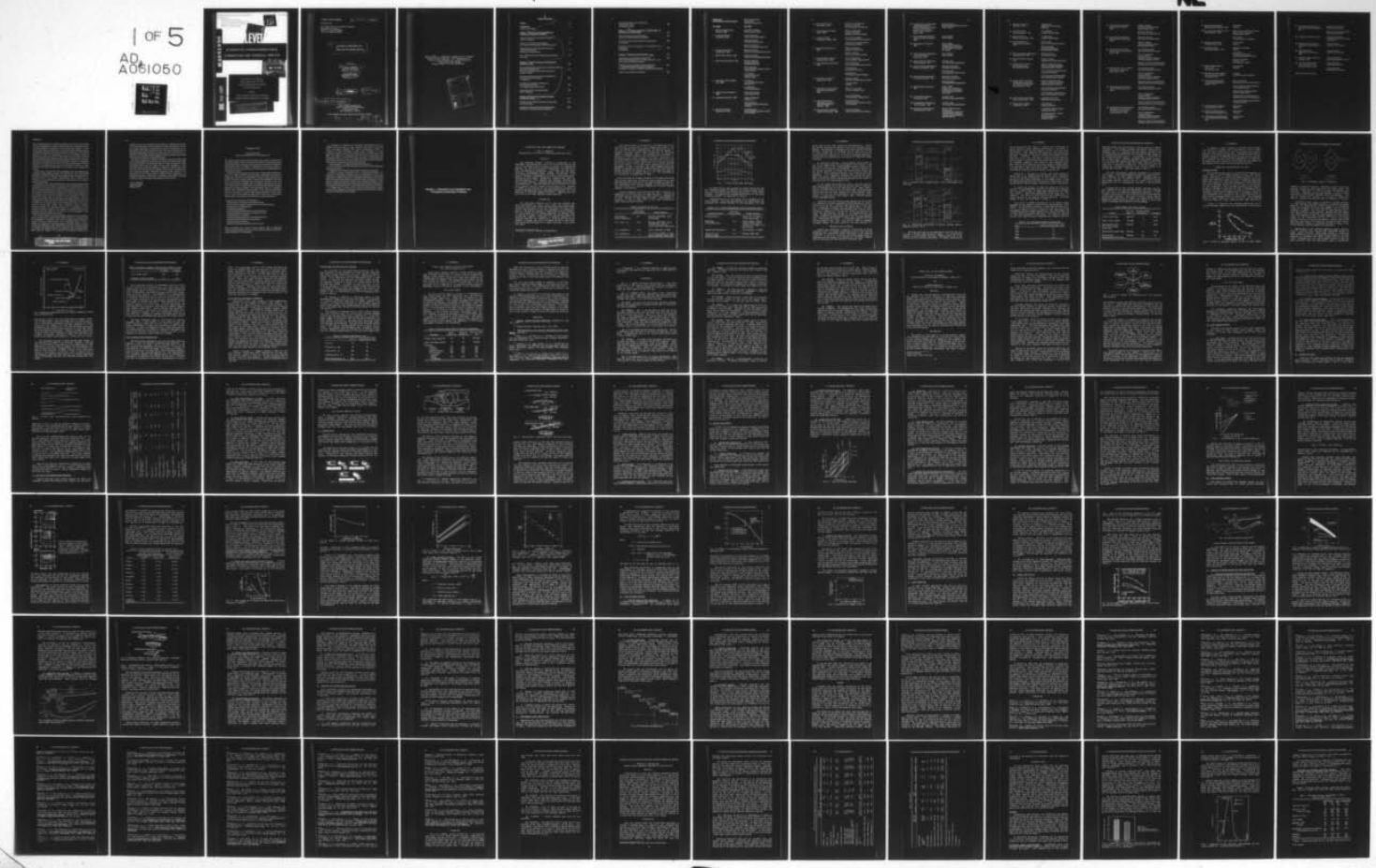
AD-A061 050 PURDUE UNIV LAFAYETTE IND PROJECT SQUID HEADQUARTERS F/G 21/4
ALTERNATIVE HYDROCARBON FUELS: COMBUSTION AND CHEMICAL KINETICS--ETC(U)
OCT 78 C T BOWMAN, J BIRKELAND N00014-75-C-1143
UNCLASSIFIED SQUID-PU-R2-78 NL

1 OF 5
AD A061050



A PROJECT SQUID (ONR) WORKSHOP
Sponsored by
Department of Energy
Air Force of Scientific Research
Naval Air Systems Command
Office of Naval Research

PU-R2-78

12

LEVEL

AD A061050

ALTERNATIVE HYDROCARBON FUELS:

COMBUSTION AND CHEMICAL KINETICS

DDC
NOV 13 1978
F

Proceedings of a Workshop
held on September 7-9, 1977
Loyola College Conference Center
Columbia, Maryland

Editors:

Craig T. Bowman (Stanford University)
Jorgen Birkeland (Department of Energy)

This document has been approved for public release and sale; its distribution is unlimited.

DDC FILE COPY

A PROJECT SQUID WORKSHOP

(14) SQUID — PU-R2-78

Sponsored by

Air Force Office of Scientific Research
Department of Energy
Naval Air Systems Command
Office of Naval Research

(6)

ALTERNATIVE HYDROCARBON FUELS: COMBUSTION AND CHEMICAL KINETICS

Edited by

(10) Craig T. Bowman
Stanford University
Stanford, California

Jorgen Birkeland
Department of Energy
Washington, D.C.

(11) Oct [redacted] 78

(12) 472 p.

(15) N00014-75-C-1143

Project SQUID Headquarters
School of Mechanical Engineering
Purdue University
West Lafayette, Indiana

This document has been approved for public release.

78 11 07 403 617 016

Project SQUID is a cooperative program of basic research relating to Jet Propulsion. It is sponsored by the Office of Naval Research and is administered by Purdue University through Contract N00014-75-C-1143, NR-098-038.

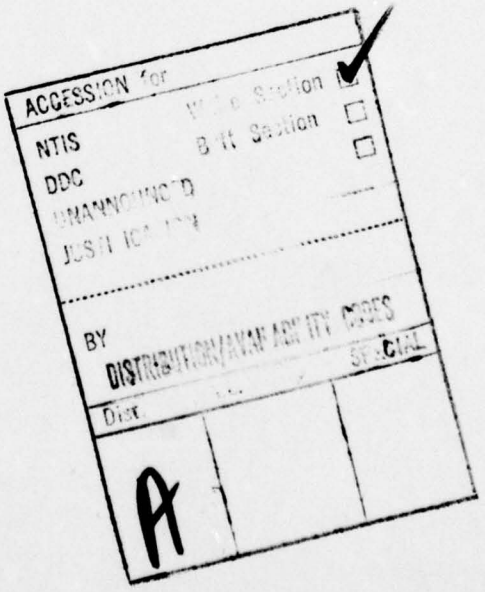


Table of Contents

Preface xiii

Introduction xv
JAMES R. PATTON JR.

Chapter I Alternative Fuel Availability and Anticipated Combustion Problems 1

Alternative Fuels and Combustion Problems 3
JOHN P. LONGWELL

Future Fuels in Gas Turbine Engines 21
WILLIAM S. BLAZOWSKI AND LAWRENCE MAGGITTI

Alternative Fuels for Reciprocating Internal Combustion Engines 74
NICHOLAS E. GALLOPOULOS

Use of Alternative Fuels in Stationary Combustors 116
M. P. HEAP

Chapter II Critical Processes in Combustion of Alternative Fuels 135

Ignition/Stabilization/Atomization: Alternative Fuels in Gas Turbine Combustors 137
ARTHUR H. LEFEBVRE, ARTHUR M. MELLOR, AND JAMES E. PETERS.

Combustion and Chemical Kinetics Problems in Internal Combustion Engines 160
F. V. BRACCO

Combustion of Droplets and Sprays of Some Alternative Fuels 180
J. B. JORDAN AND ALAN WILLIAMS

Flame Emissivities: Alternative Fuels 199
ADEL F. SAROFIM

Chapter III Pyrolysis and Oxidation Kinetics of Alternative Fuels 231

Pyrolysis and Oxidation of Aromatic Compounds 233
DAVID M. GOLDEN

Combustion Chemistry of Chain Hydrocarbons 255
FREDERICK L. DRYER AND IRVIN GLASSMAN

Liquid-Phase Reactions of Vaporizing Hydrocarbon Fuels 307
ALEXANDER VRANOS

Chapter IV Pollutant Emissions Considerations for Alternative Fuel Combustion 333

Role of Aromatics in Soot Formation 335
JAMES D. BITTNER AND JACK B. HOWARD

Kinetics of Nitric Oxide Formation in Combustion 359
B. S. HAYNES

Emission Control Techniques for Alternative Fuel Combustion 395
G. B. MARTIN

Chapter V Summary and Conclusions 423

Panel Discussion: Alternative Fuels Policy 425
JERRY GREY (MODERATOR), E. EUGENE ECKLUND, A. LEE WALLACE, AND CHARLES A. WEISEL

Panel Discussion: Alternative Fuels Technology 445
C. T. BOWMAN (MODERATOR), IRVIN GLASSMAN, HARTWELL F. CALCOTE, S. MOSIER, AND RAYMOND EDELMAN

Index to Contributors to Volume 62 463

Progress in Astronautics and Aeronautics

Martin Summerfield,
Series Editor
PRINCETON UNIVERSITY

VOLUMES	EDITORS
1. Solid Propellant Rocket Research. 1960	Martin Summerfield PRINCETON UNIVERSITY
2. Liquid Rockets and Propellants. 1960	Loren E. Bollinger THE OHIO STATE UNIVERSITY Martin Goldsmith THE RAND CORPORATION Alex W. Lemmon Jr. BATTELLE MEMORIAL INSTITUTE
3. Energy Conversion for Space Power. 1961	Nathan W. Snyder INSTITUTE FOR DEFENSE ANALYSES
4. Space Power Systems. 1961	Nathan W. Snyder INSTITUTE FOR DEFENSE ANALYSES
5. Electrostatic Propulsion. 1961	David B. Langmuir SPACE TECHNOLOGY LABORATORIES, INC. Ernst Stuhlinger NASA GEORGE C. MARSHALL SPACE FLIGHT CENTER J. M. Sellen Jr. SPACE TECHNOLOGY LABORATORIES
6. Detonation and Two-Phase Flow. 1962	S. S. Penner CALIFORNIA INSTITUTE OF TECHNOLOGY F. A. Williams HARVARD UNIVERSITY
7. Hypersonic Flow Research. 1962	Frederick R. Riddell AVCO CORPORATION
8. Guidance and Control. 1962	Robert E. Roberson CONSULTANT James S. Farrior LOCKHEED MISSILES AND SPACE COMPANY
9. Electric Propulsion Development. 1963	Ernst Stuhlinger NASA GEORGE C. MARSHALL SPACE FLIGHT CENTER

10. Technology of Lunar Exploration. 1963	Clifford I. Cummings and Harold R. Lawrence JET PROPULSION LABORATORY
11. Power Systems for Space Flight. 1963	Morris A. Zipkin and Russell N. Edwards GENERAL ELECTRIC COMPANY
12. Ionization in High-Temperature Gases. 1963	Kurt E. Stuhler, Editor NATIONAL BUREAU OF STANDARDS John B. Fenn, Associate Editor PRINCETON UNIVERSITY
13. Guidance and Control-II. 1964	Robert C. Langford GENERAL PRECISION INC. Charles J. Mundo INSTITUTE OF NAVAL STUDIES
14. Celestial Mechanics and Astrodynamics. 1964	Victor G. Szebehely YALE UNIVERSITY OBSERVATORY
15. Heterogeneous Combustion 1964	Hans G. Wolfhard INSTITUTE FOR DEFENSE ANALYSES Irvin Glassman PRINCETON UNIVERSITY Leon Green Jr. AIR FORCE SYSTEMS COMMAND
16. Space Power Systems Engineering. 1966	George C. Szego INSTITUTE FOR DEFENSE ANALYSES J. Edward Taylor TRW INC.
17. Methods in Astrodynamics and Celestial Mechanics. 1966	Raynor L. Duncombe U.S. NAVAL OBSERVATORY Victor G. Szebehely YALE UNIVERSITY OBSERVATORY
18. Thermophysics and Temperature Control of Spacecraft and Entry Vehicles. 1966	Gerhard B. Heller NASA GEORGE C. MARSHALL SPACE FLIGHT CENTER
19. Communications Satellite Systems Technology. 1966	Richard B. Marsten RADIO CORPORATION OF AMERICA

20. Thermophysics of Spacecraft and Planetary Bodies: Radiation Properties of Solids and the Electromagnetic Radiation Environment in Space. 1967	Gerhard B. Heller NASA GEORGE C. MARSHALL SPACE FLIGHT CENTER
21. Thermal Design Principles of Spacecraft and Entry Bodies. 1969	Jerry T. Bevans TRW SYSTEMS
22. Stratospheric Circulation. 1969	Willis L. Webb ATMOSPHERIC SCIENCES LABORATORY, WHITE SANDS, AND UNIVERSITY OF TEXAS AT EL PASO
23. Thermophysics: Applications to Thermal Design of Spacecraft. 1970	Jerry T. Bevans TRW SYSTEMS
24. Heat Transfer and Spacecraft Thermal Control. 1971	John W. Lucas JET PROPULSION LABORATORY
25. Communications Satellites for the 70's: Technology. 1971	Nathaniel E. Feldman THE RAND CORPORATION Charles M. Kelly THE AEROSPACE CORPORATION
26. Communications Satellites for the 70's: Systems. 1971	Nathaniel E. Feldman THE RAND CORPORATION Charles M. Kelly THE AEROSPACE CORPORATION
27. Thermospheric Circulation. 1972	Willis L. Webb ATMOSPHERIC SCIENCES LABORATORY, WHITE SANDS, AND UNIVERSITY OF TEXAS AT EL PASO
28. Thermal Characteristics of the Moon. 1972	John W. Lucas JET PROPULSION LABORATORY
29. Fundamentals of Spacecraft Thermal Design. 1972	John W. Lucas JET PROPULSION LABORATORY
30. Solar Activity Observations and Predictions. 1972	Patrick S. McIntosh and Murray Dryer ENVIRONMENTAL RESEARCH LABORATORIES, NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION

31. Thermal Control and Radiation. 1973	Chang-Lin Tien UNIVERSITY OF CALIFORNIA, BERKELEY
32. Communications Satellite Systems. 1974	P. L. Bargellini COMSAT LABORATORIES
33. Communications Satellite Technology. 1974	P. L. Bargellini COMSAT LABORATORIES
34. Instrumentation for Airbreathing Propulsion. 1974	Allen E. Fuhs NAVAL POSTGRADUATE SCHOOL Marshall Kingery ARNOLD ENGINEERING DEVELOPMENT CENTER
35. Thermophysics and Spacecraft Thermal Control. 1974	Robert G. Hering UNIVERSITY OF IOWA
36. Thermal Pollution Analysis. 1975	Joseph A. Schetz VIRGINIA POLYTECHNIC INSTITUTE
37. Aeroacoustics: Jet and Combustion Noise; Duct Acoustics. 1975	Henry T. Nagamatsu, Editor GENERAL ELECTRIC RESEARCH AND DEVELOPMENT CENTER Jack V. O'Keefe, Associate Editor THE BOEING COMPANY Ira R. Schwartz, Associate Editor NASA AMES RESEARCH CENTER
38. Aeroacoustics: Fan, STOL, and Boundary Layer Noise; Sonic Boom; Aeroacoustic Instrumentation. 1975	Henry T. Nagamatsu, Editor GENERAL ELECTRIC RESEARCH AND DEVELOPMENT CENTER Jack V. O'Keefe, Associate Editor THE BOEING COMPANY Ira R. Schwartz, Associate Editor NASA AMES RESEARCH CENTER
39. Heat Transfer with Thermal Control Applications. 1975	M. Michael Yovanovich UNIVERSITY OF WATERLOO
40. Aerodynamics of Base Combustion. 1976	S.N.B. Murthy PURDUE UNIVERSITY J. R. Osborn, Associate Editor PURDUE UNIVERSITY A. W. Barrows and J. R. Ward Associate Editors BALLISTICS RESEARCH LABORATORIES

41. Communications Satellite Developments: Systems. 1976

Gilbert E. LaVean
DEFENSE COMMUNICATIONS ENGINEERING CENTER

William G. Schmidt
CML SATELLITE CORPORATION

42. Communications Satellite Developments: Technology. 1976

William G. Schmidt
CML SATELLITE CORPORATION

Gilbert E. LaVean
DEFENSE COMMUNICATIONS ENGINEERING CENTER

43. Aeroacoustics: Jet Noise, Combustion and Core Engine Noise. 1976

Ira R. Schwartz, Editor
NASA AMES RESEARCH CENTER

Henry T. Nagamatsu, Associate Editor
GENERAL ELECTRIC RESEARCH AND DEVELOPMENT CENTER

Warren C. Strahle, Associate Editor
GEORGIA INSTITUTE OF TECHNOLOGY

44. Aeroacoustics: Fan Noise and Control; Duct Acoustics; Rotor Noise. 1976

Ira R. Schwartz, Editor
NASA AMES RESEARCH CENTER

Henry T. Nagamatsu, Associate Editor
GENERAL ELECTRIC RESEARCH AND DEVELOPMENT CENTER

Warren C. Strahle, Associate Editor
GEORGIA INSTITUTE OF TECHNOLOGY

45. Aeroacoustics: STOL Noise; Airframe and Airfoil Noise. 1976

Ira R. Schwartz, Editor
NASA AMES RESEARCH CENTER

Henry T. Nagamatsu, Associate Editor
GENERAL ELECTRIC RESEARCH AND DEVELOPMENT CENTER

Warren C. Strahle, Associate Editor
GEORGIA INSTITUTE OF TECHNOLOGY

46. Aeroacoustics: Acoustic Wave Propagation; Aircraft Noise Prediction; Aeroacoustic Instrumentation. 1976

Ira R. Schwartz, Editor
NASA AMES RESEARCH CENTER

Henry T. Nagamatsu, Associate Editor
GENERAL ELECTRIC RESEARCH AND DEVELOPMENT CENTER

Warren C. Strahle, Associate Editor
GEORGIA INSTITUTE OF TECHNOLOGY

47. Spacecraft Charging by Magnetospheric Plasmas. 1976.	Alan Rosen TRW INC.
48. Scientific Investigations on the Skylab Satellite. 1976	Marion I. Kent and Ernst Stuhlinger NASA GEORGE C. MARSHALL SPACE FLIGHT CENTER Shi-Tsan Wu THE UNIVERSITY OF ALABAMA
49. Radiative Transfer and Thermal Control. 1976	Allie M. Smith ARO INC.
50. Exploration of the Outer Solar System. 1977	Eugene W. Greenstadt TRW INC. Murray Dryer NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION Devrie S. Intriligator UNIVERSITY OF SOUTHERN CALIFORNIA
51. Rarefied Gas Dynamics Parts I and II. (two volumes) 1977	J. Leith Potter ARO INC.
52. Materials Sciences in Space with Application to Space Processing. 1977	Leo Steg GENERAL ELECTRIC COMPANY
53. Experimental Diagnostics in Gas Phase Combustion Systems. 1977	Ben T. Zinn, Editor GEORGIA INSTITUTE OF TECHNOLOGY Craig T. Bowman, Associate Editor STANFORD UNIVERSITY Daniel Hartley, Associate Editor SANDIA LABORATORIES Edward W. Price, Associate Editor GEORGIA INSTITUTE OF TECHNOLOGY James G. Skifstad, Associate Editor PURDUE UNIVERSITY
54. Satellite Communications: Future Systems. 1977	David Jarett TRW INC.
55. Satellite Communications: Advanced Technologies. 1977	David Jarett TRW INC.
56. Thermophysics of Spacecraft and Outer Planet Entry Probes. 1977	Allie M. Smith ARO INC.

57. Space-Based Manufacturing from Nonterrrestrial Materials. 1977	Gerard K. O'Neill, Editor PRINCETON UNIVERSITY Brian O'Leary, Assistant Editor PRINCETON UNIVERSITY
58. Turbulent Combustion. 1978	Lawrence A. Kennedy STATE UNIVERSITY OF NEW YORK AT BUFFALO
59. Aerodynamic Heating and Thermal Protection Systems. 1978	Leroy S. Fletcher UNIVERSITY OF VIRGINIA
60. Heat Transfer and Thermal Control Systems. 1978	Leroy S. Fletcher UNIVERSITY OF VIRGINIA
61. Radiation Energy Conversion in Space. 1978	Kenneth W. Billman NASA AMES RESEARCH CENTER
62. Alternative Hydrocarbon Fuels: Combustion and Chemical Kinetics. 1978	Craig T. Bowman STANFORD UNIVERSITY Jørgen Birkeland DEPARTMENT OF ENERGY

(Other volumes are planned.)

PREFACE

The current generation of combustion engines is the result of an extended period of simultaneous evolution of engines and fuels. During this period, the engine designer was relatively free to specify fuel properties to meet specific performance requirements, and the petroleum refining industry responded by producing fuels with the desired specifications. The resulting engine/fuel systems are appropriate to an era of abundant supply of inexpensive petroleum feed stocks. The rising cost of petroleum, coupled with a realization that petroleum supplies will not be able to meet long-term demand, has stimulated an interest in alternative liquid fuels, particularly those that can be derived from coal. An effective strategy for the efficient utilization of coal-derived fuels and for the period of transition to their utilization will require consideration of a new generation of engine/fuel systems.

A wide variety of liquid fuels can be produced from coal, ranging from methanol to high molecular weight, low-volatility oils. With the possible exception of methanol, experience in burning coal-derived liquid fuels in practical devices is very limited. Furthermore, there is almost no information on the fundamental combustion characteristics and chemical kinetics of these fuels.

In September 1977, Project SQUID sponsored a workshop on Alternative Hydrocarbon Fuels for Engines: Combustion and Chemical Kinetics. This workshop was cosponsored by the Department of Defense (the Air Force Office of Scientific Research, the Office of Naval Research, and the Naval Air Systems Command) and the Department of Energy. The objectives of this workshop were to present a perspective for the probable evolution of engine/fuel systems and, on the basis of this perspective, to identify research needs in the areas of combustion and chemical kinetics which will be required for timely transition to these systems. Although the focus of the workshop was on engines used in the transportation sector, and in particular on aircraft gas turbines, other combustion systems, including stationary devices, were considered because of a commonality in combustion and kinetics problems, the relevance of related alternative fuels experience, and the impact of these devices on the development of fuel processing techniques and fuel availability.

This volume is based on the fourteen papers presented at that workshop and on the discussions which followed them. Chapter I is concerned with the availability of alternative fuels and with engine/fuel interactions. Chapter II reviews critical aspects of the combustion process, such as ignition and stabilization, flame propagation, and flame emissivity, which are relevant to alternative fuels. Chapter III discusses the current knowledge of pyrolysis and oxidation kinetics of alternative fuels, including liquid-phase reactions. Chapter IV is concerned with pollutant emission con-

PRECEDING PAGE NOT FILMED
BLANK

siderations in the use of alternative fuels. Chapter V summarizes the results of two panel discussions which followed the formal presentations. One of these panels addressed the political and economic considerations of implementing and utilizing alternative fuels. The second summarized anticipated technological problems associated with the transition to use of alternative fuels in engines and attempted to identify specific research needs in the areas of combustion and chemical kinetics.

The editors would like to thank the authors of the various papers and those who participated in the discussions. Their contributions have made this volume possible. S.N.B. Murthy, James R. Patton, and Joseph F. Masi contributed their ideas and support in the early formulation of the workshop objectives. Special thanks go to Robert N. Hazlett who served with us on the committee which organized the workshop. Annmarie Pittman efficiently handled workshop arrangements and assisted in the preparation of this volume. Ruth F. Bryans, AIAA Administrator of Scientific Publications, and Martin Summerfield, Series Editor, provided continuous support throughout the preparation of the volume.

Craig T. Bowman
Jørgen Birkeland
February 1978

INTRODUCTION

James R. Patton Jr.
Office of Naval Research, Washington, D.C.

The Office of Naval Research and the Naval Air Systems Command were particularly happy to join with the Air Force Office of Scientific Research and the Department of Energy in sponsoring this workshop on "Alternative Hydrocarbon Fuels for Engines—Combustion and Chemical Kinetics." The sponsors have a common interest in the pursuit of knowledge relative to this important subject.

The Navy basic and applied research effort in airbreathing propulsion is planned to support research and technology requirements and the technology base necessary for development of future aircraft and missiles as well as to improve existing vehicles. Strategy for developments in this area calls for a dynamic technology base, an absolute necessity if we are to increase power plant reliability and performance and decrease life cycle costs. These types of considerations are continually placing more stringent demands on research programs. The requirement, then, is to develop a deeper, more fundamental understanding of the physical phenomena involved in all aspects of engine design and development. As part of this effort, a series of workshops has been held in recent years to emphasize problem areas. Workshops have been held on the following subjects:

Research in Gas-Dynamics of Jet Engines
Fluid Dynamics of Unsteady 3-D Separated Flows
The Use of Laser Doppler Velocimetry for Flow Measurements
Aeroelasticity in Turbomachines
Laser Raman Diagnostics
Second International Workshop in Laser Velocimetry
Turbulent Mixing in Nonreactive and Reactive Flows
Unsteady Flows in Jet Engines
Combustion Measurements in Jet Propulsion Systems
Transonic Flow Problems in Turbomachinery
Turbulence in Internal Flows
Engine-Airframe Integration-Short-Haul Aircraft

These workshops have served a useful purpose, both in improving communications between all groups involved and in the selection of specific research programs for investigation.

In planning the workshop on Alternative Hydrocarbon Fuels for Engines, the Navy sought to create a forum for discussion of the current status, anticipated problems, and research requirements relative to evolution of future fuel-engine systems under conditions of scarce petroleum supplies expected in the time period between 1990 and the year 2000. This objective is consistent with the status of alternative fuel development today. A number of meetings and other workshops have been held in recent months to review the status of alternative fuel development. The significant conclusions of these workshops were:

- A national policy is needed to develop alternative fuels.
- Use of synthetic fuels will be required in the future for both civilian and military applications.
- Engines must be designed and developed to operate on such fuels.

A number of aspects of alternative fuels - science and technology - are significant in fuel-engine matching and fuel development, such as low-temperature oxidation characteristics; physical characteristics which would affect storage, handling, injection, and ignition; high-temperature chemical kinetics of upper and middle distillates; and production problems. It was felt that chemical kinetics and its interaction with physical characteristics and combustion should deserve first attention in basic research at this time.

It is hoped that this volume will be useful in relating future research projects and investigations to particular needs and in assuring that pertinent research is undertaken in timely fashion.

Chapter I - Alternative Fuel Availability and Anticipated Combustion Problems

ALTERNATIVE FUELS AND COMBUSTION PROBLEMS

John P. Longwell*
Massachusetts Institute of Technology, Cambridge, Mass.

Abstract

The projected maximum in world oil production in the 1990-2000 time period will result in a series of shifts in the use of liquid fuels, which in turn will result in a substantial decrease in the ratio of gasoline production to diesel, jet fuel, and heating oil production. This trend, plus the introduction of low-hydrogen-content liquids from coal and shale, will reduce the hydrogen content of these "distillates." Combustion problems introduced by this trend include increased emission of carcinogenic polynuclear aromatics and soot, increased combustor liner heating, and increased ignition time lag in diesel engines. Although these problems can be avoided by hydrogenation, improved combustor design promises to be much more economical and will reduce refining energy loss. Research is needed in the formation of soot and polynuclear aromatics in droplet combustion and on the subsequent destruction of these materials in turbulent combustion systems. Opportunities also exist for use of lower hydrogen content gasoline.

Introduction

The inevitable depletion of oil and gas reserves and their replacement by, first, coal, shale, and uranium and, ultimately, by nuclear fusion and solar-based resources forces serious consideration of how the consumption of energy will adapt to the radical changes in supply which can be foreseen. For the purposes of this paper, discussion of research aimed at meeting the needs of the 1990-2000 time period seems most appropriate; however, responses to changing composition of starting materials for production of liquid fuels and to the changes in demand that can be foreseen should be consistent with the expected changes for a longer time span: say, to the year 2025.

*Professor, Chemical Engineering Department.

PRECEDING PAGE NOT FILMED
BLANK

Our interest here is primarily in the supply and use of liquid fuels, particularly in the transportation sector. For the time period under consideration, the world-wide availability of oil will be the primary driving force for change. A recently published report[1] shows projections of the world demand if adequate supplies of petroleum were available at essentially the present price structure. Obviously, if petroleum supplies were inadequate, the "gap" would be filled by substitution of other energy sources such as coal and electricity and by simply making less use of energy produced by liquid fuels. It is seen that, depending on the OPEC management of their resources, the "gap" between supply and demand is expected to be felt between 1980 and 1997, whereas before then world oil production, as is presently the case, is limited primarily by demand (see Fig. 1). The corresponding U.S. projection is summarized in Table 1.

Total use would go through a maximum in the same time period when imports would be limited by world production to some possibly constant fraction of the internationally traded oil. U.S. production could increase somewhat or hold constant during this period if a vigorous offshore drilling and recovery program is carried out.

A major response to the onset of the "gap" in the U.S. is production of liquids from oil shale and coal. During the 1990-2000 period, production of these liquids is expected to be small relative to total demand (2-10%). Rapid growth is possible, so that by 2025 half of the liquid hydrocarbons might come from these sources.

Table 1 Dynamics of oil use

	1975 Use, M barrels/day	Growth pattern
Noncommunist world production	46	Maximum 1990-2000, -80 M barrels/day
U.S. total use	16.3	Maximum 1990-1995, -23 M barrels/day; imports limited by world population
U.S. production	10.5	Fairly constant to 2000
U.S. synthetics	...	<0.5 M barrels/day in 1990; major component after 2000

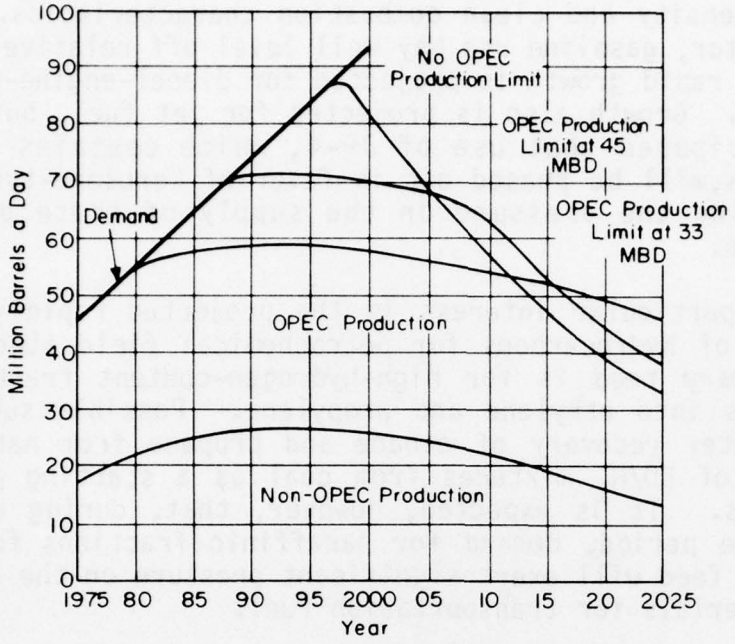


Fig. 1 Timing of petroleum shortages.

As noted earlier, the response to supply limitations must be a vigorous program of substitution of other energy sources plus use restrictions where direct substitution is not accomplished. A projection of consumption patterns for the major consuming sectors[2] is summarized in Table 2.

Transportation use is the largest and is expected to continue growing. Here the opportunities for substitution for petroleum are limited because of the requirement for high

Table 2 U.S. liquid hydrocarbons use by consuming sector

Consuming sector	1975 use, M barrels/day	Growth pattern
Transportation	9	Levels off in 1990's, -10 M barrels/day
Nonenergy (petrochemicals)	1.6	Rapid growth; second largest after transportation by 2000, -4 M barrels/day
Commercial/residential	2.4	Flat maximum in 1990's
Industrial and electric power	3.3	Maximum 1985-1990

energy density and clean combustion characteristics. Within this sector, gasoline use may well level off relatively early; however, rapid growth is projected for diesel-engine-propelled vehicles. Growth also is projected for jet fuel, but it also is anticipated that use of JP-4, which contains gasoline fractions,will be phased out in favor of kerosene-type fuels, increasing the pressure on the supply of these petroleum fractions.

Of particular interest is the projected rapid growth of the use of hydrocarbons for petrochemical field stock. Here the primary need is for high-hydrogen-content fractions for pyrolysis into ethylene and propylene. Possible substitutes are greater recovery of ethane and propane from natural gas and use of CO/H_2 mixtures from coal as a starting point for synthesis. It is expected, however, that, during the 1990-2000 time period, demand for paraffinic fractions for petrochemical feed will exert significant pressure on the supply of thse materials for transportation fuel.

In the commercial/residential sector, the fuel used for space heating makes use of the same boiling range of hydrocarbons as kerosene-type jet fuel and diesel fuel. Here, substitution of electricity plus the heat pump, coal-generated central heating, and solar heating will allow eventual reduction of oil use for this purpose so that relatively little growth is anticipated in this sector, with a maximum perhaps in the 1990-2000 period.

Industrial use and electric power generation use of fuel oil currently is growing extremely rapidly because of substitution of oil for gas. Eventual substitution of coal for fuel oil is expected to reduce this use before 1990. The heavy fuel oil used here is higher boiling than fuels used in transportation. Reduction in its use will allow its conversion to lower boiling materials falling in the transportation fuel range. A summary of these trends is as follows: 1) increased use of paraffinic hydrocarbons (diesel fuel, kerosene-type jet fuel, petrochemical feed); 2) decreased demand for high boiling aromatic fuels (fuel oil); and 3) stable or somewhat decreased demand for motor gasoline and home heating oil.

Manufacturing Efficiency

Dukek[3] has presented a general discussion of these projected shifts in product distribution and of the refining technology for converting natural petroleum to the required products. In Fig. 2, a typical petroleum composition is compared with the output of a typical U.S. refinery, together with an indication of the conversion processes used.

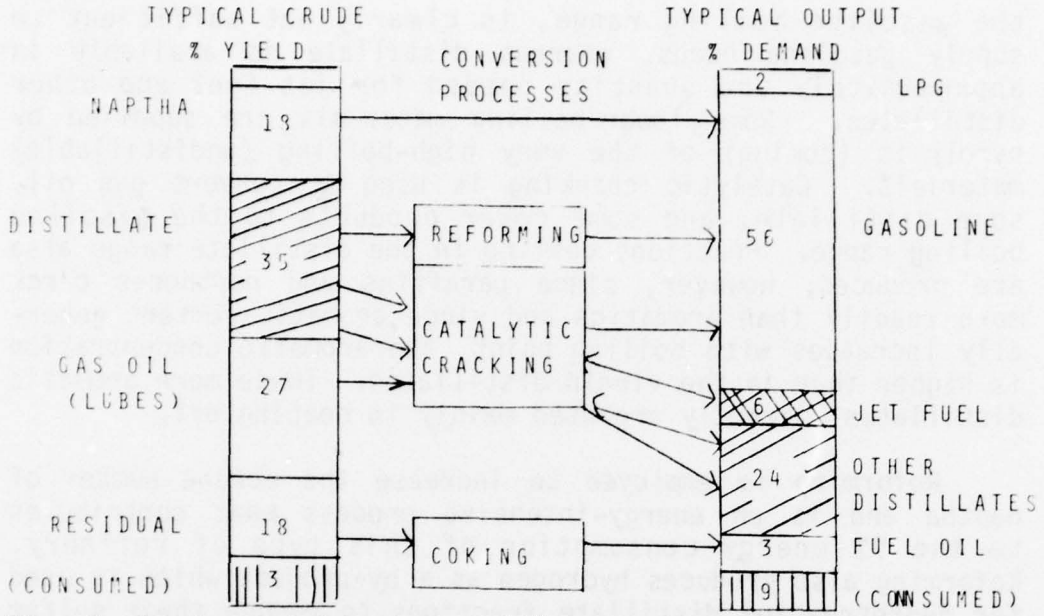


Fig. 2 Product yield vs demand (basis: 100 k barrels/day, U.S. refinery).

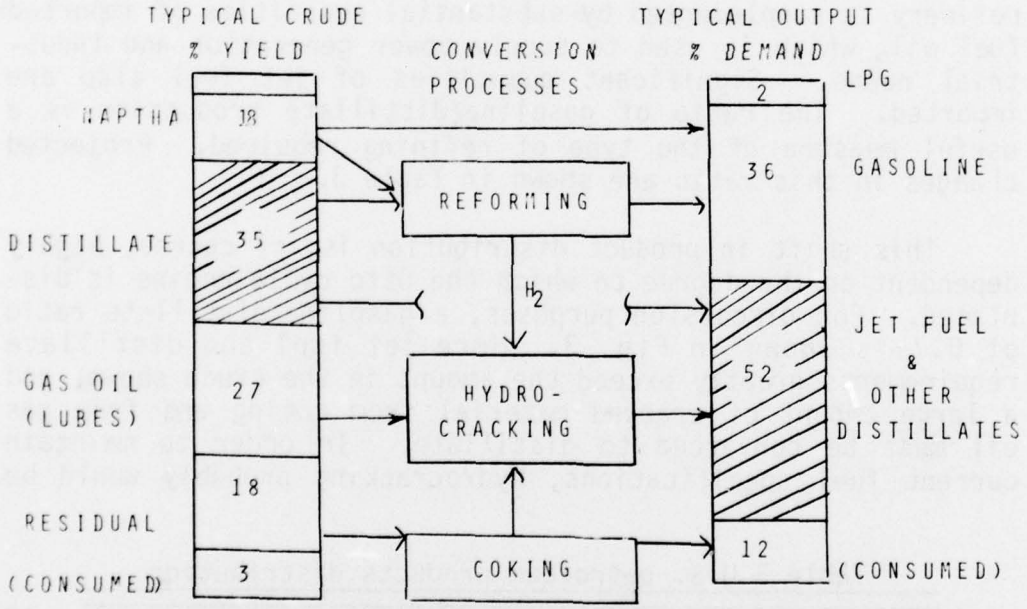


Fig. 3 Maximizing distillates in future refinery (Basis: Mogas/Dist ratio = 0.7).

The crude petroleum can be separated by distillation into the basic boiling range fractions shown. This distillation process is quite energy efficient, consuming about 3% of the heating value of the fuel petroleum. The naptha, which covers

the gasoline boiling range, is clearly not sufficient to supply gasoline needs, whereas distillate is available in approximately the quantity needed for jet fuel and other distillates. Some lower-boiling materials are supplied by pyrolysis (coking) of the very high-boiling (undistillable) materials. Catalytic cracking is used to convert gas oil, some distillate, and some coker products to the gasoline boiling range. Fractions boiling in the distillate range also are produced; however, since paraffins and napthenes carck more readily than aromatics and since aromatic content generally increases with boiling point, the aromatic concentration is higher than in the virgin distillates. These more aromatic distillates currently are used mainly in heating oil.

Reforming is employed to increase the octane number of naptha and is an energy-intensive process that contributes to the 9% energy consumption of this type of refinery. Reforming also produces hydrogen as a by-product which is used for hydrotreating distillate fractions to reduce their sulfur content and to improve thermal stability by olefin saturation.

It should be pointed out that the output of this U.S. refinery is supplemented by substantial quantities of imported fuel oil, which is used to supply power generation and industrial needs. Significant quantities of jet fuel also are imported. The ratio of gasoline/distillate production is a useful measure of the type of refining required. Projected changes in this ratio are shown in Table 3.

This shift in product distribution is, of course, highly dependent on the degree to which the Otto cycle engine is displaced. For discussion purposes, a gasoline/distillate ratio of 0.7 is shown in Fig. 3. Here jet fuel and distillate requirements greatly exceed the amount in the crude shown, and a large amount of cracked material from coking and from gas oil must be converted to distillate. In order to maintain current fuel specifications, hydrocracking probably would be

Table 3 U.S. petroleum products distribution

Year	Gasoline/distillate ratio
1975	1.7
1980	1.5
1990	1.2
2000	1.0

required rather than the catalytic cracking typical of today's refineries. This process consumes substantial quantities of hydrogen, and it is probable that the amount available from reforming would be inadequate and that hydrogen would have to be manufactured specially for this purpose, a very expensive and energy-consuming process. Introduction of shale oil or coal liquids would increase hydrogen requirements greatly. For the case shown, energy consumption increased to 12% rather than decreasing, which might have been expected from the reduction in gasoline production. From the viewpoint of combustion, the aromatic content of the various streams is of considerable interest. These are shown in Table 4.

The most efficiently produced supplement to available virgin stock is the hydrotreated catalytically cracked distillate; however, its high aromatic content (30-40%) tends to rule it out for use in paraffinic fuels. Hyrdocracking produces lower aromatic material but at a high price in energy consumption and its accompanying increase in manufacturing cost.

Introduction of coal liquids greatly increases the aromatic content of the refinery hydrocarbon pool, and, although this will help in producting high-octane gasoline, it will increase the difficulty of producing distillates meeting current specifications. Both coal and shale liquids contain substantial quantities of organic nitrogen, which can be removed by hydrotreating but which also require a very large amount of hydrogen and therefore refining energy.

Table 4 Major distillate streams

Stream	Boiling range, °C	Process energy consumption, %	% Aromatic
Virgin distillate	230-350	3	15-30
Heavy virgin naptha	130-200	3	10-20
Hydrotreated catalytically cracked distillate	200-350	6	30-40
Hydrocracked distillate	200-350	12	10-30
Hydrotreated hydrocracked distillate	200-350	20	20

In summary, a major increase in mid-distillate consumption relative to gasoline plus increased use of tars, shale oil, and coal liquids will tend to increase the aromatic content of the mid-distillate pool. Although current specifications can be met by hydrogen-intensive refining, the corresponding increase in refining energy consumption and cost will be a powerful driving force for development of combustion equipment that will allow use of the types of fuels which can be produced with minimum refining energy consumption.

Combustion Characteristics of Fuels

Hydrogen Content

The preceding discussion has pointed out the tendency for future fuels to be of higher aromatic content than today's fuels. The effect of increasing aromatic content is to increase the formation of soot in the early stages of combustion where local fuel-rich conditions occur. Experience has shown that soot formation in practical equipment is correlated better by the hydrogen content of the fuel than by the analysis for total aromatics, since individual aromatics vary considerderably in tendency to form soot and also in hydrogen content. An example of such a correlation is shown in Fig. 4[4] for fuels covering a wide range of compositions. A hydrogen content of 15% corresponds to a paraffinic fuel with specification jet fuel having a hydrogen content of around 14%. The pronounced effect on smoke formation is striking, and a similar correlation was found for linear heating from flame radiation.[4]

Figure 5 illustrates the reasoning behind the use of percent hydrogen rather than the conventional refining meas-

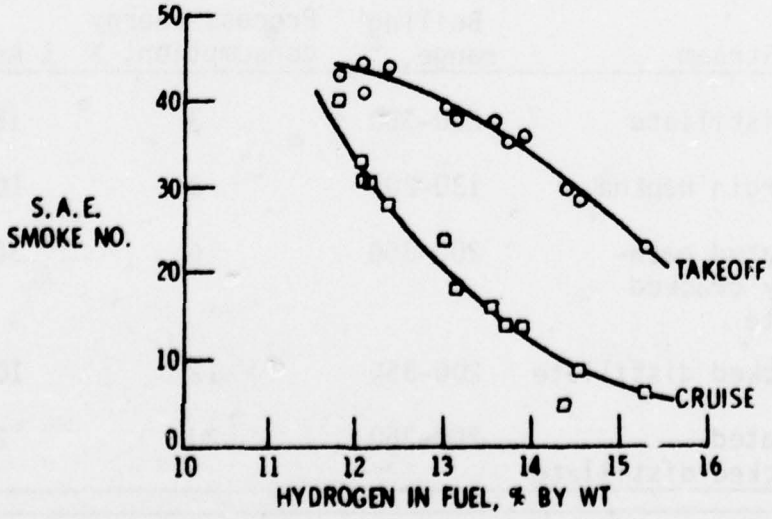


Fig. 4 Effect of hydrogen content of fuel on smoke number.

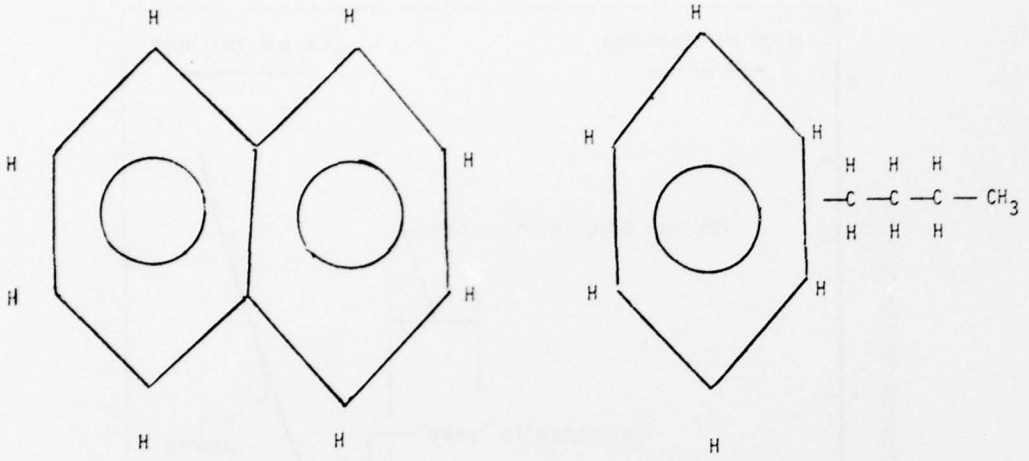


Fig. 5 Hydrogen content of aromatics.

urement of aromatics content. Napthalene (6.2% H) and butyl benzene (10.4% H), both containing 10 carbon atoms, are compared. Napthalene is known to produce considerably more soot than a compound such as butylbenzene, so that a better correlation with percent hydrogen would be expected. This type of correlation applies to a variety of combustion devices, ranging from kerosene lamps to domestic oil burners.

Formation of soot causes a variety of related problems: 1) liner heating from flame radiation; 2) combustion chamber deposits; 3) heat-transfer surface deposits; 4) smokestack fires and plugging; 5) dirty environment; and 6) possible increase in cancer. The first two of these problems are of particular interest in gas turbines. Whereas home and commercial heating units and boilers are adjusted to avoid visible smoke and, hopefully, heat exchanger deposits by setting the excess air as illustrated in Fig. 6.[5] Here a very large amount of excess air must be introduced to control soot, which decreases the thermal efficiency by increasing stack losses. This particular burner is considered typical of those in the field; however, improved designs are available.

Regulations on soot formation generally require elimination of "visible" soot and have had pronounced effects on diesel engine operation, where power output is limited by smoke formation, and on jet engine design, where it has been necessary to eliminate the highly visible soot of past designs. Although the dirty and unsightly nature of soot has been sufficient cause for regulations, there is potentially

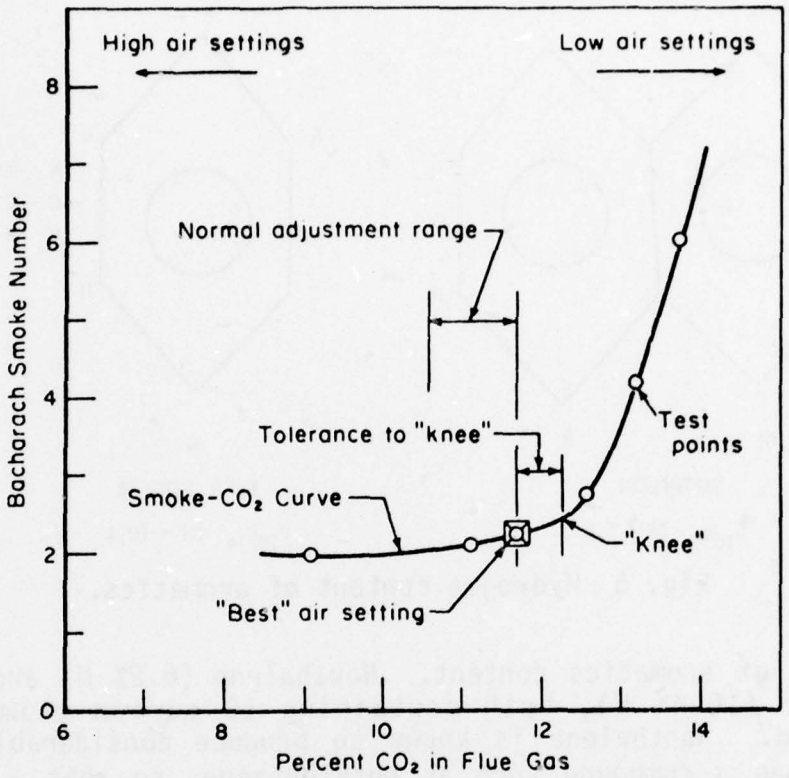


Fig. 6 Smoke-CO_2 characteristics of a typical commercial residual oil-fired boiler.

much greater concern with the established carcinogenic potential of some soots. Soots have been found to contain quantities of extractable polynuclear aromatics varying from essentially zero for samples that have been subjected to a high temperature after formation to a few percent where temperature has been reduced shortly after formation by rapid heat transfer or mixing with cold gasses. Analysis of these polynuclear aromatics shows varying content of identified carcinogens such as benzo (a) pyrene. The data in Table 5,[6] taken in a turbulent continuous flow combustor, illustrate this point.

The indicated increase in benzo pyrenes when benzene is substituted for kerosene is of particular interest. Very few data are available on the effect of fuel composition on PCAH composition or on the effect of thermal and environmental history of soot particles. Although there is little direct evidence of soot causing an increase in cancer of the respiratory system in the general population, soot is known to be in the dangerous particle-size range and to contain identified potent carcinogens and must be considered potentially hazardous.

Table 5 Polycyclic aromatic hydrocarbons (PCAH) in soot

	Kerosene	Benzene
Total PCAH, mg/m^3	603	665
% benzo (a and e) pyrene	1.1	2.0

Since soot does not form for homogenous fuel/air mixtures in the vicinity of stoichiometric, and since soot, once formed, burns out very rapidly at adiabatic flame temperatures with a modest amount of exccess air, it is generally not difficult to design for soot-free performance for a given steady-state operating condition. The problem of also designing for satisfactory performance during start-up ro during part-load or overload conditions and to design a system whose soot output does not depend on a sophisticated maintenance program has proved to be very difficult. Home heating units, for example, operate in a cyclic mode in which hydrocarbon and soot emissions are high until the combustion chamber temperature reaches steady state. Diesel engines, when operated in good condition on a test stand, can produce relatively soot-free combustion products, but poor maintenance practices in the field and a tendency to overload the egine result in the diesel having a well-established reputation for being "dirty."

The major challenge, then, is the design of practical equipment that is both capable of clean operation over the entire operating range and also not prone to produce soot before maintenance is forced on the operator by other considerations. In order to accomplish this, a much more quantitative understanding of the effect of combustion atmosphere, the mixing and turbulent combustion process, as well as the chemistry an physics of soot formation is needed.

Fuel Viscosity and Freezing Point

Refining energy consumption and cost obviously would be reduced if less boiling-point reduction were required. For distillate fuels, the upper limit on boiling point is set by the required low-temperature characteristics: viscosity and precipitation of a solid wax phase. For temperate climates, a final boiling point of around 350°C allows reasonable performance of diesel fuel and home heating oil. Wax precipitation is a potential problem, and seasonal control is achieved by a combination of additives and control of end point. Aircraft jet fuel is designed to deal with temperatures as low as

-50°C. This requirement (-40° or -50°C freeze point) has the effect of reducing the final boiling point to the 250°-230°C range, drastically reducing the fraction of petroleum which can be included in this fuel. Systems modifications such as fuel heating would allow use of distillate fuels of normal boiling ranges. Such a change would tend to decrease hydrogen content, since the higher boiling fractions are generally lower, and to increase fuel viscosity, which, particularly for start-up conditions, will increase drop size and in some cases modify spray distribution, which can result in starting or relight problems. Possible future use of antimisting additives for improvement of crash survivability also would modify the fuel viscosity and therefore atomization characteristics. Improved techniques for atomization over a wide range of flow rates and viscosities is needed.

Fuel Stability and Deposit Formation

Hydrocarbon fuels, when exposed to high temperatures, particularly in the presence of oxygen, form polymeric compounds that can cause difficulty in a variety of ways. On storage, precipitates can form which can cause filter plugging and other problems. Low-molecular-weight polymers, which remain soluble, will form films on surfaces where fuel is evaporated and can cause sticking of control valves, for example, and generally prevent the use of distillate fuels in combustion devices that evaporate the fuel on a hot surface. The development of these stability problems is a strong function of the temperatures to which the fuel is subjected in the fuel-handling system. Modern jet aircraft are particularly severe in this regard, since fuel is used to absorb heat for lubicating oil and other parts. There also can be an atomizing nozzle deposit problem from exposure of residual fuel to high temperatures after shutdown of the engine. These practices have resulted in very severe jet fuel termal stability requirements. The virgin paraffinic kerosene distillate currently used for jet fuel is a relatively stable material; however, olefins, which are a constituent of fractions formed by thermal or catalytic cracking, are highly unstable and would require hydrogenation to correct this problem. Aromatics and higher boiling fractions tend to be less stable than paraffins, so that future increase in aromatics and boiling point will require careful design to avoid thermal stress.

Organic nitrogen is a special problem in shale oil and coal liquids. Preliminary data[7] indicate that nitrogen content must be reduced to less than 100 ppm to assure meeting current stability requirements. Severe hydrogenation is required to attain such low levels, greatly increasing refining cost.

Future Fuels for Aviation Gas Turbines

As indicated in the preceding discussion, jet fuel specifications are well matched to present and past resources and manufacturing capabilities but will require increasing conversion of higher boiling and aromatic hydrocarbons in the future. Since restraints on fuel composition can, to some extent, be modified by combustor and total system design, an important opportunity exists for reoptimization of the aircraft/fuel system. In order to carry out such an optimization program, it is helpful to have a target fuel for use in research programs on both fuel production and aircraft and engine design. A NASA-sponsored workshop (June 1977) recommended a fuel for experimental use with the characteristics given in Table 6.

An increase in aromatics to 35% would appear to cover expected fuel compositions up the point where it is necessary to include significant quantities of highly aromatic coal liquids. The flash point was kept in the kerosene range for crash safety reasons, even though lowering the flash would be one of the lowest-cost and most efficient methods of increasing supplies.

The increase in freezing point to -29°C (-20°C) increase the final boiling point to a value about halfway between current jet fuel and diesel fuel or heating oil. It was felt that a higher freezing point would affect the operations of an undue number of aircraft. The fuel stability criterion was held constant and would be achievable with petroleum stocks with moderate hydrotreating. This specification would require care in order not to increase thermal stress in future jet engines. For research and development work, parametric studies of fuel composition could be carried out to develop a data base for ultimate reoptimization of the jet fuel composition.

Table 6 Proposed experimental fuel

	Jet A	Experimental fuel
% H, min	14	13
% aromatics, max	25	35
Flash point, °C	>38	>38
Freezing point, °C	-40	-29
JFTOT break point, °C	295	295

Diesel, Gas Turbines, and Stirling Engines for Ground Transportation

Since diesel engines require a fairly paraffinic fuel, some increased difficulties in supply might be encountered; however, since diesel fuel can run up to ~35 % aromatic, the problem does not appear severe until significant quantities of coal liquids are needed. The automotive gas turbine and the Stirling cycle engine could well be developed to use the equivalent of No. 2 heating oil or automotive diesel should be developed to be as flexible as possible in fuel requirements.

Otto Cycle Engine

The spark ignition engine is unique in its dependence on high octane number for high compression ratio and therefore high-efficiency operations. Conversion of paraffinic low-octane-number napthas is the largest refinery energy consumer in current refineries. This energy requirement is increasing because of the scheduled elimination of tetra-ethyl lead. The problem of knock is related closely to the combustion chamber design, with avoidance of hot spots being an important consideration. A frustrating problem, which deserves further research, is the increase in octane requiremnets with use. This increase can be quite substantial, ~5 octane number, and, if it could be avoided, would allow either use of less refining energy or an increase in engine efficiency. The problem appears to be related to surface deposits and therefore to fuel characteristics; however, the mechanism of this octane requirement increase is not understood.

Table 7 Typical octane number of gasoline components

Component	Motor octane no.	Research octane no.	Boiling range, °F
Current clear gasoline	83	91	120-430
Light petroleum naptha	65	65	150-300
Aromatics			
Toluene	112	124	230
p-xylene	124	145	280
n-butyl benzene	116	114	361
1,4 di-ethyl benzene	138	151	363
1 methyl napthalene	114	123	464

When the proportion of total petroleum used for gasoline decreases and coal liquids are used, an opportunity exists for drastically increasing the aromatic content of gasoline. Although deposit problems might be increased, this combustion system is unique in benefiting from an increase in aromatics concentration due to the high octane number of aromatics (see Table 7).

The very high octane number of aromatics is striking, and, since a gasoline octane number of ~110 would allow a 12:1 compression ratio and a 15% thermodynamic efficiency gain, a long-range possibility of resource conservation through a new engine/fuel combination exists.

In summary, the shifts in relative magnitude of the various liquid hydrocarbon uses will force re-examination of combustion system performance, particularly in the transportation area and home heating. Ability of transportation systems and home heating to make optimum use of the aromatic compounds will be of particular importance, particularly during start-up, off design, and poor maintenance condition. For large-scale stationary uses, the main problem appears to be reduction of nitric oxide from organic nitrogen found in shale oil and in coal liquids in order to avoid its removal by refining.

References

[1] Energy: Global Prospects 1985-2000, McGraw-Hill, New York, 1977.

[2] "Energy Outlook," Chrysler Corp., Oct. 1976.

[3] NASA Workship on Jet Aircraft Hydrocarbon Fuels Technology, June 1977.

[4] Butze, H. F. and Ehlers, R. C. "Effects of Fuel Properties on Performance of a Single Aircraft Turbojet Combustor," NASA TMX-71789, Oct. 1975.

[5] Locklin, D. W. and Barrett, R. E., "Guidelines for Burner Adjustments' of Commercial Oil Fired Burners," Environmental Protection Agency, EPA 600/2-76-088, NTIS PB251919, March 1976.

[6] Prado, G. P., Lee, M. L., Hites, R. A., Hoult, D. P., and Howard, J. B., "Soot and Hydrocarbon Formation in a Turbulent Diffusion Flame," Sixteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, Pa., 1977.

[7] Reynolds, T. W., "Thermal Stability of Some Aircraft Turbine Fuels Derived from Oil Shale and Coal," NASA TMX-3551, June 1977.

DISCUSSION

DR. F. L. DRYER (Princeton University): I was very interested in the process bar graphs that you presented. (Figs. 2 and 3). The percentage of residuals involved in those two cases appeared to be the same.

DR. J. P. LONGWELL (MIT): Yes, that is true. The reason is that the typical American refinery does not produce much residual fuel now. Both processes had coking which can take residual and convert it to distillate and coke.

DR. DRYER: In time, will not tertiary recovery processes increase the percentage of residuals which were in the original crude breakdown?

DR. LONGWELL: Yes. I did not dwell on that, but one of the major resources that has not been used very much in the world is what we call tars. There is a lot in the Venezuela tar belt. This Venezuelan tar contains about 60% residual. The Canadian Athabasca tars are also a major resource. There also will be more of a tendency to produce heavy crudes in the Arab countries. They have been selectively producing light crudes. One of the challenges in refining research is to find a better way of converting tars into useful distillates.

DR. R. M. FRISTROM (Applied Physics Laboratory): How big a difference does the part of the world we take the oil from make? Is geopolitics going to be a major constraining factor or just a minor one?

DR. LONGWELL: It appears that the major importable oil reserves are going to be the so-called OPEC reserves. There are two major areas to consider. One is the Mideast. There, they will be exporting more high-sulfur heavy crudes. So that will make a difference. Then, in time, Venezuela will be another major source with its tar belt reserves. Canada is not considered to be an important exportation source becuase of its internal needs.

MR. E. ECKLUND (Department of Energy, Washington): What was the basis for the use of transportation liquid fuels leveling off in the latter decade of this century?

DR. LONGWELL: Largely the proposed program on conserving gasoline. Different estimates are given, and I should have put a range on that.

MR. ECKLUND: Yes, the thinking in DOE on transportation is that the effect of the more fuel-efficient automobiles will be rather dramatic initially. Once you get to the point where you have done all the good things quickly, there is reason to believe that, with population growth, use is going to continue to increase. So the gap will get bigger and bigger with time.

DR. LONGWELL: The 1975 use that I showed was 9,000,000 barrels a day. I gave 10,000,000 for 1990-2000. I think it would have been fairer to say 10 to 14,000,000.

MR. ECKLUND: There has been a great deal of discussion in the aircraft industry on the use of the gaseous fuels, methane and hydrogen. You did not mention those fuels.

DR. LONGWELL: It is likely that these fuels will be considered for aircraft only after the 1990 to 2000 time period on which I was focusing. Hydrogen is the one gaseous fuel that really shows an advantage. From an overall energy viewpoint, it is poor compared to burning hydrocarbon fuel, but you can get better aircraft range, which can be important, particularly for supersonic flight.

MR. ECKLUND: There is a factor though, which is implied in the curves that you ahve shown and in other projections, that has not been addressed very much. Everybody seems to be pointing to the proposition of world oil production peaking out sometime in the 1990's. That says that there is going to be a gap. If a half-billion barrels a day of synthetic fuel are available to start making up that gap, we will have to start producing the synthetics by 1980. Coal synthetics will not be ready at that time. We have environmental problems with shale and only a couple of years to get something going here. If we do not, then we have to consider some other alternatives. One possibility from a liquid fuel point of view, of course, is to make up part of the shortfall with alcohol. The other aspect of the situation is that if you have to have an aircraft by the year 2000 or thereabouts, and if you have to take into account world fuel supply, you will have to start designing that aircraft somewhere in the neighborhood of 1985 or 1990. So all these things break down on us pretty rapidly.

DR. LONGWELL: They do. I presented what I would call an optimistic picture. In regard to alcohols, they, of course,

do not have much promise for aircraft use. They are one of the alternatives for ground use, there again, to make alcohols we would logically start with coal or shale. The investment and all the problems of making conventional fuels also are there for making alcohol fuels.

MR. ECKLUND: There is another factor that we are probably not prepared to address at this stage. I congratulate you on the very fine approach that you have taken to adjusting conventional fuels, but in view of the fact that we do not really know where we are going as far as an eventual finished fuel is concerned, and the price that we are going to pay in conversion efficiency, there is a need to look at the whole picture from a systems approach -- looking at the process, the engine, and the whole works. This approach may say something quite different from what you have indicated here. My point is to leave the though that we are going to be talking about here is very good and very necessary, but perhaps only part of the picture.

DR. LONGWELL: The problem does need to be worked from a systems viewpoint. My presentation was fairly qualitative. Some detail could have been added, but much remains to be done before a complete systems approach can be claimed. I think that there is going to be a real effort in the aviation area to do this, but of course it is a relatively small consumer. The NASA and Defense Department programs in this area will be at least a trial case of working the whole system problem.

FUTURE FUELS IN GAS TURBINE ENGINES

William S. Blazowski*
Exxon Research and Engineering Company, Linden, N.J.

and

Lawrence Maggitti+
Naval Air Propulsion Test Center, Trenton, N.J.

Abstract

Current cost and availability considerations along with the potential for future depletion of petroleum resources mandate the examination of obtaining liquid turbine fuels from nonpetroleum resources which may have properties that are substantially different from those of current fuels. Indeed, a significant long-range impact on combustion system design practice is envisioned. Characteristics of current petroleum-derived fuels, as well as present combustion system design requirements, are reviewed, and principal fuel effects on combustion systems are described. Fuel characteristics most likely to affect future gas turbine designs are hydrogen and nitrogen content, volatility, viscosity, metal and sulfur content, and thermal stability. Design approaches which may lead to improved fuel flexibility are described, and the research necessary for the development of those new concepts is identified. The final section describes the magnitude and time requirements for the task of achieving fuel flexibility in gas turbine engines.

Introduction

The purpose of this paper is to review potential combustion problems associated with the utilization of future fuels in gas turbine engines and to comment on the prospects for coping with these difficulties. Although much of the discussion is equally applicable to current ground-based and aircraft turbine engines, special attention has been given to turbopropulsion combustion. (It should be noted that future utility turbine technology developments may depart substan-

*Staff Engineer.
+Supervisor, Fuels Division.

tially from that of aircraft systems, e.g., fluidized bed coal combustion in combined cycles.)

Additional reasons for concentrating on the aircraft system are that jet fuel represents a much more significant consumption of energy than stationary turbine fuel and that turbopropulsion systems appear likely to be affected more seriously by future fuel changes.

Since 1973, the cost and availability of aircraft jet fuels have changed drastically. Per-gallon jet fuel costs have more than tripled for both commercial and military consumers. In addition, fuel procurement actions have encountered difficulties in obtaining desired quantities of satisfactory fuel, even though consumption levels have been reduced significantly from those of 1972. These developments have encouraged initial examinations of the feasibility of producing jet fuels from nonpetroleum resources.[1-5]

Although economics and supply are primarily responsible for this recent interest in new fuel sources, projections of available world-wide petroleum resources also indicate the necessity for seeking new means of obtaining jet fuel. Regardless of current problems, the dependence on petroleum as the primary source of jet fuel can be expected to cease sometime within the next half century.[6,7]

If the general nature of future aircraft (size, weight, flight speed, etc.) is to remain similar to today's designs, liquid hydrocarbons can be expected to continue as the primary propulsion fuel. Liquified hydrogen and methane have been studied extensively as alternatives but seem to be practical only for very large aircraft. The basic nonpetroleum resources from which future liquid hydrocarbon fuels might be produced are numerous. They range from the more familiar energy sources of coal, oil shale, and tar sands to possible future organic materials derived from energy farming. Experience to date indicates that basic synthetic crudes, especially those produced from coal, will be appreciably different from petroleum crude. Reduced fuel hydrogen content would be anticipated in jet fuels produced from these alternate sources.

Because of the global nature of aircraft operations, jet fuels of the future are likely to be produced from a combination of these basic sources. Production of fuels from blends of synthetic crudes and natural crudes also may be expected. In light of the wide variations in materials from which world-wide jet fuel production can draw, it is anticipated that economics will dictate the acceptance of future fuels

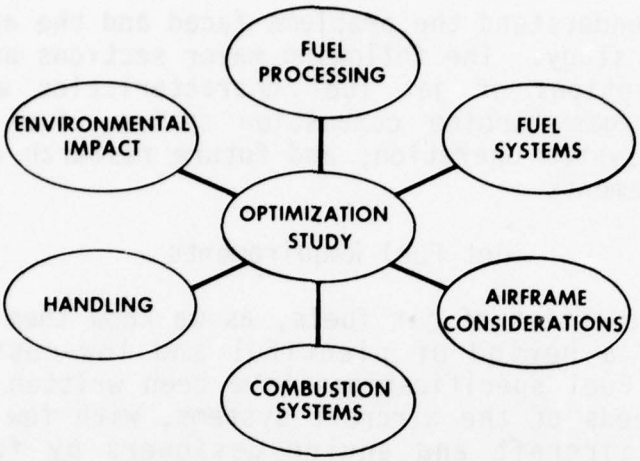


Fig. 1 Overall scheme for alternate jet fuel development program.

with properties other than those of currently used JP-4, JP-5, and Jet A. Much additional technical information will be required to identify the fuel characteristics that provide the optimum solution to the following objectives: 1) allow usage of key world-wide resources to assure availability; 2) minimize the total cost of aircraft system operation; and 3) avoid sacrifice of engine performance, flight safety, or environmental impact.

A complex program is necessary to establish the information base from which future fuel specifications can be made. Figure 1 depicts the overall nature of the required effort. Fuel processing technology naturally will be of primary importance to per-gallon fuel costs. The impact of reduced levels of refining (lower fuel costs) on all aircraft system components must be determined. These include fuel system (pumps, filters, heat exchangers, seals, etc.) and airframe (fuel tank size and design, impact on range, etc.) considerations, as well as main burner and afterburner impacts. In addition, handling difficulties (storage stability, fuel toxicity, etc.) and environmental impact (evaporative and exhaust emissions) require evaluation. The overall program must be integrated by a system optimization study intended to identify the best solution to the stated objectives.

This paper focuses on information relating to the combustion system aspects of the tradeoff. Specifically, it is intended to define the problems to be encountered and identify future directions to be undertaken in combustion research. The paper is written with sufficient background information to allow researchers not familiar with gas turbine combustion

systems to understand the problems faced and the areas requiring further study. The following major sections are concerned with descriptions of jet fuel characteristics and requirements, the gas turbine combustion system, fuel effects on combustion system operation, and future research and development requirements.

Jet Fuel Requirements

The properties of jet fuels, as we know them today, have evolved in a period of plentiful and low-cost petroleum products. Fuel specifications have been written to accommodate the needs of the aircraft systems, with few limitations placed on aircraft and engine designers by fuel quality constraints. Nevertheless, there is a direct relationship between certain properties of the fuel and the performance and durability of aircraft or associated systems. Although the primary subject of this paper is the effects of future fuels on combustion, some comments on the fuels themselves and their effects on the overall aircraft system are appropriate.

The following subsection addresses the relationships between fuel characteristics and fuel system effects. Details of combustion system effects are not included, as this topic is reserved for Sec. IV. Subsequent discussions in the current section provide a short description of current jet fuel properties and summarize recent experiences to obtain jet fuel from nonpetroleum resources.

A. Fuel System Effects

Aircraft fuel systems consist of four major components: 1) fuel tanks; 2) fuel piping, valves, pumps, meters, and filters; 3) oil/fuel heat exchangers; and 4) fuel injection equipment.

1. Fuel Tanks. Aircraft cruising at high altitude are exposed to extremely cold temperatures, and care must be taken to prevent fuel from freezing or from reaching temperatures where they attain a high viscosity. Other important fuel tank criteria relate to safety aspects of fuel handling, crash safety, and combat vulnerability. The key fuel characteristic for these factors is the flash point. This parameter is determined empirically using a controlled temperature container partially filled with fuel. A small flame is passed over the fuel/air mixture. The minimum temperature at which some evidence of ignition is observed is defined as the flash point. It has been demonstrated that this temperature corresponds approximately to conditions where the equilibrium

vapor/air mixture above the liquid fuel is at the lean flammability limit.[8]

2. Fuel Piping, Valves, Pumps, Meters, and Filters. These components must be designed to avoid excessive wear and provide reliability and easy maintainability. The system must prevent plugging from fuel impurities or vapor lock and avoid unexpected pressure drops such as those that might occur across filters. Fuel viscosity and density are key parameters that affect pumping and metering capability. The lubricating characteristics of the fuel are critical to wear and reliability of valves, pumps, and meters. Wide range in chemical composition of the fuel can give rise to additional material difficulties (e.g., seals and bearing surfaces).

3. Oil/Fuel Heat Exchangers. Cooling for the oil in the aircraft turbine engine is provided by the fuel on its way to the combustor. The temperature of the fuel in the oil/fuel heat exchanger can reach 150°C. Excessive heat load resulting in temperature exceeding this level can result in fuel breakdown and deposit formation. Such behavior can result in loss of heat-transfer effectiveness, as well as plugging problems. Special fuel quality tests for thermal stability have been established, and much effort has been expended to correlate these data with actual engine experience.

4. Fuel Injection Equipment. Both pressure-atomizing and air blast (utilizing the momentum of air flowing into the combustor) type fuel injection systems are utilized in today's aircraft turbines. In each case, the design must maintain the temperature of the liquid fuel below levels where deposits may form. This is a very difficult task in today's high-temperature systems, especially during engine shutdown, when heat is transferred to the fuel nozzle systems and nozzles under zero fuel flow conditions. Another problem associated with fuel injection is carboning or caking within the combustor (i.e., in the presence of oxygen). Carbon formation and deposition can occur if fuel is allowed to impinge on metal parts at certain temperature and pressure conditions. It is thought that this process is related to the presence of lower hydrogen content components in the fuel. Figure 2 summarizes the property/affect relationships just discussed.

B. Current Jet Fuels

Three jet fuel types are currently in wide use throughout the free world. JP-4 is the fuel used by the air forces of NATO, including the United States. Jet B, a fuel nearly

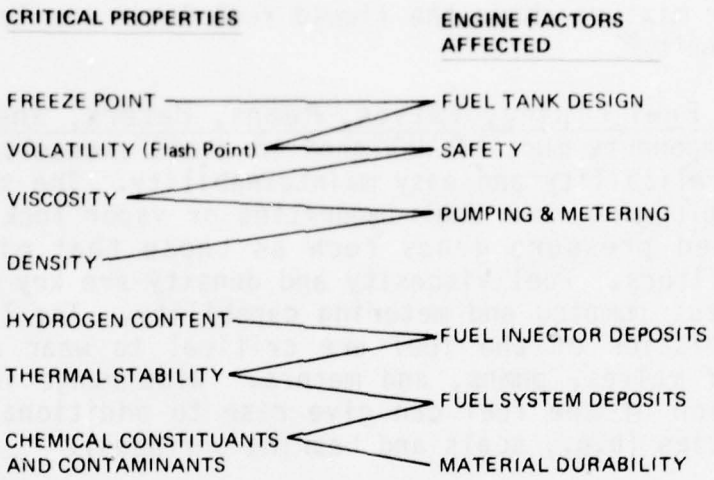


Fig. 2 Critical fuel characteristics and noncombustion effects.

identical to JP-4, is used by Canadian commercial airlines. These fuels can be represented grossly as a blend of kerosene and gasoline. The high volatility of JP-4 results in a vapor pressure of about 0.17 atm (2.5 psia) at 310K (100°F) and a flash point of approximately -25°C.

Jet A is the kerosene-based fuel used by most of the world's commercial airlines, including the United States. It has a much lower volatility than JP-4, resulting in a flash point of about 52°C. Because of the reduced probability of postcrash fires and the reduction of combat vulnerability, the NATO nation air forces are considering conversion to JP-8. This fuel is nearly identical to Jet A-1, a commercial fuel similar to Jet A in all respects except freeze point (-50°C -40°C for Jet A). The combustion characteristics of JP-8, Jet A, and Jet A-1 are virtually identical. The unique problems associated with shipboard jet fuel use cause the U.S. Navy to use a third fuel type, JP-5, which has an even higher flash point (>63°C).

Some of the physical and chemical properties of these fuels are illustrated in Table 1. Limits imposed by the various specifications[9,10] and the "typical" characteristics of delivered fuels are given. Yearly consumption figures for 1974 also are shown.

C. Jet Fuels from Nonpetroleum Resources

Recent experience with limited supplies of fuels from alternate sources has provided some insight into the devia-

Table 1 Important jet fuel properties

Property	JP-4		(Jet A-1) JP-8		JP-5	
	Spec reqm't.	Typical value	Spec reqm't.	Typical value	Spec reqm't.	Typical value
Vapor Pressure, atm, at 38°C (100°F)	0.13-0.2	0.18	...	0.007	...	0.003
Initial boiling point, °C	...	60	...	169	...	182
End point,°C	...	246	288	265	288	260
Flash point, °C	...	-25	>49	52	>63	65
Aromatic content,% vol.	<25	12	<20	16	<25	16
Olefinic content, % vol.	< 5	1	...	1	...	1
Saturates content, % vol.	...	87	...	83	...	83
Net heat of combustion, cal/g	>10,222	10,388	>10,222	10,333	>10,166	10,277
Specific gravity	0.751-0.802	0.758	0.755-0.830	0.810	0.788-0.845	0.818
U.S. yearly comsumption 10^9 gal	...	5	...	12	...	1

tions to be expected if these sources are ever exploited for aircraft use. Such fuels range from high-quality candidates obtained with routine refining to fuels that still fall short in several areas after extensive refining.

1. Fuel from Athabasca Tar Sands. A middle distillate cut (kerosene) taken from a synthetic crude oil produced by Great Canadian Oil Sands Company was found to make a JP-5 that was indistinguishable from a high-quality petroleum-derived JP-5.[11] It successfully passed all specification requirements and hardware tests. If all candidates for "future fuel" status were as amenable to aircraft operation as this one, we should not find it necessary to conduct research in their utilization.

2. Fuel from Oil Shale. The only jet fuels derived from oil shale which have been available for extensive hardware testing were part of a group of experimental products refined from 10,000 barrels of Paraho shale oil.[3] The jet fuels were intended to approach, as closely as possible, specification grades JP-4 and JP-5. The JP-4 met the specification after a minor amount of postrefining treatment; the JP-5 fell short in several characteristics.[12,13] The fuel had high gum and contamination values, a high freezing point, and poor thermal stability. The freezing point, although important, is not a factor in engine performance. The other characteristics, all related to chemical instability, caused problems during a full-scale engine test in the form of blocked filters and deposits in engine fuel injectors. However, engine performance during the test was normal. Combustor tests of the JP-4 and engine tests of the JP-5 resulted in higher than normal emissions of oxides of nitrogen because of high fuel nitrogen content.[12,13] The effects of fuel-bound nitrogen on emissions will be covered in detail later in this paper. Recent investigations in the area of shale oil refining[14] have indicated that it may be possible to minimize these problems without excessively intensive refining.

3. Fuel from Coal. A JP-5 type of fuel refined from crude coal liquids has been tested on a gas turbine engine[15] and a research combustor.[16] Although this fuel received rather intensive hydrogen treatment in both the liquefaction and refining stages, it still failed to meet the specification requirements in several respects. The thermal stability was poor, heat of combustion marginal, density too high, and smoke point too low. None of these factors had any noticeable effect on the performance of the engine. Although density is a factor in the operation of the fuel control, it did not deviate enough to cause a problem. Smoke point and thermal

stability can have long-range effects on durability which were not apparent in this short test (4 hr). In the combustor test, the effect of the low smoke point, which is related to hydrogen content, was to increase the total flame radiation. This phenomenon also will be explored in the sections on combustors. The fuel tested represented only one coal type, one liquefaction process, and a particular level of refining severity. A different set of circumstances might produce a fuel of higher or lower quality which results in different effects on an engine.

Gas Turbine Combustion System

The gas turbine employs the Brayton thermodynamic cycle: adiabatic compression, constant-pressure heat addition, and adiabatic expansion. The function of the combustion system is to accomplish the heat release with complete combustion and minimum pressure loss and to satisfy numerous engine operational requirements. This section describes the type of hardware used and the requirements that must be satisfied.

A. Description

Turbine engine combustors have undergone continuing development over the past 40 years, resulting in the evolution of a variety of basic main combustor configurations. Contemporary aircraft combustion systems may be classified broadly into one of the three types schematically illustrated in Fig. 3.

The function of the main burner is to provide for the mixing of fuel and air within the proper environment to insure their nearly complete reaction to desirable combustion products. Operation of can, cannular, and modern annular combustors is described adequately through consideration of Fig.

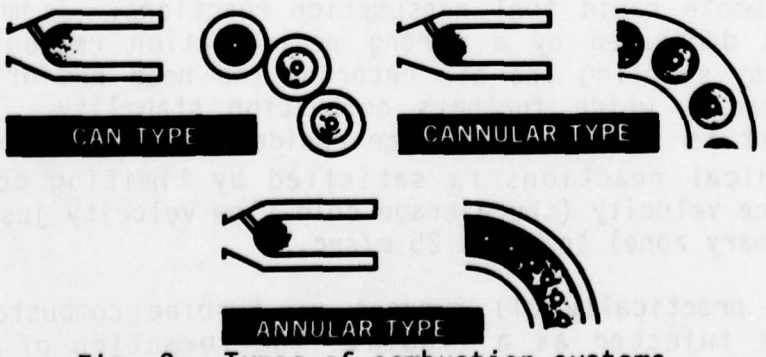


Fig. 3 Types of combustion systems.

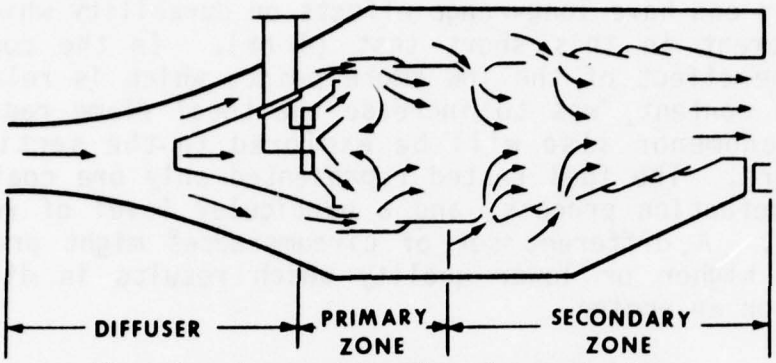


Fig. 4 Conventional main combustor.

4. In the "primary zone," fuel and oxidizer are mixed, usually in slightly fuel-rich proportions. Approximately 90% of the fuel is burned in this zone. Fuel oxidation is completed in the "secondary zone." In modern engines, turbine inlet temperatures are close to the temperature at which significant chemical reactions cease (~1600 K), and no dilution is required. However, older designs with reduced turbine inlet temperatures utilize a "dilution zone" to reduce temperature further. No significant reaction occurs within this zone.

The fuel-air ratio typically required for the combustor temperature increase is less than one-third the stoichiometric quantity: that resulting in complete O_2 consumption upon fuel conversion to CO_2 and H_2O. The equivalence ratio parameter $\emptyset$, defined as the ratio of the actual fuel-air mixture strength to that required for stoichiometric combustion, provides a convenient way of describing mixture variations through the combustor. Current primary zone equivalence ratios are about one, whereas combustor exit values are less than one-third.

The purpose of the primary zone is to stabilize combustion. High temperatures resulting from stoichiometric operation promote rapid fuel consumption reactions. Primary zone flow is dominated by a strong recirculation region (established by swirling the air entering the head end or dome of the burner), which furthers combustion stability. The requirement to insure an adequate residence time for completion of chemical reactions is satisfied by limiting combustor reference velocity (the average cold-flow velocity just behind the primary zone) to about 25 m/sec.

In practically all current gas-turbine combustors, the fuel is injected as a liquid. The formation of a well-distributed dispersion of small droplets is desirable to

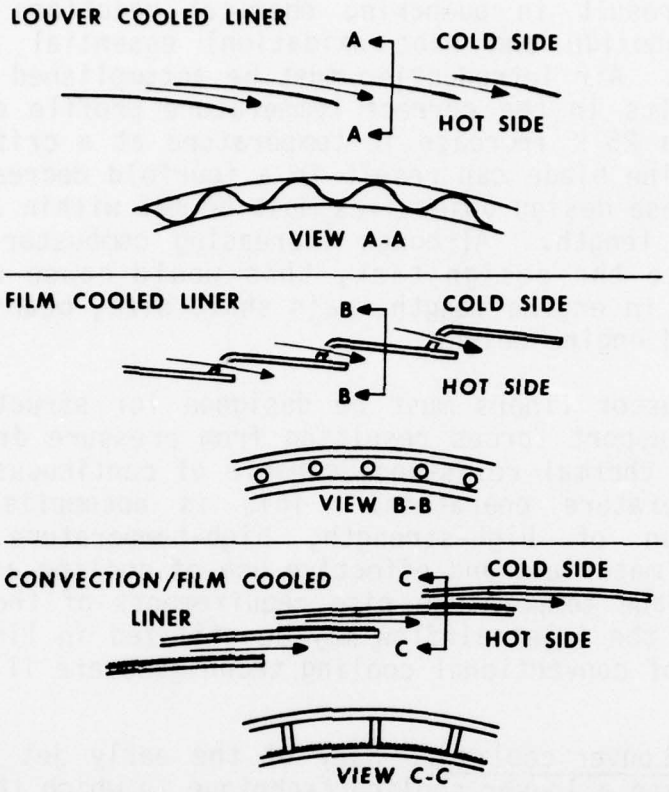


Fig. 5 Conventional combustor liner cooling techniques.

promote rapid evaporation of the fuel and intimate mixing of the fuel and air. Two general categories of fuel injectors currently are employed. Pressure atomizers utilize a large fuel pressure drop (greater than 100 psi) across a nozzle to create a finely dispersed spray of small ($<50\mu$) fuel droplets, which quickly vaporize. Air-blast atomizers create strong swirling motions of a small portion of the combustor airflow into which fuel is introduced. The severe shearing motion of the air disperses the fuel and results in small fuel droplets.

The secondary zone introduces additional air to provide for the chemical reactions that consume the products of incomplete combustion passing from the primary zone. Air participating in these chemical reactions is introduced normal to the main flow direction. The remaining air enters parallel to the main flow at the combustor walls to provide a film of cool air which protects the combustor liner and to tailor the temperature profile exiting the combustor. Design of the combustor liner hole pattern to accomplish this requirement traditionally involves a costly development effort to avoid a number of possible detrimental effects. Excessive addition of

air may result in quenching chemical reactions (especially carbon monoxide and soot oxidation) essential in reducing emissions. Air introduction must be accomplished in a manner that results in the correct temperature profile entering the turbine; a 25 K increase in temperature at a critical region of a turbine blade can result in a fourfold decrease in blade life. These design objectives must be met within a prescribed combustor length. Although increasing combustor size might facilitate the design task, this would cause undesirable increases in engine length, main shaft size, bearing requirements, and engine weight.

Combustor liners must be designed for structural integrity to support forces resulting from pressure drop and must have high thermal resistance capable of continuous and cyclic high-temperature operation. This is accomplished through utilization of high-strength, high-temperature oxidation-resistant materials and effective use of cooling air. Depending upon the temperature rise requirements of the combustor, 20-50% of the inlet airflow may be utilized in liner cooling. A number of conventional cooling techniques are illustrated in Fig. 5.

1. Louver cooling. Many of the early jet engine combustors used a louver cooling technique in which the liner was fabricated into a number of cylindrical panels. When assembled, the liner contained a series of annular air passages at the panel intersection points, the gap heights of which were maintained by simple wiggle-strip louvers. This permitted a film of air to be injected along the hot side of each panel wall, providing a protective thermal barrier. Subsequent injection downstream through remaining panels permitted replenishment of this cooling air boundary layer. Unfortunately, the louver cooling technique did not provide accurate metering of the cooling air, which resulted in considerable cooling flow nonuniformity, with attendant variations in combustor exit profiles and severe metal temperature gradients along the liner.

2. Film Cooling. This technique is an extension of the louver cooling technique but with machined injection holes instead of louvers. Consequently, airflow metering is more accurate and uniform throughout the combustion chamber. Most current combustors use this cooling technique. However, increased operating gas temperatures of future combustors will result in less air for cooling, and more advanced cooling techniques/materials will be required.

3. Convection/Film Cooling. This relatively new technique (patent pending: patent application Nos. SN 876,264 and

SN 298,434, titled "Combustion Liner," Detroit Diesel Allison Division of General Motors) permits much reduced cooling airflow (15-25%) while providing high cooling effectiveness and uniform metal temperatures. It is particularly suited for high-temperature rise combustion systems where cooling air is at a premium. The convection/film-cooled liner takes advantage of simple but controlled convection cooling enhanced by roughened walls while providing the protective boundary layer of cool air at each cooling panel discharge plane. Although somewhat similar in appearance to the louver and film-cooled liners, the convection/film coolant passage length is several times greater; more accurate coolant metering is provided, and a more stable coolant film is established at the panel exit. Principal disadvantages of this design are somewhat heavier construction, increased manufacturing complexity, and repairability difficulties.

B. System Requirements

A broad list of combustion system performance and design objectives is required of all combustors. Although this list can be quite lengthy, the more important requirements, some of which were alluded to previously, are discussed below; these focus on the aircraft application but are adaptable to the industrial/utility turbine combustors, with obvious modifications that recognize ground utilization:

1) Performance objectives: a) high combustion efficiency (100%) at all operating conditions; b) low overall system total pressure loss; c) stable combustion at all operating conditions; and d) reliable ground-level ignition and altitude relight capability.

2) Design objectives: e) minimum size, weight, and cost; f) combustor exit temperature profile consistent with turbine design requirements; g) good durability, maintainability, and reliability; and h) minimum exhaust emissions consistent with current specified limitations and regulations.

These demands are discussed in more detail in the following subsections.

1. Combustion Efficiency. Since propulsion system fuel consumption has a direct affect on aircraft system range, payload, and operating cost, it is imperative that design point combustor efficiency be as close to 100% as possible. Combustion efficiency at the high-power/high-fuel-consumption conditions of takeoff and cruise is always near 100% (usually greater than 99.5%). However, off-design efficiency, particularly at idle, can be in the low nineties.

2. Overall Pressure Loss. The combustion system total pressure loss from the compressor discharge to the turbine inlet normally is expressed as a percent of compressor discharge pressure. Losses of 5-8% typically are encountered in contemporary systems. Combustion system pressure loss is recognized as necessary to achieve certain design objectives (pattern factor, effective cooling, etc.) and also can provide a stabilizing effect on combustor aerodynamics. However, pressure loss also impacts engine thrust and specific fuel consumption. Each additional percent increase in pressure loss will result in approximately a 1% decrease in thrust and a 0.5-0.75% increase in specific fuel consumption. Consequently, design goals for pressure loss represent a compromise among the preceding factors.

3. Combustion Stability. Combustion stability is defined as the ability of the combustion process to sustain itself in a continuous manner. Stable, efficient combustion can be upset by the fuel-air mixture become too lean so that temperatures and reaction rates drop below the level necessary to heat and vaporize the incoming air and fuel effectively. Such a situation causes blowout of the combustion process. In addition to these extinction considerations, oscillatory combustion (sometimes called acoustic instability) must be avoided.

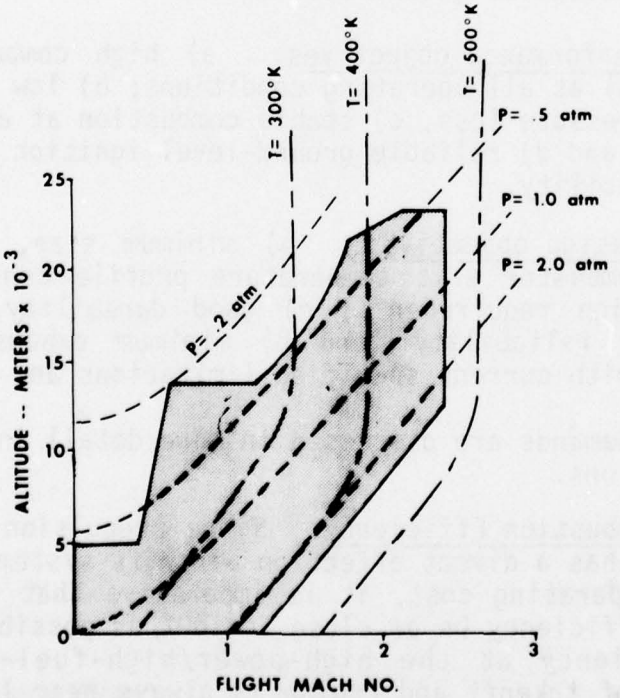


Fig. 6 Ignition/relight envelope.

4. Ignition. Ignition of a fuel-air mixture in a turbine engine combustor requires inlet air and fuel conditions within flammability limits, sufficient residence time of the potentially burnable mixture, and the location of an effective ignition source in the vicinity of the burnable mixture. Reliable ignition in the combustion system is required during ground-level startup and for relighting during altitude windmilling. The broad range of combustor inlet temperature and pressure conditions encompassed by a typical ignition/relight envelope is illustrated in Fig. 6. It is well known that ignition performance is improved by increases in pressure, temperature, fuel-air ratio, and ignition-source energy. In general, ignition is impaired by increases in reference velocity, poor fuel atomization, and low fuel volatility.

5. Size, Weight, Cost. The main combustor of a turbine engine, like all other main components, must be designed within constraints of size, weight, and cost. The combustor diameter usually is dictated by the engine casing envelope provided between the compressor and turbine and never is allowed to exceed the limiting diameter defined for the engine. Minimization of combustor length allows reduction of engine bearing requirements and permits substantial reductions in weight and cost. Advancements in design technology have permitted major reductions in combustor length. With the advent of the annular combustor design, length has been reduced by at least 50% when compared to contemporary cannular systems.

6. Exit Temperature Profile. A critical turbine-life-determining parameter controlled by the combustor design is related to the temperature uniformity of the combustion gases as they enter the turbine. In order to insure that the proper temperature profile has been established at the combustor exit, combustion gas temperature often are measured by means of high-temperature thermocouples or via gas sampling techniques employed at the combustor exit plane. A detailed description of the thermal field entering the turbine both radially and circumferentially can be determined from these data.

7. Durability, Maintainability, Reliability. A principal combustor design objective is to provide a system with sufficient durability to permit continuous operation for an acceptably long time period between scheduled major engine overhauls, at which time it becomes cost-effective to make necessary repairs and/or replacements. In the case of the main burner, durability is related predominantly to the struc-

tural and thermal integrity of the dome and liner. The combustor must exhibit good oxidation resistance and low stress levels at all operating conditions if durability is to be achieved.

A maintainable component is one that is easily accessible, repairable, and/or replaceable with a minimum of time, cost, and labor. Although most combustor liners can be weld-repaired if damaged or burned, turbine removal is required for replacement of combustors in many cases. Combustor cases and diffuser sections require minimal maintenance, and fuel nozzles and ignitors generally can be replaced and/or cleaned with minimal effort.

Reliability can be defined as the probability that a system or subsystem will perform satisfactorily between scheduled maintenance and overhaul periods. Component reliability is highly dependent on the aircraft mission, geographical location, and pilot operation, since these factors strongly affect the actual combustor temperature-pressure environment and cyclic history of the components. In that the combustor has virtually no moving parts, its reliability is related strongly to fuel nozzle and ignitor performance. Although fouling and carboning of these subcomponents are common causes for engine rejection, these problems are relatively easy to correct through normal inspection and replacement field maintenance procedures.

8. Exhaust Emissions. With the advent of environmental regulations and goals for aircraft gas turbine systems[17,18] the levels of carbon monoxide (CO), unburned hydrocarbons (HC), oxides of nitrogen (NO_x), and smoke in the engine exhaust become important. Naturally, the environmental constraints directly impact the combustion system: the principal source of nearly all pollutants emitted by the engine. Major changes to combustor design philosophy have evolved in recent years to provide cleaner operation at all conditions without serious compromise to engine performance. Further emissions reductions are being sought in efforts such as the NASA Experimental Clean Combustion Program (ECCP).[19-21]

CO and HC are the products of incomplete combustion in a gas turbine system. At design conditions (near full load or at cruise conditions), both of these emissions are negligible. However, during engine idle conditions when combustor inlet temperatures and fuel-air ratios are low, combustion efficiency decreases, and CO and HC emissions increase. Techniques to minimize these emissions focus on control of fuel-

air distribution at idle to optimize temperature and residence time conditions to provide for maximum combustion efficiency.

NO_x emissions from continuous combustion processes result from three formation mechanisms. The best-understood mechanism involves "thermal NO," which arises primarily from combination of N_2 and O present during combustion at near-stoichiometric conditions. N_2 and O equilibrium concentrations can be utilized to predict thermal NO. The second contribution "prompt NO," is not predictable by equilibrium concentration assumptions. Prompt NO is formed at the very beginning of the combustion process and is thought to be associated with active radical concentration levels far in excess of equilibrium formed during the fuel pyrolysis and chain branching, which initiates the combustion process. The third and final mechanism for NO formation is that where nitrogen chemically bonded to the fuel is converted to NO_x. Fuel nitrogen has been found to be converted very effectively to NO_x (30-100% conversion) in laboratory studies and in actual gas turbine combustion testing. This mechanism for NO_x formation is thought to be very rapid, occurring early in the combustion process during fuel pyrolysis.

The importance of each of these three contributions in gas turbine combustors is illustrated in Fig. 7. An assumed fuel nitrogen concentration of 0.3% and a 100% conversion efficiency have been used in developing this figure. Thermal and prompt NO_x values were determined with the analytical correlation of Ref. 22. At low power, combustion inlet temperature corresponding to large engine idle or small (<1000 hp) engine operation, fuel nitrogen is the predominant contribution, followed by prompt and then thermal NO_x. At high inlet temperature operation, corresponding to stationary or aircraft high-power conditions, thermal NO is the primary contribution, followed by fuel NO_x and, finally, prompt NO_x. It should be noted that current aircraft jet fuels have fuel nitrogen contents far below this level (usually less than 20 ppmw), and NO_x from fuel nitrogen is not a present concern.

Smoke is formed at higher power conditions when the primary zone of the combustor operates with its highest fuel-air ratio. The carbon particle formation processes that occur in the primary zone and the limits of soot formation will be described in Sec. IV. A.1. Techniques that have been employed to reduce smoke emission depend on the introduction of additional air into the primary zone (to achieve leaner operation) and the improvement of mixing to avoid rich fuel-air pockets.[23-28]

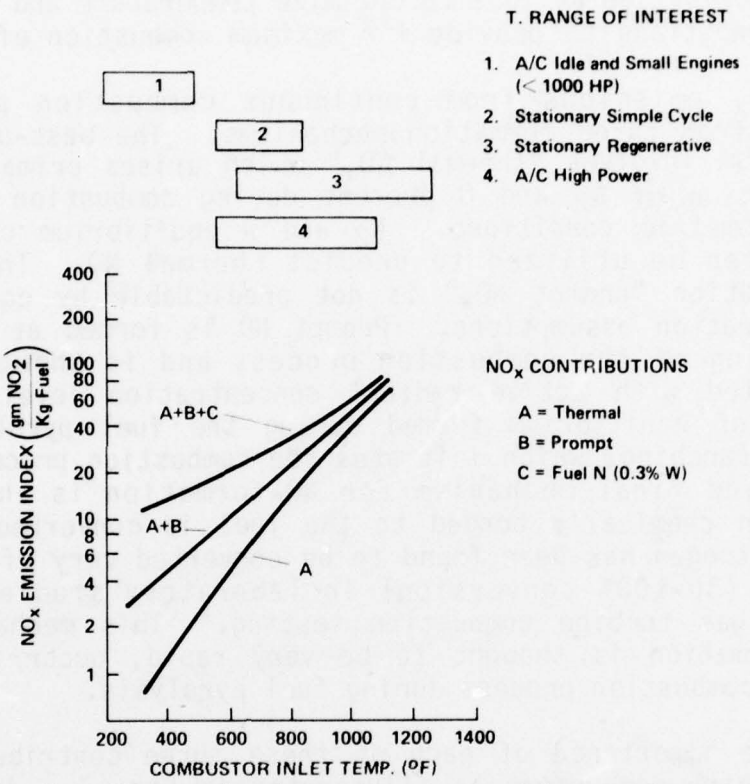


Fig. 7 NO_x mechanisms in gas turbine combustion.

Beyond the difficulty of exhaust visibility is the ill-defined issue of the health effects of emitted particulates. Although there has been some general discussion of the effects on humans of particulates of various size ranges, none of the existing regulations addressed this potential problem. It should be noted that some limited work has indicated the possibility that carcinogenic compounds may be present in gas-turbine-emitted particulates.[29]

Fuel Effects on Combustion Systems

Fuel characteristics that are most likely to affect the gas turbine combustor designer in the future are fuel hydrogen and nitrogen content and fuel thermal stability. In addition, the designer may be confronted with changes in fuel characteristics influencing volatility, viscosity, sulfur, and trace metal content. Each of these topics is discussed below.

A. Fuel Hydrogen Content

The impacts of reduced fuel hydrogen content are associated with increased rates of carbon particle formation.

Effects include increased flame luminosity, leading to higher combustion liner temperatures and increased smoke emission. The following subsections focus on the carbon particle formation process, smoke emission dependence on hydrogen content, and the effects of increased flame luminosity.

1. Carbon Particle Formation Process. Although both carbon formation and carbon consumption processes occur in continuous combustion systems, the latter are very much slower. The optimum approach for preventing hardware distress and avoiding serious environmental consequences is to develop technology to avoid carbon formation while satisfying other system requirements (efficiency, gaseous emissions, hardware reliability, etc.).

The predominance of fundamental research activity has involved laminar premixed flames. Street and Thomas' work, published in 1955, is extremely thorough in experimental detail and breadth of hydrocarbons examined;[30] it has become the classical paper in the field. Other publications are Refs. 31-42. These investigations have confirmed universally that soot formation is a kinetically controlled process. Equilibrium calculations indicate that soot should not be present at fuel-air mixture conditions where the oxygen-to-carbon atomic ratio (O/C) is greater than one. That is, the general chemical equation

$$C_xH_y + (x/2\ O_2) \rightarrow XCO + (y/2)\ H_2$$

should define a soot formation threshold. All experimental results have shown soot formation at O/C substantially in excess of unity.

Another very important premixed flame experiment conducted at the British National Gas Turbine Establishment (NGTE) attempted to evaluate the effect of pressure on soot formation.[37] All previously mentioned work with premixed flames concerned atmospheric or subatmospheric conditions. The combustion system employed took special precautions to prevent flashing back to upstream locations, an additional difficulty associated with the high-pressure operation. In addition to sooting limits, the amount of soot formed was determined and expressed as a "soot formation ratio" (the percent of fuel carbon evident as soot). The index of the soot quantity was found to increase with the cube of pressure. Very useful plots of pressure equivalence ratio for various values of soot formation ratio were presented. Examples are shown in Fig. 8 for cyclohexane, cyclohexene, and benzene.

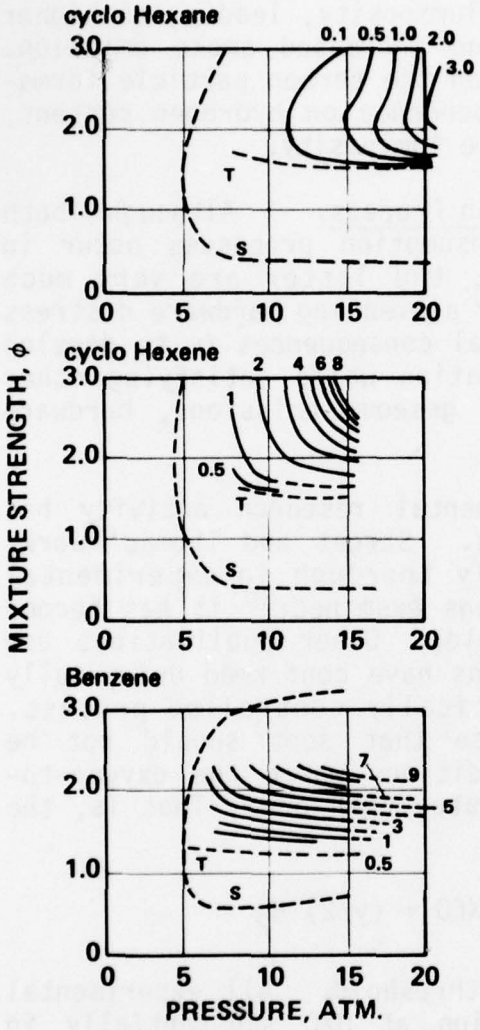


Fig. 8 Effects of pressure and mixture strength on soot formation. (S denotes flame stability limit, T the soot formation threshold, and numbers indicate conditions producting a constant "soot formation ratio.")[37]

Gas-phase species also were determined during this testing, and it was concluded that H_2O and CO_2, oxygenated compounds not predicted by equilibrium for the system $[C_xH_y + (y/2)O_2 \rightarrow XCO + (y/2)H_2]$, are formed in substantial quantities and deplete the system of oxygen prior to consumption of all fuel.

Soot formation in laminar diffusion flames also has been studied.[43-46] The direct utility of this information for the gas turbine combustion application has been questioned, as the mixing rates and characteristic times for chemical reaction are very much different from those in the typical combustor. Shirmer[47] has discussed the significant differences between such experiments and the actual combustion process. He is particularly critical of the use of the smoke point test as an index of fuel tendency to form carbon particulates. Turbulent diffusion flame results would appear to be more

applicable.[48] Wright[46] has examined soot formation in a diffusion flame burner and has published results of soot measured when the fuel side of the flame is supplemented with oxygen at concentrations well below O/C = 1. Surprisingly, it was found that the addition of oxygen increases soot formation up to an optimal rate at which the influence abruptly reverses, and soot suppression is accomplished at higher O_2 concentrations.

Wright's work involving soot formation in the jet-stirred reactor[49,50] is perhaps of most interest to this discussion; it is a combustion process similar to that at which soot forms in the primary zone of an actual continuous combustion system. As in the previously mentioned studies, it was determined that soot forms at O/C > 1, but the strong backmixing of the jet-stirred reactor did afford some broadening of the soot-free O/C ratio. In addition to the establishment of sooting limits, as determined by the color of the flame (luminous yellow blue), Wright determined the concentra-

Table 2 Carbon formation limits for various fuels

Fuel	Critical O/C ratio for incipient carbon formation		f/a mass ratio for carbon formation at well-stirred conditions
	Premixed Bunsen flame[30]	Well-stirred condition[49]	
Ethane	2.10	<1.56	>0.140
Propane	2.14	<1.41	>0.151
Hexane	2.18	<1.75	>0.119
Ethylene	1.67	1.43	0.1426
Propylene	1.79	1.40	0.146
Butene	2.08	1.48	0.138
Benzene	1.75	1.75	0.116
Toluene	1.92	1.71	0.112
Xylene	2.08	1.80	0.107
Tetralin	2.27	1.81	0.106
1-methyl napthalene	2.38	1.62	0.116

tions of soot formed for some limited conditions of O/C below the soot limit. No analysis of this "yield" data to determine soot formation kinetics was undertaken, but it is recognized that more such data might provide the basis for global carbon formation chemical models.

The key fundamental data just discussed have been summarized in Table 2. These results indicate that all hydrocarbons soot at O/C > 1. The table also illustrates broadened soot limits afforded by backmixing in the jet-stirred reactor. Figure 9 illustrates the difference in soot production between the jet-stirred reactor and a premixed laminar flame.[50] Since the troublesome aromatic compounds are present in relatively small amounts in practical fuel blends, the fuel-air ratio to achieve the design temperature rise is dominated by the balance of the fuel composition which may be relatively high in hydrogen content. Therefore, the fuel-air mass ratio for incipient soot formation is most important to the combustor designer. This information, based on the jet-stirred reactor sooting limits,[49] also has been included in Table 2. The fuel-air ratio representation emphasizes the soot-forming tendencies of the aromatic-type compounds. Consequently, attempts to utilize reduced hydrogen content fuels with increased aromatic compounds would be expected to experience the difficulties associated with soot formation.

2. Smoke and Particulate Emission Effects. Visible smoke from new gas turbine systems is not permitted by existing Federal Environment Protection Agency (EPA) regulations in the case of aircraft gas turbines and is forbidden by local regulations in the case of stationary utility and industrial

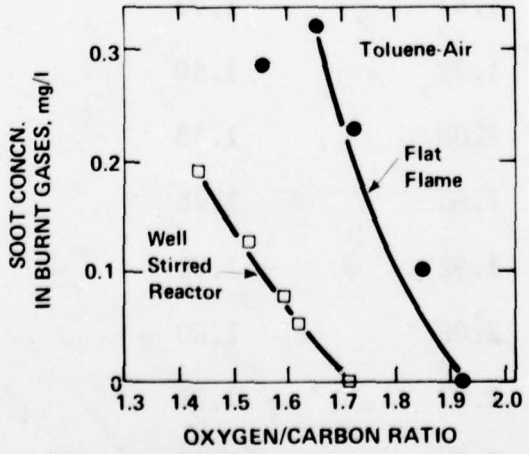


Fig. 9 Soot production in laminar and backmixed system for a toluene-air flame.[50]

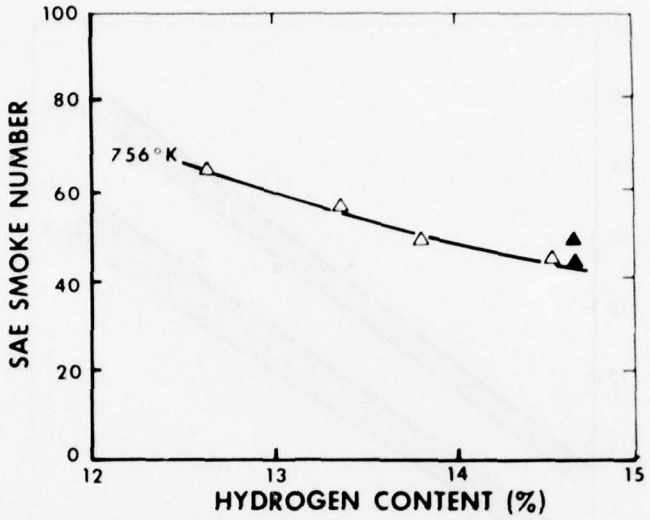


Fig. 10 Impact of reduced hydrogen content on smoke emission.[51]

turbines. Reductions in fuel hydrogen content can handicap the designer severely in his goal of attaining exhaust invisibility.

Figure 10 illustrates the relationship between smoke emission and fuel hydrogen content. These data were acquired at a combustor inlet temperature of 756 K using a T56 single-combustor rig.[51] Substantial increases in the SAE smoke number (SN) (determined from the reflectance of a smoke spot formed on filter paper after passing a known volume of exhaust sample[52]) with decreasing hydrogen content are noted at each combustor inlet temperature. These changes can cause serious visibility problems in engines with current SN values near the visibility threshold. (Depending on engine size, the threshold varies from SN = 20 to 40.) Furthermore, since the relationship between SN and particulate mass loading (gravimetric exhaust concentration) is exponential,[53] these increases represent very substantial increases in absolute particulate emission levels.

Even smaller changes in fuel hydrogn content can affect smoke emission significantly. Setting of combustion systems on both JP-4 and either JP-5 or Jet A has indicated that smoke levels are substantially lower with JP-4.[54] The higher hydrogen of JP-4 (about 14.5 vs 13.9 wt% for Jet A) is thought to be primarily responsible for the increase. The increased volatility of JP-4 also contributes toward lower smoke emission; increased volatility yields more rapid vaporization which may give better fuel/air mixing. Figure 11 illustrates one example of this type of result for the case of the CJ005 (J79) engine.[55]

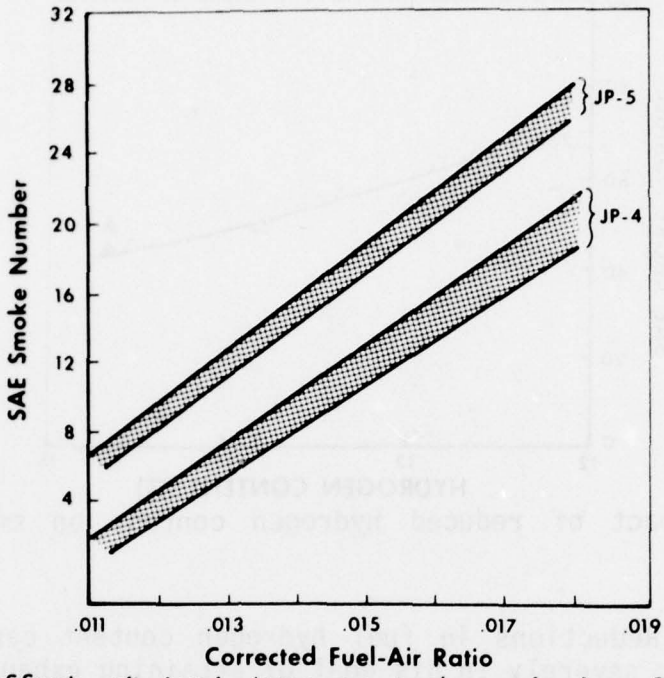


Fig. 11 Effect of fuel type on smoke emission from a CJ805 (J79) engine with low-smoke combustor.[55]

3. Flame Luminosity Effects. The flame in a gas turbine combustion system radiates energy to the combustor liners, which must be cooled with substantial quantities of compressor discharge air.[47,51,56-62] Radiation may be considered both luminous and nonluminous. The nonluminous infrared emission is due to CO_2 and H_2O band radiation, whereas the luminous component is due to radiation from carbon particles within the flame. The nonluminous portion of the flame emissivity can be calculated from[56,59]

$$\varepsilon_{n\ell} = 1 - \exp\left[-2.86 \times 10^2 \, P \, (r\ell)^{0.5} \, T_f^{-1.5}\right]$$

where

P = combustor pressure, kN/m^2

r = fuel-air mass ratio

ℓ = radiation path length, m

T_f = flame temperature, K

The conditions that would result in the highest value of $\varepsilon_{n\ell}$ correspond to high-power operation of a modern high-bypass-ratio engine: P = 30 atm = 3039 kN/m^2, r = 0.05, ℓ = 7.5

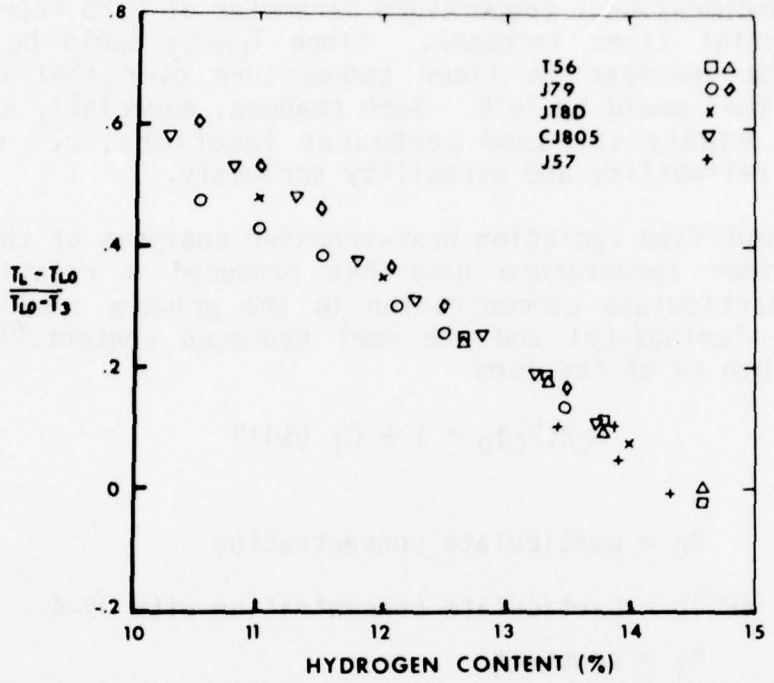


Fig. 12 Impact of reduced hydrogen content on combustor liner temperature. (T_L = combustor liner temperature with test fuel, T_{LO} = combustor liner temperature with 14.5% hydrogen JP-4, and T_3 = combustor inlet temperature).[51]

cm = 0.075 m, and T_f = 2500 K. Even under these conditions, $\epsilon_{n\ell}$ is only 0.346. Consequently, nonluminous radiation does not approach optically thick conditions. Increases in luminous emissivity resulting from use of a low-hydrogen-content fuel can have substantial heat-transfer impact.

Many investigators have studied the effect of fuel characteristics on flame luminosity and the resulting effects on liner temperature and durability.[51,63-69] Figure 12 illustrates a correlation of many of these data. This figure illustrates the relationship between hydrogen content and combustor liner temperatures for a number of aircraft gas turbine engines. The ordinate in Fig. 12 is a nondimensional temperature parameter;[51] T_L-T_{LO} is the difference between liner temperature with a given hydrogen content fuel and that obtained with a standard fuel (in this case JP-4 with 14.5% hydrogen content), and T_{LO}-T_3 is the difference between the JP-4 liner temperature and the combustor inlet temperature. The parameter is representative of the fractional increase in liner temperature (over the baseline JP-4 case). Thinking of the liner as a radiative heatflux gage, the parameter is also representative of additional radiative loading.

A nondimensional temperature parameter of 0.25 represents a substantial liner increase. Since T_{LO}-T_3 could be about 300°C, the increase in liner temperature over that of the standard fuel would be 75°C. Such changes, especially as they occur at highly stressed combustor locations, can reduce hardware reliability and durability seriously.

A simplified radiation heat-transfer analysis of the combustor liner temperature data has produced a relationship between particulate concentration in the primary zone (which increased luminosity) and the fuel hydrogen content.[68] The relationship is of the form

$$P_C/(P_C)_o = 1 + C_1 (\Delta H)^n$$

where

P_C = particulate concentration

$(PC)o$ = particulate concentration with JP-4

C_1 = constant

$\Delta H = 14.5 - H$, where 14.5 = JP-4 hydrogen content, and H is the hdyrogen content ot the test fuel

$n = 0, 1, 2,$ etc.

The best fit of the data of Fig. 12 indicated that n = 1.

More detailed evaluations of hydrocarbon type on the enhancement of luminous radiation have been pursued.[68] Figure 13 illustrates the influence of single- and double-ring aromatic compounds on the previously described nondimensional temperature parameter using results from testing with a T56 single combustor. Different hydrocarbon compounds were added to the fuel to achieve reduction in hydrogen content: napthalene is an unsaturated double-ring compound, tetralin is double ring with one saturated and one unsaturated ring, decaline is a saturated double-ring compound, and xylene is a single-ring unsaturated compound with two methyl groups. The figure illustrates that, in this instance, hydrogen content is a sufficient correlating parameter, and hydrocarbon-type influences are secondary.

B. Fuel Nitrogen Content

1. Fuel Nitrogen → NO_x Chemistry. A number of researchers have studied the fuel nitrogen problem from a fundamental standpoint.[70-79] All indications point toward

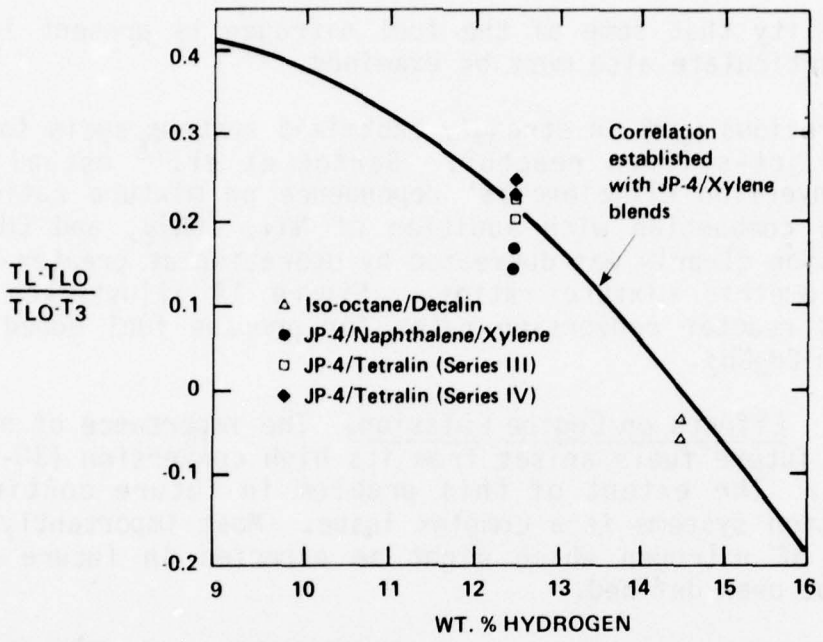


Fig. 13 Effect of low hydrogen content blending compounds on correlation.[68]

extremely rapid conversion of the fuel nitrogen to a nitrogen-containing intermediate with subsequent rapid oxidation to NO. Some correlations and models have been suggested, but it seems certain that only at rich mixture ratio conditions can minimization of NO formation be possible.

Equilibrium conditions at rich mixture conditions call for the fuel nitrogen to be converted largely to N_2. Sufficient time for the approach to equilibrium must be allowed; otherwise large quantities of the nitrogen containing intermediates can enter the burnout stage and be converted to NO_x during that process. Consequently, the kinetics of the initial fuel pyrolysis and partial oxidation process must be evaluated.

The key research needs in this area focus on 1) how to accomplish rich combustion without detrimental side effects (smoke, hardware carboning, flame radiation), and 2) what the products of rich combustion are which must be accommodated in the second-stage combustion process. The time requirements, volumetric loading limitation, inlet temperature influence, and fuel-type variations all must be considered in establishment of the rich operating limits. The form of the nitrogen compounds as they exit this first stage (i.e., NH_3, CHN, NO, etc.) as a function of operating conditions will be important to the design of the second-stage burnout process. The

possibility that some of the fuel nitrogen is present in the soot particulate also must be examined.

Previous work in strongly backmixed systems again focuses on the jet-stirred reactor. Bartok et al.[75] established NO_x conversion efficiencies' dependence on mixture ratio for methane combustion with addition of NH_3, $(CN)_2$, and CH_3NH_2. Conversion clearly was decreased by operation at greater-than-stoichiometric mixture ratios. Figure 14 illustrates jet-stirred reactor conversion rates for propane fuel doped with 500 ppm CH_3NH_2.

2. Effects on Engine Emission. The importance of nitrogen in future fuels arises from its high conversion (30-100%) to NO_x. The extent of this problem in future continuous combustion systems is a complex issue. Most importantly, the levels of nitrogen which might be expected in future fuels have not been defined.

Discussion at the recent NASA Hydrocarbon Fuels Workshop[80] indicated that the impact of fuel nitrogen on the storage and thermal stability of jet fuels may dictate levels, which, even if completely converted to NO_x, would be nearly undetectable. This conclusion, however, was drawn in consideration of petroleum-derived fuels and current technology aircraft systems and refining methodology. A more long-range look at the jet fuel nitrogen issue, where nonpetroleum fuels and improved techniques for coping with stability difficulties are considered, may alter this assessment.

The effect of increased fuel-bound nitrogen in actual engine systems is evaluated by determining the additional NO_x

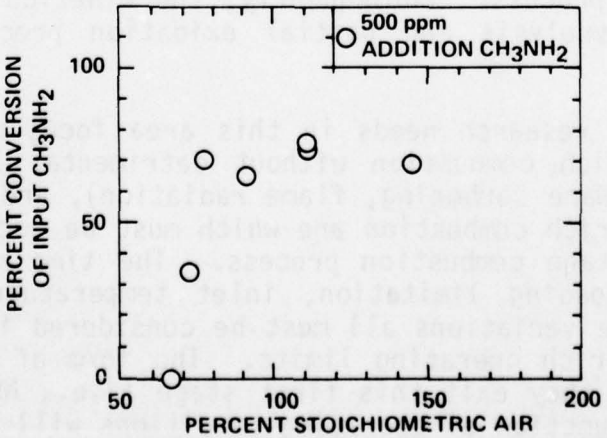


Fig. 14 Conversion of CH_3NH_2 to NO_x.[75]

emission occurring when nitrogen is present in the fuel and calculating the percent of fuel nitrogen conversion to NO_x necessary to cause this increase. Current petroleum jets fuels that have near zero (< 10 ppmw) fuel nitrogen usually are used as the zero fuel nitrogen baseline. Results presented in Fig. 15 were acquired using a standard JP-4 fuel doped with pyridine to fuel nitrogen levels of 0.1, 0.3, and 1.0 wt%.[51] A T56 single combustor was utilized in this testing. These results indicate the importance of two variables. First, as combustor inlet temperature is increased, conversion is reduced. Secondly, as fuel nitrogen concentrations are increased, conversion decreases. Other V gas turbine results of combustor testing have reached these same conclusions.[66,67,81-84]

Another observation to be made with the information presented in Fig. 15 is the conversion achieved with nitrogen naturally present in a refined jet fuel from a nonpetroleum source. In this case, the fuels were derived from Colorado oil shale resources, and nitrogen contents of 250-800 ppm resulted. The oil shale jet fuel results are shown on a band in Fig. 15 because of difficulties in accurately measuring small NO_x increases.

Stationary turbines using heavy distillate or residual fuels can be expected to be confronted more directly by fuel nitrogen considerations. Levels in some currently consumed fuels will cause significant difficulties satisfying the proposed NO_x emission requirements for ground-based turbines (75 ppmv at 15% O_2). Further fuel nitrogen increases with the use of coal or shale-derived fuels will compound this difficulty. In recognition of this problem, EPA has established a substantial contractual effort with the Pratt and Whitney Florida Research and Development Center to develop technology to limit fuel nitrogen-to-NO_x conversion.[83]

C. Fuel Stability

In many aircraft applications, the fuel is used as a coolant prior to being combusted. Subsonic applications use the fuel to cool engine oil, whereas supersonic-cruise aircraft also may require the fuel to serve as a heat sink for aerodynamic heating effects. As the fuel enters the combustor, it flows through hardware (fuel nozzles, fuel pipes, manifolds, etc.) exposed to high temperature due to heating by the compressor discharge air and often radiant heating from the combustion zone. For these reasons, the thermal stability is a closely monitored fuel quality.

The combustor designer must recognize this fuel limitation and take appropriate precautions to prevent the fuel from reaching temperatures where thermal breakdown leading to deposition can occur. Designs for low emissions involving fuel staging are especially troublesome in this respect. As the fuel flow to a stage of the combustor is started or stopped, the fuel is exposed to a transient heating. After starting, the hardware may be at an initial temperature corresponding to the compressor discharge, and thus the fuel is exposed to very high wall termperatures for a brief period. After stopping, the fuel may reach high temperatures as it slowly drains from the system with no supplemental cooling.

Another potential difficulty is the formation of carbon deposits within the combustion system. These would be distinctly different from those within the fuel system which are formed in the absence of oxygen. Unplanned impingement of fuel on combustor walls with the use of air-blast fuel injection techniques can result in substantial carbon deposit buildup. In addition to the difficulties associated with a distorted aerodynamic situation, fragments of deposit can separate from the hardware, pass through the combustor, and impinge on the turbine.[85]

The introduction of lower-hydrogen-, higher-nitrogen-content fuels would aggravate further the design difficulties of coping with the fuel's limitations. The technique that would be expected to offer improved fuel flexibility (e.g., air-blast atomization and staged combustion) may experience especially difficult problems because of liquid fuel contact with metal surfaces and intermittent fuel nozzle usage.

D. Other Fuel Factors

Volatility affects the rate at which liquid fuel introduced into the combustor can vaporize. Since important heat-release processes do not occur until gas-phase reactions take place, reduction of volatility shortens the time for chemical reaction within the combustion system. In the aircraft engine, this can result in difficulty in ground or altitude ignition capability, reduced combustor stability, increased emissions of carbon monoxide (CO) and hydrocarbons (HC), and the associated loss in combustion efficiency. Moreover, carbon particle formation is aided by the formation and maintenance of fuel-rich pockets in the hot combustion zone.[86] Low volatility allows rich pockets to persist because of the reduced vaporization rate. Again, increased particulates can cause additional radiative loading to combustor liners and increased smoke emission between JP-4 and

JP-5. Some of the differences between JP-4 and JP-5 smoke levels (Fig. 11) can be attributed to the volatility effect.

The desired formation of a finely dispersed spray of small fuel droplets is affected adversely by viscosity. Consequently, the shortened time for gas-phase combustion reactions and prolonging of fuel-rich pockets experienced with low volatility also can occur with increased viscosity. The ignition, stability, emissions, and smoke problems previously mentioned also increase for higher-viscosity fuels.

Both sulfur and trace metals are at very low concentrations in current jet fuels. Sulfur is typically less than 0.1% because the petroleum fraction used for jet fuel production is nearly void of sulfur-containing compounds. Although syncrudes from coal or oil shale may contain higher sulfur levels, it is not likely that the current specification limit of 0.4% would be exceeded with the processed jet fuel. The nature of modern turbine blade design and the operating temperatures in this component require that the trace metals be removed. Because of the way in which future jet fuels are expected to be produced, trace metals also are expected to continue to be present at low concentrations (less than 1 ppmw). Should higher levels appear possible, the necessity to preserve the high fuel efficiency benefits of the advanced technology turbine blade would justify additional expense for removal.

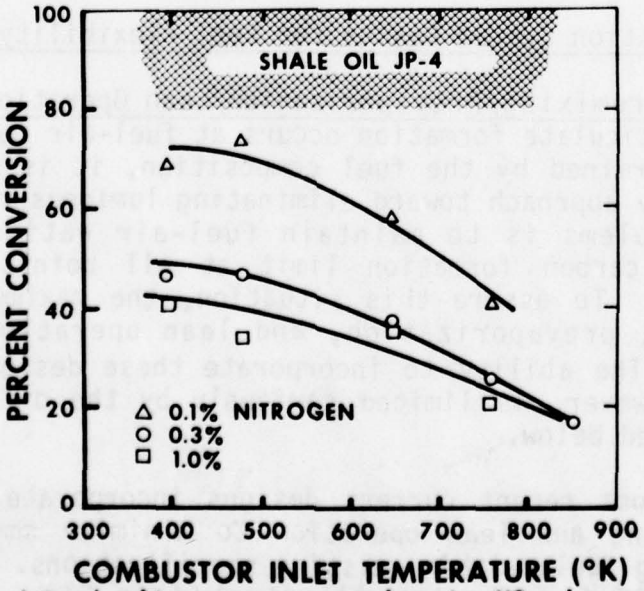


Fig. 15 Fuel-bound nitrogen conversion to NO_x in an aircraft gas turbine combustor.[51]

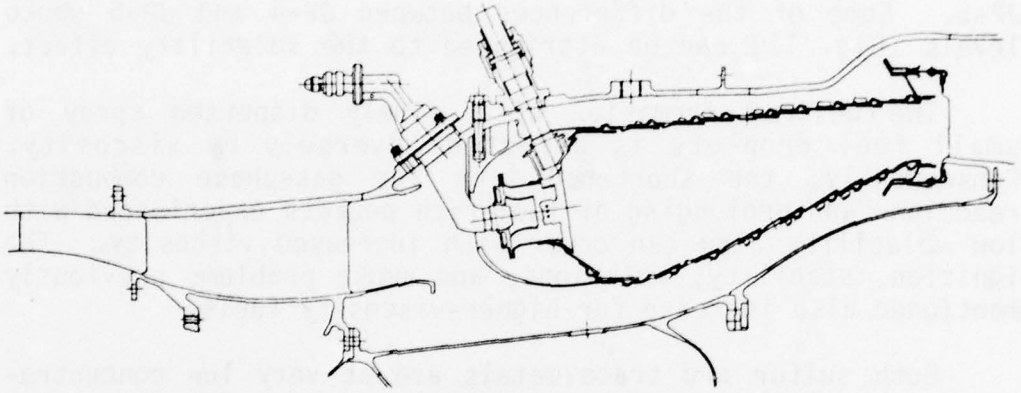


Fig. 16 CF6-50 standard combustor.[87]

Future Research and Development Requirements

In consideration of future research and development requirements, this section presents three types of information. First, the types of designs which might be expected to afford some fuel flexibility are described. Secondly, the research and technology development requirements that must be satisfied to move toward this goal are summarized. Third, the implications of the development cycle through which new technological approaches must proceed are described. This final section provides important information on time requirements for development of new engines that might have greater fuel flexibility.

A. Combustion System Design for Fuel Flexibility

1. Premixing/Prevaporization/Lean Operation. Since carbon particulate formation occurs at fuel-air ratios above a limit determined by the fuel composition, it is evident that the primary approach toward eliminating luminous radiation and smoke problems is to maintain fuel-air ratios below the incipient carbon formation limit at all points within the combustor. To assure this situation, the maximum degree of premixing, prevaporization, and lean operation should be pursued. The ability to incorporate these design characteristics, however, is limited seriously by the difficulties to be described below.

The most recent current designs incorporate some degree of premixing and lean operation to minimize smoke emission while using fuels within existing specifications. The General Electric CF-6 combustor illustrated in Fig. 16 utilizes air-blast atomization and a lean primary zone. Testing of the

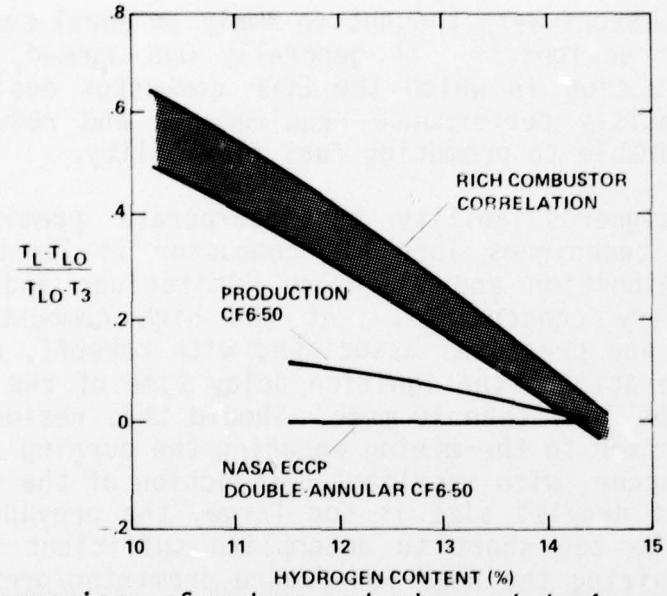


Fig. 17 Comparison of modern and advanced designs with rich combustor correlation (CF6-50 and NASA ECCP data from Ref. 87).

CF-6 combustor has produced results that indicate combustor liner temperature dependencies on fuel hydrogen content significantly below that of older designs.[87] Figure 17 compares the nondimensional temperature parameter for the CF-6 with that of the older designs established as Fig. 12. Interpreting the nondimensional temperature parameter in terms of a heat flux parameter, it is clear that the fractional increase in combustor thermal loading resulting from luminous radiation is far less for the CF-6 combustor.

Low NO_x emissions designs tested in the NASA Experimental Clean Combustor Program have a leaner, more premixed design. These advanced combustors make use of a staged design, as illustrated in Fig. 18. The first stage, being the only one fueled at idle, is designed for peak idle combustion efficiency. The second stage is only utilized at higher power conditions. This main combustion zone is designed with the primary motivation of NO_x control and operates fuel-lean. It has been found that some of these designs indicate nearly no sensitivity to fuel type; the behavior of such systems as expressed in the manner of Fig. 17 would be a horizontal line.[87] That is, all fuel-air ratios in the combustion zone must have been below the incipient sooting limit.

It should be noted that not all evidence points to greater fuel flexibility for modern engines. During the recent NASA Hydrocarbon Fuels Technology Workshop, combustor liner temperature results from the testing of some of the ECCP

advanced combustors were thought to imply an equal sensitivity to the older designs.[72] It generally was agreed, however, that the direction in which the ECCP combustor designs proceeded to satisfy performance requirements and reduce emissions is favorable to promoting fuel flexibility.

The designer's ability to incorporate premixing/prevaporization techniques into his combustor is limited seriously by preignition and flashback limitations and by combustor geometry constraints. At the high combustor inlet temperatures and pressures associated with takeoff, climbout, or cruise operations, the ignition delay time of the fuel air mixture may be less than 10 msec. Should this residence time be achieved prior to the mixing entering the burning zone, ignition will occur, with resultant destruction of the combustor hardware. If droplet size is too large, the prevaporization passage may be too short to accomplish sufficient vaporization. Recognizing the need for future premixing/prevaporization systems, a number of efforts have begun to collect fundamental information of methods of best achieving this condition in practical systems.[88,89]

2. Combustor Liner Cooling. A second, or perhaps additional, approach to avoiding hardware distress resulting from increased flame luminosity is the use of advanced combustor liner cooling techniques. Three concepts are to be reviewed

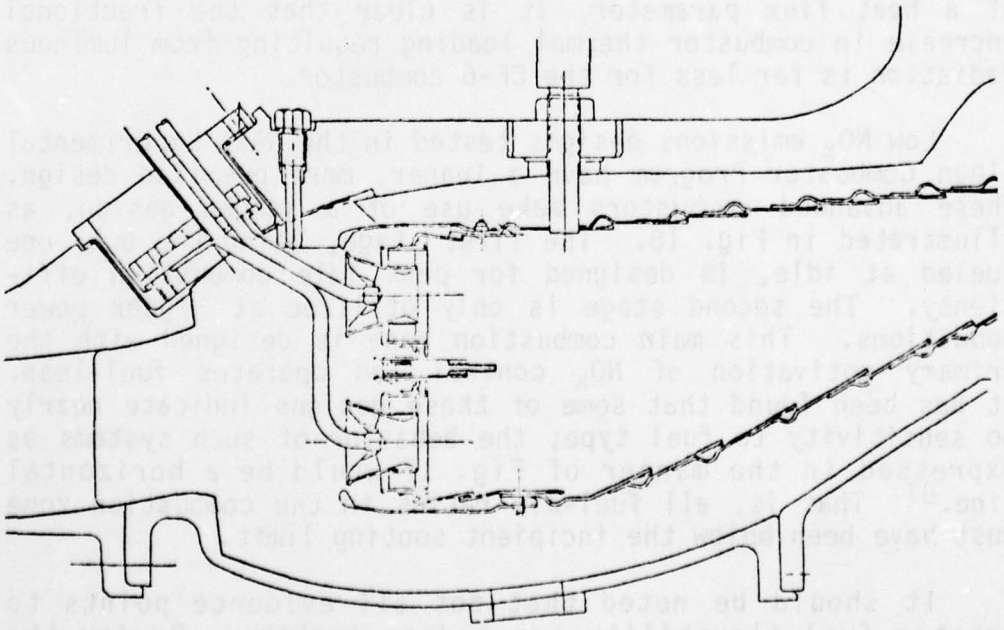


Fig. 18 General Electric double annular combustor developed during NASA ECCP program.[87]

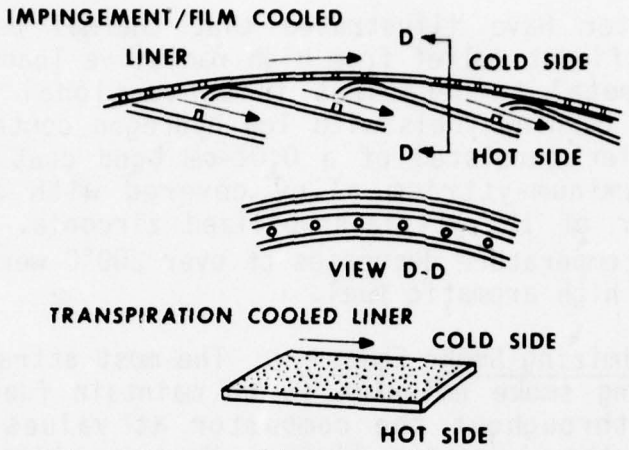


Fig. 19 Advanced combustor liner cooling techniques: a)impingement/film cooling; and b) transpiration cooling.

here: impingement/film cooling, transpiration cooling, and thermal barrier coatings. Figure 19 illustrates characteristics of each of these techniques.

The impingement/film-cooling technique is well suited for applications involving high radiative flux and minimum availability of cooling air. Small jets of air impinge on the hot side of the combustor liner, providing very effective heat transfer. When combined with the additional film-cooling feature (see Fig. 5), impingement cooling provides for excellent thermal protection of a high-temperature liner. Its disadvantages, however, are similar to those of the film/convection liner: heavier construction, manufacturing complexity, and repairability difficulties.

Transpiration cooling is the most advanced cooling scheme available and is particularly well suited for future high-temperature applications. Cooling air flows through a porous liner material, uniformly removing heat from the liners while providing an excellent thermal barrier to high combustion gas temperature. Both porous (regimesh and porolloy) and fabricated porous transpiring materials (Lamilloy, developed by Detroit Diesel Allison, Division of General Motors Corporation, Patent No. 3,584,972, titled "Laminated Porous Material," June 15, 1971) have been examined experimentally. Fabricated porous materials tend to alleviate plugging and contamination problems, inherent disadvantages of the more conventional porous materials. As can be seen in Fig. 19, transpiration cooling offers better temperature control and uniformity than any other cooling technique.

Beyond these techniques are other approaches involving coatings and thermal barriers. Recent efforts at NASA Lewis

Research Center have illustrated that thermal barriers can provide significant relief from high radiative loads, allowing acceptable metal temperatures in conventional combustion designs when burning fuels with low hydrogen content.[90] The thermal barrier consisted of a 0.01-cm bond coat of nickel-chromium-aluminum-yttrium alloy covered with a 0.025-cm ceramic layer of 12% yttria-stabilized zirconia. Combustor liner metal temperature decreases of over 200°C were indicated when using a high aromatic fuel.

3. Minimizing Smoke Emission. The most attractive means of controlling smoke emission is to maintain fuel-air ratio conditions throughout the combustor at values below the incipient carbon formation limit. However, because of the practical problems presented by premixing, prevaporization, and lean combustion, this may not be possible. In such a case, the previously discussed liner cooling techniques will be of value in handling the increased amounts of luminous radiation.

Carbon particulates that are formed will have to be oxidized within the secondary zone. Close control of mixture ratio, temperature, and residence time within this zone will be necessary to achieve maximum consumption. Radcliffe and Appleton[91] have determined that optimum consumption of particulates occurs at $\phi = 0.75$. Their particle surface consumption rates of 1-20 μm/sec indicate that particles whose initial diameter is less than 0.04 μm will be consumed in a typical residence time of 5 msec. Even with optimum conditions, however, it may not be possible to consume sufficient amounts of soot to provide acceptable exhaust levels, especially if significant agglomeration has occurred to form particles larger than 400 Å.

4. Fuel Nitrogen Conversion. The primary approaches to minimizing fuel nitrogen conversion to NO_x involve rich combustion to react fuel nitrogen to N_2, followed by lean burnout of the rich zone products. The necessity for the rich combustion zone creates substantial difficulty in the task of preventing carbon particulate formation. In brief, this limits the "window" of premixed prevaporized conditions which the designer must satisfy and creates the necessity for a sequentially staged design (rather than spatially or parallel staged design, as in the NASA ECCP combustors). Difficulties associated with the conflicting approaches to soot minimization and fuel nitrogen $\rightarrow NO_x$ control, coupled with thermal stability requirements, certainly will contribute toward a preference to remove nitrogen from future aviation fuels.

The situation is ground-based turbines, although still very difficult, is more flexible. Combustion system size and weight constraints and methods of fuel preparation might offer enough flexibility to deal successfully with the fuel nitrogen problem. It may be possible, for example, to utilize "reburn" techniques, where the injection of a reducing agent at the proper location for a sufficient time might reduce the high NO levels.[92] Such a solution would not be a quick fix, as it may be necessary to place the injection point between turbine stages and thus alter the entire turbomachinery structure.

5. Other Fuel Characteristics. Fuel thermal stability, volatility, viscosity, and sulfur and trace metal content would have significant impacts. As previously discussed, thermal stability might become a more significant problem in staged designs where fuel introduction systems are started and shut down frequently, thus undergoing substantial thermal transients. Cautious design of fuel system components and control of fuel quality will be required to overcome this difficulty.

Reduced volatility and increased viscosity would impact ground and altitude ignition capabilities. It must be emphasized that the system must be designed for and qualified at the most stringent operating parameters (in this case, lowest temperature), and future fuels might have very difficult properties at such conditions.

B. Research and Technology Requirements

Much fundamental research and technology development is required before significantly different fuels can be utilized in the gas turbine engine. Key research requirements are listed below:

1) With the exception of Wright's work,[49,50] soot formation has been studied under conditions where fuel and air were premixed, and, with the exception of the NGTE data,[37] experiments have been conducted at atmospheric pressure. Existing knowledge, based largely on the information from the premixed flame data, must be re-examined, and pressure effects must be investigated.

2) Additional information concerning the effects of mixture ratio, fuel type, pressure, and other relevant variables is necessary for the development of a better understanding of carbon particle formation.

3) Soot chemical composition, physical properties, and its radiative characteristics have not been analyzed suffi-

ciently. Each of these must be determined at the appropriate combustion conditions with representative fuels for application in environmental assessment, as well as flame heat-transfer modeling. The possible existence of polynuclear aromatic material in soot particulate size distribution and particulate contribution to luminous emissivity are of interest.

4) With respect to the determination of soot radiative properties, it should be noted that optical methods of measuring emissivity, reaction temperature, and particle size have not been applied widely. Such experiments should be conducted to satisfy a number of the informational requirments described here.

5) The effect of imperfect mixing on soot formation has not been studied in fundamental experiments. Such information is of direct practical interest. In addition, all of the fundamental information previously developed has involved completely vaporized fuels. Further studies to investigate the influences of percent vaporization and droplet size are required.

6) Evaluation of the impact of viscosity on ignition should be undertaken. An improved understanding of droplet atomization and distribution with high-viscosity fuels should be developed, and modeling of the process should be accomplished.

7) New methods of fuel injection must be developed which provide optimum liquid fuel vaporization and fuel-air mixing to avoid carbon particle formation difficulties in rich fuel-air pockets. To this end, an improved understanding of preignition and flashback must be developed.

While these research requirements are being satisfied, a number of technology development tasks will demand attention:

1) An assessment of the impact of fuel characteristics on existing combustion systems is required. This data base will define the limits of fuel flexibility and any associated performance or durability penalties that might be expected of in-use designs. Since most of this assessment would be conducted using combustor rigs, some extension or verification testing in actual engines is necessary.

2) Retrofit technology may be necessary to maintain current performance levels (especially altitude and ground

ignition characteristics) while avoiding problems of smoke emission and excessive combustor liner temperature when fuels of significantly different type are used. This new technology should be defined.

3) Advanced technology combustors, such as those developed in the NASA Experimental Clean Combustor Program (ECCP), must be assessed in the same manner, and technology must be defined to accommodate fuels of significantly different character while achieving the reduced emission levels.

4) Modeling capability to allow prediction of fuel effects in the combustor system (especially smoke emission, ignition characteristics, and radiant loading) will be necessary. Current analytical capabilities to predict gaseous exhaust emissions should prove to be a worthwile starting point for these efforts.

5) Improved methods of describing fuel characteristics are required; current test methods do not correspond to conditions within the modern gas turbine combustion system. Solution of fuel-related difficulties in the future will be impeded by this situation if not corrected. Furthermore, existing measurement methods are often not sufficiently accurate. Since fuel hydrogen contents from 12-14% wt are of interest to aircraft fuel effects studies,[80] a method of measurement with accuracy to 0.02% wt should be developed. Currently used methods produce results far from this level of confidence.

6) Methods to relate combustion system data to final information for tradeoff assessments are required. For example, the commonly measured parameter combustor liner temperature is not in itself meaningful; this information must be related to the reduced durability of the component and to the increased costs of operation with the new fuel.

7) Tradeoff studies to define the optimum fuel characteristics for the future must be undertaken. Combustion difficulties are but one aspect of this complicated problem, which also includes the cost of fuel refining, world-wide availability considerations, and handling considerations.

C. Development Cycle Implications

Depending upon the state-of-the-art of existing technology, the period required for implementation of fuel flexible concepts may range from as little as seven years to more than 13 years. Under this subsection, the timing for implementing

the three basic technology categories (current technology, midterm technology, and advanced technology) is considered.

1. Current Technology. Technology concepts that involve minor changes to conventional hardware design would require a minimal development period. Modifications to the combustor hardware for existing engines or engines in development normally would begin with combustor rig testing (not involving the actual engine). Any planned engine developments would follow this testing. These activities would be included in an advanced development program (ADP). Although the time required is dependent on complexity and degree of risk, a period of about three years normally is required. Other techniques not involving combustor hardware modifications (e.g., improved fuel distribution control) would not require this long development and demonstration period; a six-month to one-year period of investigation would be suitable.

The results then are incorporated into an engine for ground testing where performance, endurance, and other problems are analyzed and appropriate design changes are made. Flight suitability and propulsion system performance impact and compatibility will have been investigated thoroughly after this engineering development program (EDP), which generally requires an additional three years.

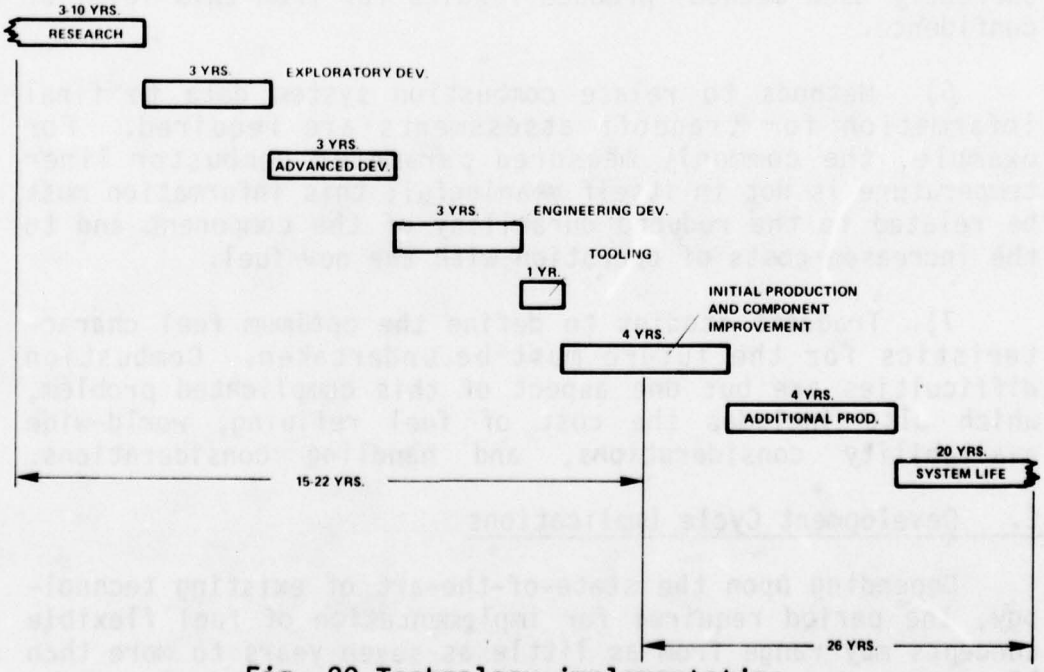


Fig. 20 Technology implementation.

Implementation into the aircraft plant may be delayed yet an additional year for acquisition of special tooling and establishment of the production routine. Figure 20 illustrates that, when technology is considered ready for advancement development, the total time to production will be approximately seven years.

2. Midterm Technology. Technology concepts that have been defined generally but not yet developed to the point where benefits are substantiated fully and hardware approaches are defined fall into the midterm technology category. These concepts will require considerably more development than those state-of-the-art techniques discussed previously. Midterm technology control measures normally will begin with an exploratory development effort (similar to the NASA ECCP efforts previously discussed) to establish firmly component capabilities and limitations. This effort typically requires three years to complete.

Once the technology has been established firmly through exploratory development, subsequent steps similar to those described for current technology may be undertaken. Figure 20 illustrates these phases and indicates a total time to production for midterm technology hardware of approximately 10 years.

3. Advanced Concepts. Advanced techniques for fuel flexibility will require even longer technology development periods. The advanced technology candidates will require a period of 3-10 years of basic and/or fundamental concept research. Once a sound understanding has been established relative to how this new emissions control concept functions, an exploratory research and development program may be established to develop and apply this new technology further. Progress beyond the research stage then would be similar to the schedule described for midterm technology. Total time in this case would be 13-20 years, as indicated in Fig. 20.

Beyond development of the production design and tooling is production itself. The production phase might be considered in two stages. First is that stage where production is accompanied by significant component improvement: changes in design which respond to field problems. Substantial engineering involvement occurs during the first half of this period. Second comes the period of production with only minor changes. These have been shown in Fig. 20 as two four-year periods. Naturally, the demand for each engine can cause this time period to vary significantly, and this total eight-year time period is chosen only for purposes of illustration. The

engine finally produced during this process has an anticipated lifetime on the order of 20 years.

This discussion reminds us of the time requirements to realize benefits of our research. Today's finding may result in a concept that can be accomplished with minor hardware modification (production realized in seven years) or one that is categorized as a midterm concept (realized in 10 years). Significant increases in fuel flexibility, however, are likely to require research, and, in this case, time periods of 13-20 years will be required before production. The engines based on concepts generated in research programs are begun today and will be in the inventory of aircraft 41-48 years beyond initiation of this work.

It may be that some fuel flexibility can begin to be acquired with minor system changes in the relative near term (beyond 1985). Greater flexibility could be the target for the fleet of aircraft to be produced in the far term (beyond 2000), consistent with the long lead times required to develop and implement truly new technology. The tradeoff studies discussed previously should consider the suitability of this implementation schedule vis-a-vis the availability and cost-effectiveness of projected future energy resources.

Summary

Increased cost and reduced availability of jet fuels, along with the potential future depletion of world-wide petroleum resources, has created an interest in the feasibility of obtaining jet fuel from nonpetroleum resources. Crude oils from coal, oil shale, and tar sands, alone or in mixtures with petroleum crudes, are likely possibilities. Because of basic chemical differences in these crudes, and processing economics, future fuels may have properties that are different from those of current fuels. Programs are necessary to provide the information base for future specifications. The end objective is to optimize the factors of availability, cost, aircraft performance, and safety.

The properties of modern jet fuels have evolved over a number of years in response to the operational requirements of aircraft and economic/supply factors connected with petroleum refining. The aircraft systems for which performance and durability are sensitive to fuel properties are the pumping and metering systems and the combustion/turbine system. Density, viscosity, lubricity, volatility, thermal stability, freeze point, and material compatibility all impact on the fluid flow systems. Volatility, hydrogen content, thermal

stability and viscosity, and the presence of certain minor constituents are related to combustor performance and/or combustor and turbine durability. Military and commercial specifications controlling the important fuel properties have been developed in an era of plentiful natural petroleum, and changes may be required in order to assure an adequate supply of economical fuel in the future. The combustion process is one of the most sensitive areas to changes in fuel properties.

Fuel characteristics that are most likely to affect future gas turbine combustor design are the hydrogen and nitrogen content and the thermal stability. The impacts of reduced fuel hydrogen content are associated with increased rates of carbon particle formation. Effects include increased flame luminosity, leading to higher combustor liner temperatures and increased smoke emission. The carbon particle information process is discussed, and data are presented to show the dependency of smoke emission on hydrogen content and the effects of hydrogen content on flame luminosity and liner temperature.

The nitrogen content of the fuel can have a strong effect on the emission of oxides of nitrogen (NO_x). Conversion efficiency of fuel-bound nitrogen to NO_x varies with fuel nitrogen concentration and variations in combustion conditions but has been found to be high in conventional fuels to which N-containing compounds have been added, as well as in fuels derived from shale oil (30-100%). Although there is no substantial contribution to NO_x emission from the fuel nitrogen in conventional jet fuels (the nitrogen contents being extremely low), future jet fuels derived from synthetic crude sources may have higher nitrogen contents, which could contribute to total NO_x emissions. The thermal stability of the fuel also is affected by nitrogen content, as well as by other possible differences in future fuels. Because of high convective and radiative heat loads on parts of the fuel injection system, careful design will be required to avoid harmful deposits. Other factors to be considered in combustors for future fuels are volatility, viscosity, sulfur, and trace metals.

Combustor research and development is needed to accommodate future fuels. Fuel flexibility is provided in recent designs with the use of premixing of fuel and air, partial prevaporizing of the fuel, and operation at lean fuel/air mixtures. New techniques in combustor liner cooling have the potential to reduce the impact of the higher flame luminosity caused by low hydrogen content. The primary approaches to

minimizing fuel nitrogen conversion involve rich combustion, followed by lean burnout. Much fundamental research and technology development still is required. Additional information is needed on the effects of all of the important fuel and combustor variables on soot formation and on the chemical and physical characteristics of the soot. Evaluation of the impact of viscosity on ignition should be undertaken, and new methods of fuel injection must be developed to improve droplet atomization and mixing. Modeling capability for predicting fuel effects is needed. Improved ways of describing fuel characteristics also are required. Finally, tradeoff studies are needed to identify the optimum fuel characteristics that maximize availability, minimize cost, and preserve flight safety.

It should be noted that the development of tommorrow's sophisticated gas turbine engines requires a complex and costly process. New concepts derived from research and development require from seven to 10 years before actual production occurs. Even longer time periods (up to 20 years) are required if research is necessary to accomplish goals. Furthermore, because of the typical 20-year lifetime of a new engine, significant impact on the fleet of operational engines will require a very long time period beyond the time of initial production. These factors encourage the research and development community associated with gas turbines to assess the potential for fuel flexibility and to evaluate the related cost/availability tradeoffs. This task is one requiring immediate attention. From these results, the general direction for future technology direction can be identified, and movement toward realization of these advantages can begin.

References

[1]Goen, R. L., Clark, C. F., and Moore, M. A., "Synthetic Petroleum for Department of Defense Use," Air Force Aero Propulsion Lab., AFAPL-TR-74-115, Nov. 1973.

[2]Shaw, H., Kalfadelis, C. D., and Jahnig, C. E., "Evaluation of Methods to Produce Aviation Turbine Fuels from Synthetic Crude Oils, Phase I," Air Force Aero Propulsion Lab., AFAPL-TR-75-10, Vol. I, March 1975.

[3]Bartick, H., Junchal, K., Switzer, D., Bowen, R., and Edwards, R., "The Production and Refining of Crude Shale Oil into Military Fuels," Office of Naval Research, Arlington, Va., Final Rep. for Contract N00014-75-C-0055.

[4]Jaarsma, F., "Impact of Future Fuels on Military Aero Engines," AGARD Annual Meeting, 1974.

[5]Antoine, A. C. and Gallagher, J. P., "Synthesis and Analysis of Jet Fuels from Shale Oil and Coal Syncrudes," NASA TM X-73399, Aug. 1976.

[6]Longwell, J. P., "Synthetic Fuels and Combustion," Sixteenth International Symposium on Combustion, The Combustion Institute, Pittsburgh, Pa., Aug. 1976.

[7]Pinkel, I. I., "Future Fuels for Aviation," AGARD Advisory Rept. 93, Jan. 1976.

[8]Nestor, L. J., "Investigation of Turbine Fuel Flammability Within Aircraft Fuel Tanks," Federal Aviation Agency, Rept. DS-67-7, July 1967.

[9]Military Specification MIL-T-5624K, Turbine Fuel, Aviation, Grades JP-4 and JP-5.

[10]Standard Specification for Aviation Turbine Fuels, D1655, American Society for Testing and Materials.

[11]Maggitti, L., "Interim Progress Report on Development of Alternate Sources of JP-5 Fuel," Naval Air Propulsion Test Center Rep., Aug. 1974.

12Blazowski, W.S., Fahrenbruck, F. W., and Tackett, L. P., "Combustion Characteristics of Oil Shale Derived Jet Fuels," WSS/CI Fall Technical Meeting, Palo Alto, Calif., Paper 75-13, Oct. 20-21, 1975.

[13]Solash, J., Nowack, C. J., and Delfosse, R. J., "Evaluation of a JP-5 Type Fuel Derived from Oil Shale," Naval Air Propulsion Test Center, NAPTC-FE-82, May 1976.

[14]Kalfadelis, C. D., "Evaluation of Methods to Produce Aviation Turbine Fuels from Synthetic Crude Oils, Phase 2," Air Force Aero Propulsion Lab., AFAPL-TR-75-10, Volume II, May 1976.

[15]Nowack, C. J., Solash, J., and Delfosse, R. J., "Evaluation of Coal-Derived JP-5 Fuels," CEP Technical Manual, Vol. 3, 1977, pp. 122-126.

[16]Moses, C. and Naegeli, D., "Investigation Into the Effects of Extending JP-5 Fuel Specifications on Combustor Performance," Southwest Research Inst. (to be published).

[17]"Control of Air Pollution from Aircraft and Aircraft Engines," Federal Register, Vol. 38, July 17, 1973.

[18]Blazowski, W. S. and Henderson, R. E., "Aircraft Exhaust Pollution and its Effect on the U.S. Air Force," Air Force Aero Propulsion Lab., AFAPL-TR-74-64, Aug. 1974.

[19]Roberts, R., Peduzzi, A., and Niedzwiecki, R. W., "Low Pollution Combustor Designs for CTOL Engines--Results of Experimental Clean Combustor Program," AIAA Paper 76-762, Palo Alto, Calif., July 1976.

[20]Gleason, C. C. and Niedzwiecki, R. W., "Results of the NASA/General Electric Experimental Clean Combustor Program," AIAA Paper 76-763, July 1976.

[21]Roberts, R., Fiorentino, A. J., and Diehl, L., "The Pollution Reduction Technology Program for Can-Annular Combustor Engines--Description and Results," AIAA Paper 76-761, Palo Alto, Calif., July 1976.

[22]Blazowski, W.S., Walsh, D. E., and Mach, K. D., "Operating and Ambient Condition Influences on Aircraft Gas Turbine NO_x Emissions," Journal of Aircraft, Vol. 12, Feb. 1975, pp. 110-115.

[23]Faitani, J. J., "Smoke Reduction in Jet Engines Through Burner Design," Society of Automotive Engineers, Paper 680348, April 1968.

[24]Durrant, T., Fiorello, S. C., Faitani, J. J., Hochheiser, S., and Lozano, E. R., "Combustor Design Changes Reduce Smoke from Gas Turbine Engines," SAE Journal, Vol. 77, June 1969, pp. 61-64.

[25]Taylor, W.G., Davis, F.F., Jr., DeCorso, S. M., Hussey, C. E., and Ambrose, M. J., "Reducing Smoke from Gas Turbines," Mechanical Engineering, Vol. 90, July 1968, pp. 29-35.

[26]Hilt, M. B., Fenimore, C. P., and Johnson, R. H., "Hydrocarbon Combustion Smoke and its Elimination from Heavy Duty Gas Turbines," American Society of Mechanical Engineers, Paper 70-PWR-14, Sept. 1970.

[27]Nelson, A. W., "Development of a Reduced Smoke Combustor for the JT3D Engine," Society of Automotive Engineers, April 1974.

[28]Bahr, D. W., Smith, J. R., and Kenworthy, M. J., "Development of Low Smoke Emission Combustors for Large Aircraft Turbine Engines," AIAA Paper 69-493, U.S. Air Force Academy, Colo., June, 1969.

[29]Shabod, L. M. and Smirnov, G. A., "Aircraft Engines as a Source of Carcinogenic Pollution of the Environment (Benzo-a-pyrene Studies)," Atmospheric Environment, Vol. 6, No. 2, 1972, pp. 153-164.

[30]Street, J. C. and Thomas, A., "Soot Formation in Premixed Flames," Fuel, Vol. 34, 1955, pp. 4-36.

[31]Daniels, P. H., "Carbon Formation in Premixed Flames," Combustion and Flame, Vol. 4, March 1960, pp. 45-49.

[32]Tesner, P. A., "Formation of Dispersed Carbon by Thermal Decomposition of Hydrocarbons," 7th Symposium (International) on Combustion, Williams and Wilkins, Baltimore, Md., 1959.

[33]Chakraborty, B. B. and Long, R., "The Formation of Soot and Polycyclic Aromatic Hydrocarbons in Diffusion Flames III; Effect of Additions of Oxygen to Ethylene and Ethane Respectively as Fuels," Combustion and Flame, Vol. 12, Oct. 1968, pp. 469-476.

[34]Homann, K. H., "Carbon Formation in Premixed Flames," Combustion and Flame, Vol. 11, Aug. 1967, pp. 265-287.

[35]Gill, D. W., "Review No. 182 - Luminosity and Soot Formation in Hydrocarbon Flames," BCURA Monthly Bulletin, Vol. XXII, Nov. - Dec. 1958, pp. 487-506.

[36]Clarke, A. E., Hunter, T. G., and Garner, F. H., "The Tendency to Smoke of Organic Substances on Burning," Journal of the Institute of Petroleum, Vol. 32, pp. 627-642.

[37]MacFarlene, J. J., Holderness, F. H., and Whiteher, F. S. E., "Soot Formation Rates in Premixed C_5 and C_6 Hydrocarbon-Air Flames at Pressure Up to 20 Atmospheres," Combustion and Flame, Vol. 8, Sept. 1964, pp. 215-229.

[38]Schalla, R. L. and Hibbard, R. R., "Smoke and Coke Formation in the Combustion of Hydrocarbon-Air Mixtures," Basic Considerations in the Combustion of Hydrocarbon Fuels with Air, Chap. IX, NACA Rept. 1300, 1957, pp. 242-255.

[39]Fenimore, C. P., Jones, G. W., and Moore, G. E., "Carbon Formation in Quenched Flat Flames at 1600°K," 6th Symposium (International) on Combustion, Williams and Wilkins, Baltimore, Md., 1956, pp. 247-254.

[40]Stehling, F. C., Frazee, J. E., and Anderson, R. C., "Carbon Formation from Acetylene," 6th Symposium (Interna-

tional) on Combustion, Williams and Wilkins, Baltimore, Md., 1956, pp. 247-254.

[41]D'Alessio, A., DiLorenzo, A., Sarofim, A. F., Beretta, F., Masi, J., and Venitozzi, C., "Soot Formation in CH_4-O_2 Flames," 15th Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, Pa., 1974, pp. 1427-1438.

[42]Palmer, H. B. and Cullis, C. F., "The Formation of Carbon from Gases," Chemistry and Physics of Carbon, Vol. 5, edited by P. L. Walker, Marcel Dekker, Inc., 1975.

[43]Schalla, R. L. and McDonald, G. E., "Mechanism of Smoke Formation in Diffusion Flames," 5th Symposium (International) on Combustion, Williams and Wilkins, Baltimore, Md., 1954, pp. 316-323.

[44]Arthur, J. R. and Napier, D. H., "Formation of Carbon and Related Materials in Diffusion Flames," 5th Symposium (International) on Combustion, Williams and Wilkins, Baltimore, Md., 1954, pp. 303-315.

[45]Gaydon, A. G. and Fairbairn, A. R., "Carbon Formation for C_2H_2 and CO in Dishcharge Tubes," 5th Symposium (International) on Combustion, Williams and Wilkins, Baltimore, Md., 1954, pp. 324-328.

[46]Wright, F. J., "Effect of Oxygen on the Carbon Forming Tendencies of Diffusion Flames," Fuel, Vol. 53, Oct. 1974, pp. 232-235.

[47]Schirmer, R. M., "Effect of Fuel Composition on Particulate Emissions from Gas Turbine Engines," Emissions from Continuous Combustion Systems, edited by W. Cornelius and W. G. Agnew, Plenum Publishing Corp., N.Y., 1972.

[48]Magnusson, B. F., "An Investigation into the Behavior of Soot in a Turbulent Free Jet C_2H_2 Flame," 15th Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, Pa., 1974, pp. 1415-1425.

[49]Wright, F. J., "The Formation of Carbon Under Well-Stirred Conditions," 12th Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, Pa., 1968, pp. 867-875.

[50]Wright, F. J., "Carbon Formation Under Well-Stirred Conditions, Part II," Combustion and Flame, Vol. 15, Dec. 1970 pp. 217-222.

[51]Blazowski, W. S., "Combustion Considerations for Future Jet Fuels," 16th Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, Pa., Aug. 1976.

[52]"Aerospace Recommended Practice 1179: Aircraft Gas Turbine Smoke Measurement," Society of Automotive Engineers Committee E-31, 1970.

[53]Champagne, D. L., "Standard Measurement of Aircraft Gas Turbine Exhaust Smoke," American Society of Mechanical Engineers, Paper 71-GT-88, March-April 1971.

[54]Blazowski, W. S., "The Impact of JP-4/JP-8 Conversion on Aircraft Engine Exhaust Emissions," Air Force Aero Propulsion Lab., AFAPL-TR-76-20, May 1976.

[55]Bernier, T. R., "T5 and T6 Profile Studies of Fleet Leader Reduced Smoke Combustors," General Electric Co., Aircraft Engine Group, Evandale, Ohio, TM 75-214, March 1975.

[56]Reeves, D., "Flame Radiation in an Industrial Gas Turbine Combustion Chamber," National Gas Turbine Establishment, Memo. M285, Oct. 1956.

[57]Schirmer, R. M. and Aldrich, E. W., "Microburner Studies of Flame Radiation as Related to Hydrocarbon Structure," Phillips Petroleum Co., Research Div., Rept. 3752-64R for NAVY BUWEPS Contract 63-0406-d, May 1964.

[58]Quigg, H. T., "Effect of Prevaporized JP-5 Fuel on Combustor Performance," Phillips Petroleum Co., Research and Development, Rept. 6413-72 for Naval Air Systems Command Contract N00019-71-C-0486, Oct. 1972.

[59]Lefebvre, A. H., "Radiation from Flames in Gas Turbines and Rocket Engines," 12th Symposium (International) on Combustion, Williams and Wilkins, Baltimore, Md., 1969, pp. 1247-1254.

[60]MacFarlane, J. J., "Flame Radiation Studies Using a Model Gas Turbine Primary Zone," 12th Symposium (International) on Combustion, Williams and Wilkins, Baltimore, Md., 1969, pp. 1255-1254.

[61]Marsland, J., Odgers, J., and Winter, J., "The Effects of Flame Radiation on Flame Tube Temperatures," 12th Symposium (International) on Combustion, Williams and Wilkins, Baltimore, Md., 1969, pp. 1265-1276.

[62]Colket, M. B., Stefucza, J. M., Peters, J. E., and Mellor, A. M., "Radiation and Smoke from Gas Turbine Flames, Part II Fuel Effects on Performance," TACOM Systems Lab., U.S. Army Tank Automotive Command, Warren, Mich., TR 12163, Jan. 1977.

[63]Schirmer, R. M., McReynolds, L. A., and Daley, J. A., "Radiation from Flames in Gas Turbine Combustors," SAE Transactions, Vol. 68, 1960, pp. 554-561.

[64]Macaulay, R. W. and Shayeson, M. W., "Effects of Fuel Properties on Liner Temperatures and Carbon Deposition in the CJ805 Combustor for Long Life Applications," American Society of Mechanical Engineers, Paper 61-WA-304, Oct. 1961.

[65]McClelland, C. C., "Effects of Jet Fuel Constituents on Combustor Durability," Naval Air Propulsion Test Center, Rept. NAEC-AEL-1736, May 1963.

[66]Butze, H. F. and Ehlers, R. C., "Effect of Fuel Properties on Performance of a Single Aircraft Turbojet Combustor," NASA TM-X-71789, Oct. 1975.

[67]Stettler, R. J. and Hardin, M. C., "Initial Evaluation of Coal Derived Liquid Fuels in a Low Emission and Conventional Turbine Combustor," General Motors Engineering Publ. 6544, April 1976.

[68]Jackson, T. A. and Blazowski, W. S., "Fuel Hydrogen Content as an Indicator of Radiative Heat Transfer in an Aircraft Gas Turbine Combustor," 1977 Winter Annual Meeting, American Society of Mechanical Engineers, Nov. 1977.

[69]Blazowski, W. S., Fahrenbruck, F. S., and Tackett, L. P., "Evaluation of Future Jet Fuel Combustion Characteristics," Air Force Aero Propulsion Lab. (to be published).

[70]Fenimore, C. P., "Formation of NO from Fuel Nitrogen in Ethylene Flames," Combustion and Flame, Vol. 19, Oct. 1972, pp. 289-296.

[71]Sternling, C. V. and Wendt, J. O. L., "On the Oxidation of Fuel Nitrogen in a Diffusion Flame," AIChE Journal, Vol. 20, Jan. 1974, pp. 81-87.

[72]Duxbury, J. and Pratt, N. H., "A Shock Tube Study of NO Kinetics in the Presence of H_2 and Fuel-N," 15th Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, Pa., 1975, pp. 843-855.

[73]Sarofim, A. F., Williams, G. C., Modell, M., and Slater, S. M., "Conversion of Fuel Nitrogen to NO in Premixed and Diffusion Flames," AIChE Symposium Series, Vol. 68, 1975, pp. 51-61.

[74]Axworthy, A. E., "Chemistry and Kinetics of Fuel Nitrogen Conversion to NO," AIChE Symposium Series, Vol. 68, 1975, pp. 43-50.

[75]Bartok, W., Engleman, V. S., Goldstein, R., and del Valle, E. G., "Basic Kinetic Studies and Modeling of NO Formation in Combustion Processes," AIChE Symposium Series, Vol. 68, 1975, p. 30.

[76]Fenimore, C. P., "Reactions of Fuel-Nitrogen in Rich Flame Gases," Combustion and Flame, Vol. 26, April 1976, pp. 249-256.

[77]Nelson, H. F. , "Nitric Oxide Formation in Combustion," AIAA Journal, Vol. 14, Sept. 1976, pp. 1177-1182.

[78]Morley, C., "The Formation and Destruction of Hydrogen Cyanide from Atmospheric and Fuel Nitrogen in Rich Atmospheric Pressure Flames," Combustion and Flame, Vol. 27, Oct. 1976, pp. 187-204.

[79]Haynes, B. S., "Reactions of Ammonia and Nitric Oxide in the Burnt Gases of Fuel-Rich Hydrocarbon-Air Flames," Combustion and Flame, Vol. 28, 1977, pp. 81-91.

[80]Longwell, J. P., Proceedings of the NASA Lewis Research Center Workshop on Hydrocarbon Fuel Technology," (to be published).

[81]Wilkes, C. and Johnson, R. H., "Effect of Fuel Nitrogen on NO_x Emission from Gas Turbines," Proceedings of the No_x Control Technology Seminar, Electric Power Research Institute, Palo Alto, Calif., Special Rept. 39, Feb. 1976.

[82]Hung, W. S. Y., "The NO_x Emission Levels of Unconventional Fuels for Gas Turbines," American Society of Mechanical Engineers, Paper 77-GT-16, March 1977.

[83]Mosier, S. A. and Pierce, R. M., "Progress in Development of Low-NO_x Gas Turbine Combustors," 69th Annual AIChE Meeting, Chicago, Ill., Dec. 1976.

[84]Dilmore, J. A. and Rohrer, W., "Nitric Oxide Formation in the Combustion of Fuels Containing Nitrogen in a Gas Turbine

Combustor," American Society of Mechanical Engieners, Paper 74-GT-37, April 1974.

[85]Tomlinson, J. G. and Montgomery, L. N., "Elimination of Turbine Erosion in the T56 Turboprop Engine," American Society of Mechanical Engineers, Paper 65-WA/GTT-9, 19656.

[86]Dodds, W. J., Peters, J. E., Colket, M. B., and Mellor, A. M., "Preliminary Study of Smoke Formed in the Combustion of Various Jet Fuels," Journal of Energy, Vol. 1, March-April 1977, pp. 115-120.

[87]Gleason, C. C. and Bahr, D. W., "Experimental Clean Combustor Program Alternate Fuels Addendum Phase II Final Report," NASA-CR-134972, Jan. 1976.

[88]Plee, S. L. and Mellor, A. M., "Preliminary Investigation of Flashback in Prevaporizing Premixing Combustor," Western States Section of the Combustor Institute Meeting, Paper TI-22, 1977..

[89]"Autoignition of Fuels Program," NASA Lewis Research Center, Request for Proposals, May 25, 1976.

[90]Butze, H. F. and Liebert, C. H., "Effect of Ceramic Coating of JT8D Combustor Liner on Maximum Liner Temperatures and Other Combustor Performance Parameters," NASA TM X-73581, Dec. 1976.

[91]Radcliffe, S. W. and Appleton, J. P., "Soot Oxidation Rates in Gas Turbine Engines," NASA CR-125404, Massachusetts Inst. of Technology, Fluid Mechanics Lab., Rep. 71-12, June 1971.

[92]Myerson, A. L., "The Reduction of Nitric Oxide in Simulated Combustion Effluents by Hydrocarbon-Oxygen Mixtures," 15th Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, Pa., 1975, pp. 1085-1092.

DISCUSSION

DR. A. H. LEFEBVRE (Purdue University): I am concerned about your Fig. 12, which relates liner wall temperature to the hydrogen content of the fuel. I attended a meeting almost 20 years ago where there was at least one paper which showed quite conclusively that you get a variation of liner wall temperature with fuel type only if you make the mistake of having an over-rich primary zone. I thought this lesson had

been learned, and I have never heard anyone argue with that view.

As you well know, if you make the primary zone over-rich, then the bulk of the heat transfer from the flame to the wall occurs by radiation which is sensitive to fuel type. However, if you make the primary zone fairly weak, then most of the heat transfer to the wall is by convection which is insensitive to fuel type. I thought it had been fully established that the best way to design a combustion chamber is to avoid rich combustion. It seems to me that by introducing this slide, you are highlighting a problem that should not exist.

DR. BLAZOWSKI (Exxon Research and Engineering Company): Perhaps it is valid to say that these problems should not exist since the fuel-air ratios required for incipient soot formation are far in excess of that necessary for gas turbine engine operation. The fact is that the combustion systems which I considered in Fig. 12 are significantly affected in terms of both smoke emission and liner temperature.

DR. LEFEBVRE: Yes, but you are talking about engines or combustors that were designed many years ago. If one were sitting down now to face the problems of alternative or synthetic fuels, then I think you would agree that one would not use a rich primary zone.

DR. BLAZOWSKI: That is right, but even in the case of the CF-6, which utilizes a leaner primary zone, there is sensitivity (albeit a reduced sensitivity) of smoke emission and liner temperature to fuel hdyrogen content.

DR. LEFEBVRE: I cannot remember when the CF-6 was designed.

DR. BLAZOWSKI: The important point is that the CF-6 was designed after smoke abatement became a design goal. This development illustrates that, although it may be theoretically possible to operate at a fuel-air ratio below the incipient soot formation limit, this goal is difficult to achieve in a real engine because of the many other requirements the combustor designer must satisfy.

ALTERNATIVE FUELS FOR RECIPROCATING INTERNAL COMBUSTION ENGINES

Nicholas E. Gallopoulos*
General Motors Research Laboratories, Warren, Mich.

Abstract

Investigations of fuels for internal combustion engines usually are aimed at one of three objectives: to improve the efficiency and performance of engines; to widen the availability of natural resources for fuel production and thus avoid fuel shortages; and to reduce pollutants in engine exhaust gases. Most recent research in fuels for internal combustion engines has been motivated by the desire to attain all three objectives. Consequently, this review examines recent literature that reports efficiency, performance, and exhaust emissions of Otto and diesel cycle engines burning various fuels derived from several natural resources. Included in this review are liquid gaseous hydrocarbons derived from oil shale or coal; alcohols; ammonia; hydrogen; powdered coal; and blends of some of these fuels. Experimental findings with respect to engine efficiency, performance, and exhaust emissions are reviewed and compared to identify the advantages and shortcomings of the various fuels in Otto and diesel cycle engines. The review also suggests that, to conserve natural resources, one of the criteria for the commercialization of fuel-engine combinations should be the maximization of overall energy efficiency, which is the product of the efficiencies of all of the steps involved in converting a natural resource to a usable fuel and burning that fuel in an engine.

Introduction

That the United States has insufficient petroleum to satisfy its energy needs is a matter of fact reflected most vividly in the precipitous increase in petroleum imports from 26% of consumption in 1970 to almost 43% in 1976.[1] Whether and when the world will run out of petroleum is discussed seriously, but it generally is conceded that by the year 2000 world petroleum production will have passed its peak, and world petroleum demand will have outstripped supply.[2,3] These circumstances, therefore, compel the search for fuels not

*Assistant Head, Fuels and Lubricants Department.

derived from petroleum, which usually are referred to as alternative fuels.

The search for alternative fuels involves all consuming sectors, but this paper will concentrate only on fuels suitable for reciprocating internal combustion engines. However, decisions to produce a given alternative fuel commercially will have to be based on whether it satisfies other energy needs in addition to those of internal combustion engines and meets stringent social, economic, technological, and environmental requirements.

The viability and desirability of an alternative fuel depends on several factors: 1) the size of the resource from which it is to be derived; 2) the maturity of the technology for converting the resource to the alternative fuel; 3) the social, economic, and environmental considerations associated with the resource-to-fuel conversion; 4) the transportation and distribution requirements of the fuel; and 5) the suitability of the fuel for its intended application. In this paper, the first four factors will be discussed briefly for each alternative fuel. The fifth factor, the suitability of each fuel for use in reciprocating internal combustion engines, will be examined in greater detail by focusing on engine power and efficiency, exhaust emissions, compatibility of engine materials with the fuel, and safety. In addition, the volumetric energy density and the storability of fuels on vehicles will be discussed, since these properties affect the operating range and weight of vehicles that usually are powered by reciprocating internal combustion engines.

This literature review will be comprehensive in terms of the number and types of alternative fuels which it will consider, but it will be eclectic in terms of the references from which information will be extracted. In particular, most of the engine and vehicle data that will be shown will be those generated by the author's colleagues at the General Motors Research Laboratories. However, the General Motors work will be compared with that which has been reported in the literature, and discrepancies will be identified. An additional limitation of this review is that it deals only with conventional spark ignition and diesel engines.

Inorganic alternative fuels will be reviewed first, and organic fuels second. Following the review of individual fuels, the paper will address future research needs in the evaluation of alternative fuels. The paper will close with a discussion of the application of the overall energy efficiency

Table 1 Physical and chemical properties of fuels (based on Refs. 22 and 34)

	Gasoline (typical)	Hydrogen	Ammonia	Coal powder	Methane	Acetylene	Methanol	Ethanol
Chemical formula	...	H_2	NH_3	...	CH_4	C_2H_2	CH_3OH	C_2H_5OH
Atomic H/C	1.80	...	...	0.8	4.0	1.0	4.0	3.0
Molecular weight	91.4 av	2.02	17.03	...	16.04	26.04	32.04	46.07
Heat of combustion (net)								
MJ/kg	43.4	120.1	18.6	25.8	50.0	48.3	20.1	26.9
MJ/l (liquid)	31.8	8.41	12.7	34.7	20.8	53.9	15.9	21.3
Stoichiometric Mixture								
Mass air/mass fuel	14.5	34.3	6.1	10.4	17.2	13.2	6.5	9.0
Vol. air/vol. fuel	45.79	2.38	3.57	...	9.53	11.93	7.14	14.3
kJ/l, gaseous fuel	3.78	3.20	3.09	...	3.40	4.34	3.53	3.61
kJ/l, liquid fuel	3.86	...	...	3.2	...	...	3.98	3.85
Mole products/mole reactants[a]	1.04	0.85	1.16	...	1.00	0.96	1.06	1.06
Mole products/mole air[b]	1.07	...	...	1.04	...	...	1.21	1.14
Flammability limits in air								
Vol. %	1.3-7.6	4.1-74	16-25	...	5-15.4	2.5-81	6.0-37	3.5-19
Ø	0.60-3.8	0.10-6.8	0.68-1.2	0.43-?	0.50-1.7	0.31-51.0	0.45-4.2	0.52-3.4
Maximum laminar flame speed, m/sec	0.37	2.91	0.010	...	0.37	1.55	0.52	...
Adiabatic flame temperature, °C	2637[c]	2756	2484	...	2603	2870	2576	2594
Autoignition temperature, °C	257	574	651	593	632	305	470	392

Table 1 (continued)

	Gasoline (typical)	Hydrogen	Ammonia	Coal powder	Methane	Acetylene	Methanol	Ethanol
Octane Number								
Research	91-100	130+	130	...	130	~50	110	106
Motor	82-94	...	...	...	105	...	87	89
Cetane number	0-5	...	<0	...	<0	...	10	15
Boiling point, °C	32-221	-253	-33	...	-161.5	-83	64.6	78.5
Vapor pressure at 37.8°C, kPa	48-103	...	1642	...	...	6500	31.7	15.2
Heat of vaporization, MJ/kg	0.272[c]	0.447	1.370	...	0.509	...	1.102	0.856
Liquid density, g/cm^3 (at °C)	0.734 (15.6)	0.07 (-78.9)	0.817 (-78.9)	1.346[d] ...	0.415 (-163.9)	0.618 (-32)	0.795 (15.6)	0.792 (15.6)

[a] For gaseous fuel.

[b] For liquid or solid fuel.

[c] Isooctane.

[d] Solid.

criterion to the selection of alternative fuels for commercial development.

Inorganic Fuels

Of the alternative fuels, those that are inorganic provide opportunities but also challenges and problems. The opportunities arise because most of the inorganic fuels can be derived from inexhaustible or renewable resources, and when burned they tend to contribute fewer air pollutants than organic fuels. Also, combustion of inorganic fuels does not produce carbon dioxide. Some scientists contend that the burning of fuels that produce carbon dioxide will have to be limited because an excess of carbon dioxide in the Earth's atmosphere will increase the Earth's temperature (greenhouse effect), which could have severe climatological effects.[4] Such a limitation also would apply to certain production methods for inorganic fuels which release carbon dioxide to the atmosphere. The challenges and problems, on the other hand, result from the physical and chemical properties (Table 1) of these inorganic fuels, which make them dissimilar and incompatible with current fuels and reciprocating internal combustion engines. (In the remainder of the text, whenever fuel properties are referenced, it should be understood that their values will be found in Table 1.) Since hydrogen is the inorganic fuel that has received the greatest attention in the literature, this section will emphasize hydrogen, whereas ammonia and hydrazine will be discussed briefly.

Hydrogen

Hydrogen has been studied as an alternative fuel because it can be produced from water via either electrolysis or thermochemical cycles and from coal via gasification. Salzano and Brown recently have assessed hydrogen's prospects[5] and conclude that, in the next 30 years, hydrogen from coal will be used in those industrial markets currently served by hydrogen derived from petroleum and natural gas. Production of hydrogen from water either by electrolysis or through thermochemical cycles may become viable only after the year 2000, but this possibility is inextricably connected with the uncertainties of nuclear power.[5]

An additional attraction of hydrogen for any application is its minimal contribution to air pollution, since its combustion with air produces only water and nitrogen oxides.

Efficiency, Power, and Emissions. Experimental work with hydrogen-fueled internal combustion engines has been surveyed in detail by Escher.[6] Cole[7] compared much of the available

thermal efficiency and power data of hydrogen-fueled engines with calculations based on fuel/air cycle analysis. These two reviews cover most of the available literature of hydrogen-fueled engines. Both reviews state that hydrogen is unsuitable for diesel engines because of its large ignition delay. However, successful diesel operation using a glow plug has been reported.[7,8]

Results of several investigations[6,7] have shown that hydrogen-fueled Otto cycle engines are efficient because of hydrogen's high flame speed and because they can operate at very lean equivalence ratios. [Equivalence ratio (Ø) is the actual fuel-air ratio. Equivalence ratios less than one (Ø < 1.0) indicate fuel-lean conditions.] The latter is a consequence of hydrogen's wide flammability limits. For example, Fig. 1 shows Stebar's results.[9] He found an indicated thermal efficiency advantage of five percentage points for hydrogen over isooctane. Both were tested at their respective lean limits, where indicated thermal efficiency is near its maximum value for either fuel.

The ability of hydrogen-fueled engines to operate lean also permits running the engine unthrottled, whith power regulation being accomplished by changes in fuel flow. Unthrottled operation further enhances overall engine efficiency by decreasing pumping work. With throttled engines, high efficiencies at lean equivalence ratio, however, are obtained at the expense of power output, which decreases very rapidly as equivalence ratio decreases (leaner). This effect is particularly troublesome for hydrogen because of its very low

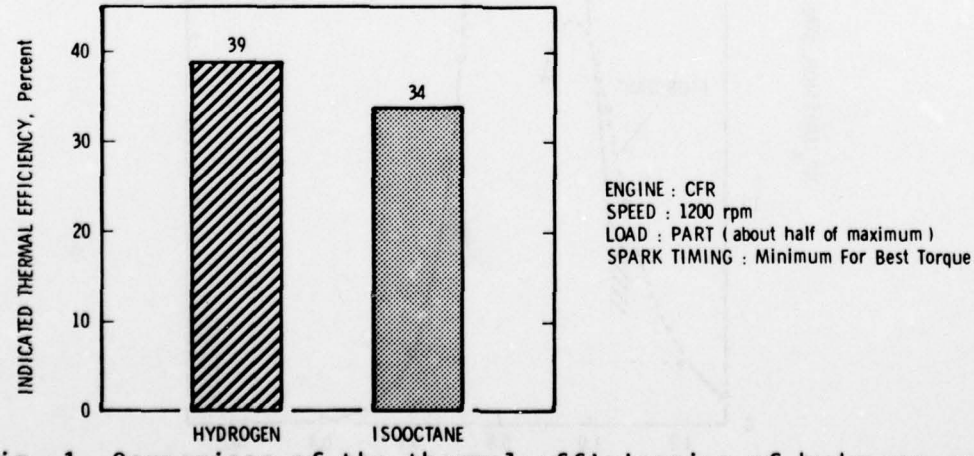


Fig. 1 Comparison of the thermal efficiencies of hydrogen and isooctane at their respective lean limits (Ø = 0.2 for hydrogen; Ø = 0.9 for isooctane).[9]

charge energy density even at stoichiometric conditions. A potential solution to this problem is to inject hydrogen directly into the engine's cylinder.[7,9]

The power output of hydrogen-fueled engines also is restricted by preignition and backflash problems, which limit engine operation to low compression and lean equivalence ratios.[10] Operation at low compression ratio decreases not only power but also engine efficiency. Preignition and backflash can be minimized by water injection and exhaust gas recirculation, which also can reduce nitrogen oxide (NO_x) emissions.[10]

Without those NO_x control methods, burning hydrogen with air in Otto cycle engines under peak power conditions ($\phi \approx 1$), such as those encountered during vehicle accelerations, produces more NO_x than burning hydrocarbon fuels.[9] Figure 2, which was developed from Stebar's data,[9] illustrates this point and also shows the preignition and backflash limits. Under low power conditions (vehicle cruising at moderate

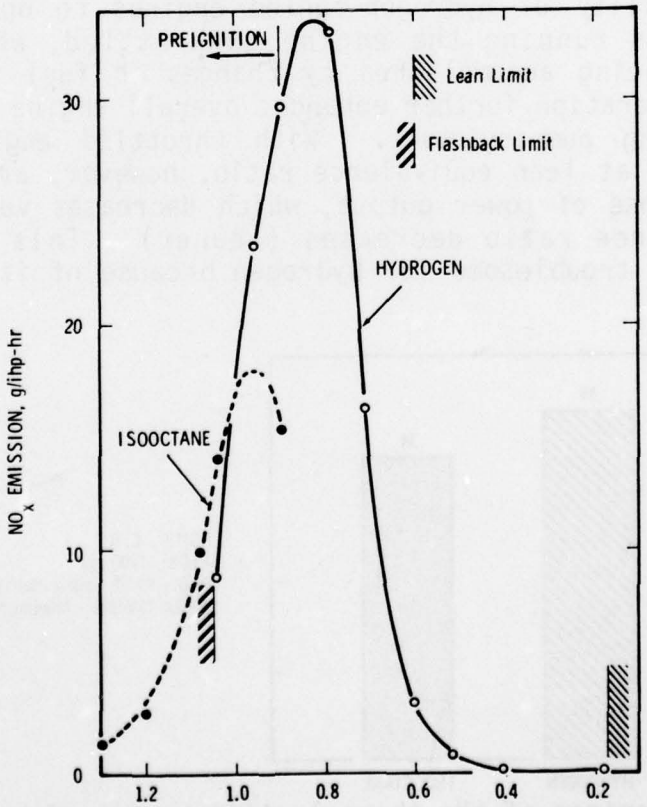


Fig. 2 Comparison of NO_x emissions from hydrogen and isooctane combustion: single-cylinder engine.[9]

speeds), however, NO_x can be kept at low levels by operating with very lean mixtures, as shown in Fig. 2.

As mentioned previously, combustion of hydrogen does not produce carbon monoxide (CO) and hydrocarbons (HC). Any traces of these pollutants found in hydrogen-fueled engine exhaust are due to the engine's lubricating oil.[9]

Distribution, Storage, and Other Concerns. The metal embrittlement caused by hydrogen under high pressure may be a problem for hydrogen distribution systems. Hydrogen is compatible with materials used in automotive engines and fuel systems[6] but incompatible with fuel carburetion or injection systems used with gasoline. Consequently, such systems will have to be developed specifically for hydrogen before it can be used widely.

Bowen[11] discussed safety hazards associated with hydrogen. The wide flammability limits and other unique properties

Table 2 Vehicular storage requirements of fuels (Based on Ref. 35)[a]

	Fuel Alone		Fuel + Container	
	kg	L	kg	L
Gasoline (typical)	54	75	61	79
Hydrogen, Gas[b]	20	1150	1020	1870
Liquid	20	289	160	289
as M_gH_2	262	187	314	306
Ammonia, liquid	129	203	206	380
Coal powder	94	70	105	75
Methane, Gas[b]	48	351	227	782
Liquid	48	115	109	456
Acetylene, dissolved in acetone	54	400	362	416
carbide-water reaction	200	125		
Methanol	120	149	130	161
Ethanol	88	112	97	135

[a] Basis: Energy equivalent of 75 L (20 gal) gasoline (2.4 GJ).

[b] At 20 MPa.

AD-A061 050 PURDUE UNIV LAFAYETTE IND PROJECT SQUID HEADQUARTERS F/G 21/4
ALTERNATIVE HYDROCARBON FUELS: COMBUSTION AND CHEMICAL KINETICS--ETC(U)
OCT 78 C T BOWMAN, J BIRKELAND N00014-75-C-1143
UNCLASSIFIED SQUID-PU-R2-78 NL

2 OF 5
AD
A061050



of hydrogen present some safety problems, but their seriousness generally has been overdramatized.[11] Distribution to and storage on vehicles are, however, serious problems. Even if existing natural gas pipelines could be used for long-distance hydrogen transport, refueling automobiles with hydrogen would require the construction of a completely new distribution (service station) system, which could not utilize current gasoline and diesel fuel distribution facilities. The low volumetric energy density of hydrogen makes its storage on vehicles a difficult problem to solve, particularly for passenger cars and other small vehicles, because any of the three storage methods (compressed gas, cyrogenic liquid, metal hydride) require heavy and bulky containers (Table 2). Even in the best installations to date, the amount of hydrogen which was stored on vehicles was insufficient for the vehicle to travel a reasonable distance before refueling. Escher[9] and Salzano[5] have reviewed progress in this area. Research by Daimler-Benz to develop hydrogen-fueled vehicles utilizing metal hydrides for hydrogen storage was reviewed by Buchner and Saufferer.[12]

Hydrogen As a Supplement

Supplementation of gasoline with hydrogen generated from the gasoline onboard a vehicle is not a subject that fits this paper's definition of alternative fuels. However, for completeness, the following references dealing with the subject are cited: 6, 9, and 13-15.

Ammonia and Hydrazine

Ammonia can be synthesized from hydrogen and nitrogen, and hydrazine is, in turn, derived from ammonia. Consequently, ammonia and hydrazine have been considered as alternative automotive fuels mainly because they are hydrogen carriers that may be easier to store on vehicles than hydrogen.[16] Whether this is indeed an advantage is debatable, as shown in Table 2. Unquestionable disadvantages of the production of these nitrogenous fuels are dependence on hydrogen availabilty, which is subject to the uncertainties of nuclear power; and reduction of overall fuel production efficiency, since energy must be expended to convert hydrogen to ammonia or hydrazine. An advantage that these two fuels share with hydrogen, however, is the absence of CO_2, CO, and HC from their combustion products.

Efficiency, Power, and Emissions. Operation of engines with ammonia has been reported by several investigators.[17-19] Hydrazine, on the other hand, has not been used in engines,

except as reported in the very preliminary study of Schmidt.[20] Consequently, hydrazine will not be discussed further.

Compared to hydrocarbon fuels, ammonia combustion in normally aspirated Otto cycle engines yields very low efficiency and power because of its low energy density and slow flame speed.[21] At wide-open-throttle conditions, increasing engine compression ratio and supercharging can alleviate these problems, but at part-throttle conditions the addition of hydrogen is required to overcome the slow flame speed effects, which restrict operation to low engine speeds.[18,21] Operation at high compression ratios and supercharging are possible with ammonia because it has a high octane number. However, the high octane number (low cetane number) makes ammonia unsuitable for diesel engines,[19] unless either glow plugs or supplementary fuels are used to help ignite the mixture.

Ignition of ammonia is difficult in Otto cycle engines, also. Ignition systems to overcome this problem and the adverse effects of ammonia's slow flame speed can be devised.[21] Another problem which ammonia is its high latent heat of vaporization; vehicles will have to be equipped with ammonia vaporizers.[16]

Ammonia and NO_x are pollutants found in the exhause of ammonia-fueled engines.[21] Unfortunately, no definitive ammonia-fueled engine studies of these two nitrogenous pollutants have been reported.

Distribution, Storage, and Other Concerns. As in the case of hydrogen, distribution of ammonia to vehicles presents serious problems because of its incompatibility with systems designed for hydrocarbon fuels. Ammonia also shares with hydrogen the weight and bulk problems associated with storage on vehicles (Table 2). In addition, ammonia is corrosive to materials such as brass and zinc[16] which are found in many automotive fuel systems.

The narrow flammability limits of ammonia reduce fire hazards with this fuel. However, ammonia is toxic, and its release into the atmosphere either from fuel storage systems or from unburned ammonia in engine exhaust gases could be a problem. Additional safety problems are local freezing if ammonia contacts skin and fuel tank rupture (if overfilled) due to liquid ammonia's high coefficient of expansion.[16] This latter problem could be resolved through proper fuel tank design.

Organic Fuels

Because of their similarity with current petroleum-derived fuels, many of the organic alternative fuels present

fewer technical challenges than inorganic fuels. In addition, the use of organic fuels in reciprocating internal combustion engines has been investigated extensively. However, the combustion with air of all organic fuels produces CO, NO_x, unburned fuel components such as HC, aldehydes, and particulate matter. The greatest challenge presented by the organic alternative fules for the near future is not associated with either their use in engines or their contribution to air pollution, but with the technology and economics of converting various natural resources to organic automotive fuels.

This paper will review organic alternative fuels in two groups: hydrocarbons and oxygenated hydrocarbons. Each group will be introduced by a brief section on the natural resources available for the production of these fuels.

Hydrocarbons

Alternative hydrocarbon fuels can be produced from such domestic natural resources as biomass (plants, manure, and other wastes), oil shale, and coal. Biomass can be converted to hydrocarbon fuels by a number of processes, including anaerobic digestion to produce methane, pyrolysis to produce heavy oil, and gasification to produce synthesis gas (CO and H_2), which can be converted to either gaseous or liquid hydrocarbons. For best results, the type of biomass must be matched with the appropriate process. For example, manure and giant kelp may be more suitable for anaerobic digestion because of their large water content, whereas municipal wastes and crop residues may be more appropriate for pyrolysis or gasification.[22] As suggested by Calvin,[23] another, albeit long-range, possibility is to cultivate plants (Euphorbia) that generate hydrocarbons biologically.

The kerogen in oil shale yields hydrocarbons upon heating. The product, shale oil, is a viscous liquid with a hydrogento-carbon ratio lower than that of crude petroleum. Refining of the shale oil, including hydrogenation, yields various hydrocarbon fuels including those suitable for automotive applications.[24]

Coal itself can be considered a solid hydrocarbon fuel with some potential for direct combustion in reciprocating internal combustion engines. In addition, coal can be either converted to liquid hydrocarbons (liquefaction) or gasified to synthesis gas, from which both liquid and gaseous hydrocarbons can be made.[25] With suitable processing, the products of coal liquefaction and gasification can be made into acceptable automotive fuels.[25] The remainder of this section will review

studies in reciprocating internal combustion engines of hydrocarbon alternative fuels derivable from the aforementioned resources.

Solid Coal

The burning of solid (powdered) coal in reciprocating internal combustion engines has not been studied intensively. Existing studies are very old and limited to modified diesel engine applications. A recent assessment by the Thermo-Electron Corporation for the National Science Foundation[26] reviews the scant literature on the subject. Thermo-Electron concluded that powdered coal could be burned efficiently in large-bore, very slow-speed, stationary diesel engines that can be designed to circumvent the wear problems caused by coal and ash particles. The selection of very slow-speed engines is justified further on the basis of the very low combustion rate of coal.

Review of the Thermo-Electron assessment, as well as of other studies of coal-fueled engines, strongly suggests that powdered coal, despite the high energy efficiency associated with its production, would not be a suitable fuel for automotive engines. Additional problems with powdered coal as an automotive fuel are on-vehicle storage due to its low mass energy density and the complex mechanisms required for feeding the coal to the engine.

Gaseous Hydrocarbons

Methane, propane, butane, and acetylene are among the alternative gaseous fuels that have been studied. Since these are individual chemical compounds now extracted from petroleum in industrial quantities, their study has not been hampered by availability. Furthermore, methane, propane, butane, and liquefied mixtures of propane and butane (liquefied petroleum gas or LPG) are currently used to fuel spark ignition engines in special commercial applications. In the future, these gases could be made from coal, shale, or biomass. However, of these gaseous hydrocarbons, only methane and acetylene would be likely alternative fuels to be made from the aforementioned natural resources. Methane is a likely candidate because it can be made directly by anaerobic fermentation of biomass and from synthesis gas produced by gasification of either coal or biomass. Acetylene appears feasible because it can be made by a series of reactions involving coal, calcium oxide, and water. Synthesis of the other gaseous hydrocarbons, although possible, involves large energy losses and high costs. Consequently, the remainder of this section will be devoted to methane and acetylene.

Methane. Methane, usually as natural gas (~90% methane), currently is used to fuel reciprocating internal combustion engines predominantly in stationary applications. Methane is recognized as an excellent Ottocycle engine fuel for specialized applications, and its combustion and exhaust emissions have been studied.

Efficiency, power, and emissions. Lee and Wimmer[27] compared methane to gasoline in engines. Workers at the Bureau of Mines[28] used natural gas in comparable studies. As expected from its properties shown under "Stoichiometric Mixture" in Table 1, methane produces less power[27] than does gasoline under comparable operating conditions. Methane's ability to burn at leaner conditions than gasoline would allow engines to operate with high efficiency and low exhaust emissions (see pp. 144, 145 of Ref. 22 and Refs. 27 and 28). However, use of methane does not reduce emissions sufficiently to eliminate the need for emission controls.

Distribution, storage, and other concerns. Fueling automobiles with methane presents problems: on-vehicle storage requires either high pressure or cryogenic tanks, which increase the weight (Table 2), complexity, and cost of the car; and distribution to vehicles would require a complete revamping of the service station network. Of course, distribution of methane from the generation plant to distribution terminals now is practiced by public utilities. Methane by itself is not suitable for fueling diesel engines[29] because it is very difficult to ignite in a diesel engine.

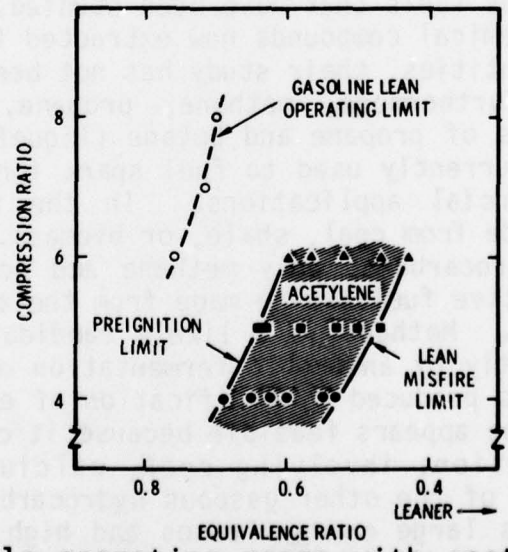


Fig. 3 Stable operating range with acetylene: single-cylinder engine.[30]

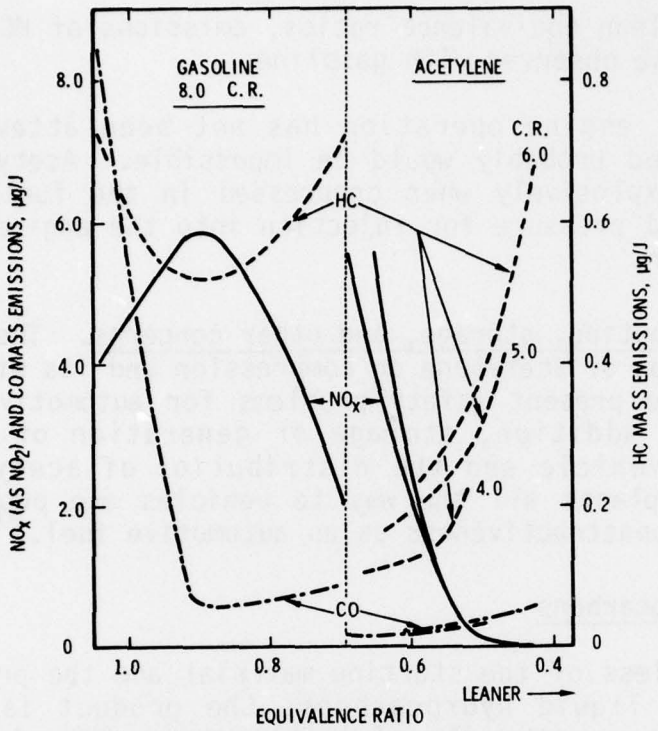


Fig. 4 Mass emissions comparison between acetylene and gasoline: single-cylinder engine.[30]

Acetylene. Whereas methane received early and thorough attention as a fuel for reciprocating internal combustion engines, acetylene was studied in depth only recently.[30] This neglect was mainly due to acetylene's very low octane number (which was determined many years ago) and knowledge that acetylene explosively decomposes upon compression.[30]

Efficiency, power, and emissions. Hilden and Stebar[30] found that the power and efficiency of an acetylene-fueled Ottocycle engine cannot match those attained by gasoline-fueled engines, because with acetylene the engine operates only in a very narrow range of compression and equivalence ratios, as shown in Fig. 3. The low values of the compression ratio and rich limit equivalence ratio observed for acetylene are due to its low octane quality, which, in turn, probably is related to the ease with which acetylene decomposes upon compression. In contrast, the fast flame speed of acetylene allows engine operation at much leaner equivalence ratios than are possible with gasoline.

As shown in Fig. 4, very lean operation (ϕ = 0.5 to 0.4) with acetylene reduces emissions of CO and NO_x to levels lower than those found with gasoline. However, at

these very lean equivalence ratios, emissions of HC can be as high as those observed with gasoline.

Diesel engine operation has not been attempted with acetylene and probably would be impossible. Acetylene would decompose explosively when compressed in the fuel system to the required pressure for injection into the engine's combustion chamber.

Distribution, storage, and other concerns. The explosive decomposition of acetylene on compression and its wide flammability range present safety problems for automotive applications. In addition, storage or generation of acetylene onboard a vehicle and the distribution of acetylene from generation plants all the way to vehicles are problems that add to its unattractiveness as an automotive fuel.[30]

Liquid Hydrocarbons

Regardless of the starting material and the process used to produce liquid hydrocarbons, the product is always a complex mixture not only of hydrocarbons, but also of many organic compounds of oxygen, nitrogen, and sulfur. The starting material and conversion process, however, greatly influence both the composition and properties of these complex liquid mixtures. For example, coal-derived liquids usually contain more aromatic compounds than oil shale-derived liquids. Liquids produced from synthesis gas via the Fischer-Tropsch and related methods are complex mixtures of hydrocarbons; however, most nitrogen and sulfur compounds are absent because purification of the synthesis gas precedes the Fischer-Tropsch synthesis.

Production of liquid hydrocarbons from coal, oil shale, or biomass is still in the developmental stage in the United States. Thus, the raw material from which automotive fuels can be made is generally unavailable. In a few instances, synthetic crude from either coal or oil shale has been refined to gasoline and diesel fuel, but serious efforts along these lines are awaiting more definitive developments in conversion technologies. This is a logical attitude, since changes in the technology to produce liquids from coal, shale, or biomass will affect the properties of the liquid product and consequently the type and severity of refining which this liquid product will require for conversion to automotive fuels. Thus, very little research has been conducted in reciprocating internal combustion engines with liquid hydrocarbons not derived from petroleum.

Hurn[31] reported preliminary results from spark-ignition engine tests using coal- and oil shale-derived gasoline. He found no unusual results with these gasolines and remarked that their properties were either very close to their petroleum-derived counterparts or could be made more comparable by more severe refining. Several other authors[24,31-34] also have observed that liquid hydrocarbon fuels derived from nonpetroleum resources are likely to resemble those derived from petroleum. Consequently, nonpetroleum-derived liquid hydrocarbons refined to meet current specifications for gasoline and diesel fuel should not present any unforeseen or unique combustion and exhaust emissions problems when burned in reciprocating internal combustion engines. In addition, they should be compatible with current distribution and storage systems, and their safety and toxicity properties also should be similar to those of petroleum-derived automtotive fuels.

However, the closer one tries to duplicate the properties of petroleum-derived fuels, the more numerous and severe will be the refining steps required for the liquids dervied from nonpetroleum resources. This increased refining complexity

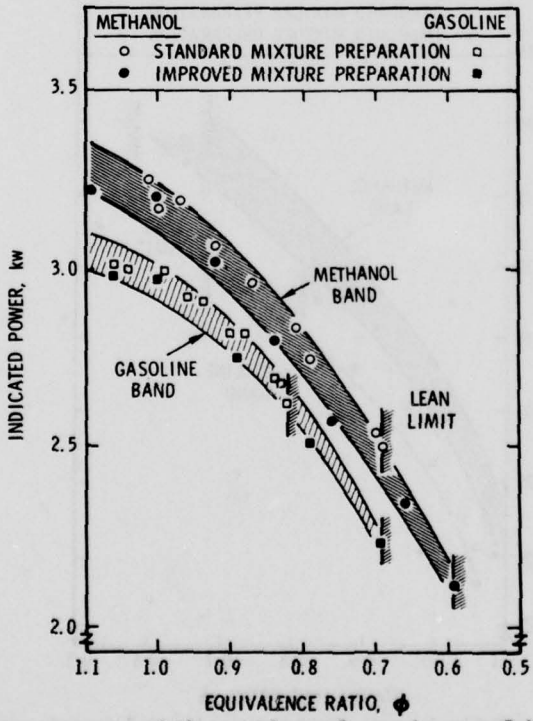


Fig. 5 Engine power with methanol and gasoline fuels; standard and improved mixture preparation systems: single-cylinder engine.[40]

and severity cost both energy and money. This was recognized by Hurn,[31] who recommended as a remedy the mutual adaptation of fuels and engines. Also, Stebar[35] recommended that engine-fuel combinations be selected for development on the basis of maximum overall efficiency (fuel processing efficiency times engine efficiency) consistent with good engine performance and durability, low exhaust emissions, and favorable economics. This concept will be explored further later in this paper.

Oxygenated Hydrocarbons

The only oxygenated hydrocarbons viable as alternative fuels are methanol and ethanol, which can be produced directly, and not after production of a hydrocarbon. Another oxygenated hydrocarbon that has received some attention is methyl tertiary-butyl ether (MTBE). However, MTBE requires the availability of both a hydrocarbon (isobutene) and methanol for its manufacture. In addition, it has not been considered as a fuel by itself, but as an octane-improving component of gasoline.[36]

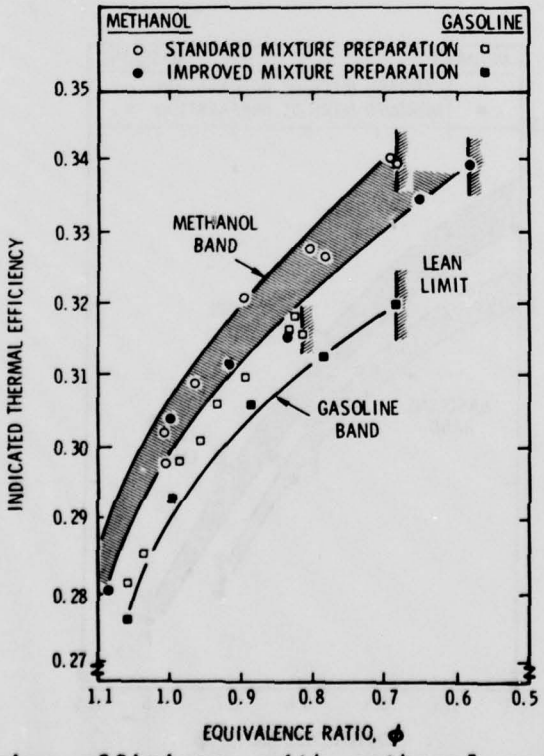


Fig. 6 Engine efficiency with methanol and gasoline fuels; standard and improved mixture preparation systems: single-cylinder engine.[40]

Alcohols: Neat

Methanol and ethanol, either neat or as alcohol-gasoline blends, have been suggested as alternative fuels primarily because they can be made readily from a number of nonpetroleum resources. In addition, as will be shown later, alcohols have some attractive characteristics as automotive fuels. This section will review work with neat alcohols, which properly can be labeled alternative fuels, whereas alcohol-gasoline blends represent a transition phase to alternative fuels. A comprehensive review of publications through 1975 related to alcohols as automotive fuels has been prepared by the American Petroleum Institute.[37] Alcohols are generally unsuitable for fueling diesel engines without the use of auxiliary fuels or ignition sources.[29]

Methanol. Methanol is the more versatile of the two alcohols as far as resources for its manufacture are concern ed. Methanol can be produced directly by passing compressed synthesis gas through a suitable catalyst. The source of the synthesis gas can be coal, various natural wastes, or even liquid and gaseous hydrocarbons. Methanol also can be manufactured by the destructive distillation of wood. However, the source most frequently considered for methanol production is coal,[38] although production from various wastes also has been considered.[39] Because coal is such an abundant domestic resource and the technology for methanol manufacture from coal is relatively mature, and because methanol is available now in industrial quantitites, it has been studied by many investigators not only in laboratory engines, but also in cars.

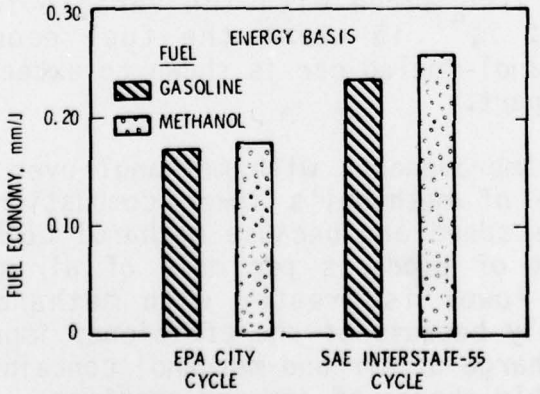


Fig. 7 Comparison of gasoline and methanol: fuel economy. Electronic Fuel Injection car with production spark timing and $\emptyset_a = 0.96$.[47]

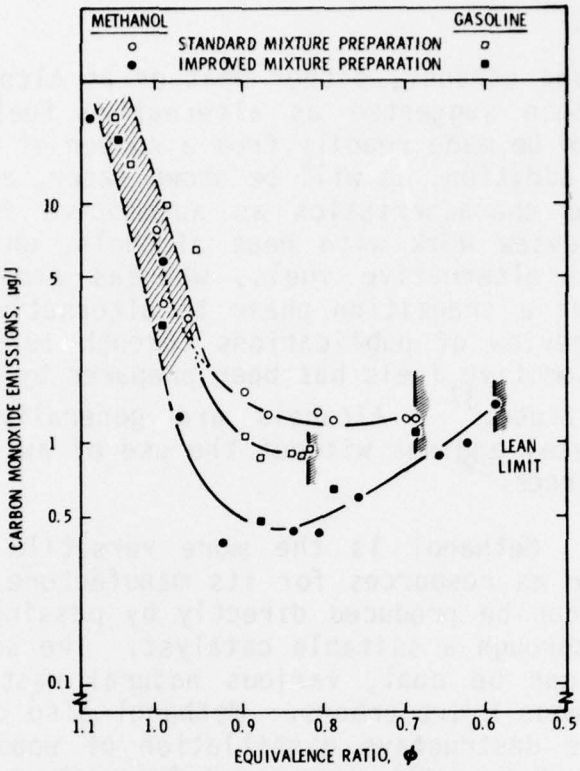


Fig. 8 Mixture preparation effects on CO exhaust emissions with methanol and gasoline fuels: single-cylinder engine.[40]

Efficiency, power, and emissions. As shown in Figs. 5 and 6, compared to gasoline, methanol burns with greater efficiency, and this produces more power.[40] This was true for either standard or improved mixture preparation. (Hilden and Parks improved intake mixture homogeneity by improving mixture preparation.) The single-cylinder engine test efficiency results also agree with the vehicle tests results plotted in Fig. 7,[41] in which the fuel economy (energy basis) of a methanol-fueled car is shown to exceed that of its gasoline counterpart.

Efficiency improvements with methanol over gasoline are obtained because of methanol's lower combustion temperature and higher flame speed and because methanol combustion generates more moles of products per mole of air than gasoline combustion.[40] Power is greater with methanol than with gasoline, not only because of the efficiency improvements but also because a charge of air and methanol contains more energy than the comparable charge of air and gasoline.

Carbon monoxide emissions are primarily a function of equivalence ratio; therefore, they should not differ greatly

between fuels as long as fuels are compared at the same equivalence ratio. As shown in Fig. 8, this applies to methanol and gasoline, provided that for each fuel the air-fuel mixture approaches homogeneity.[40] Similar results have been found in vehicle tests, as shown in Fig. 9.[41]. In comparison to gasoline, the lower flame temperature and higher heat of vaporization of methanol are responsible for the lower emissions of NO_x observed both in single-cylinder engine (Fig. 10) and vehicle (Fig. 9) tests.

Until recently, confusion existed in the literature concerning the organic emissions from methanol combustion. Hilden and Parks[40] put this issue in perspective. First, they defined the term unburned fuel (UBF) emissions. For methanol combustion, UBF emissions consist of methanol mixed with small amounts of hydrocarbons. In the case of gasoline, UBF emissions are virtually all hydrocarbons. Second, they found that methanol and gasoline combustion produce comparable amounts of UBF emissions when the preparation of the air-fuel

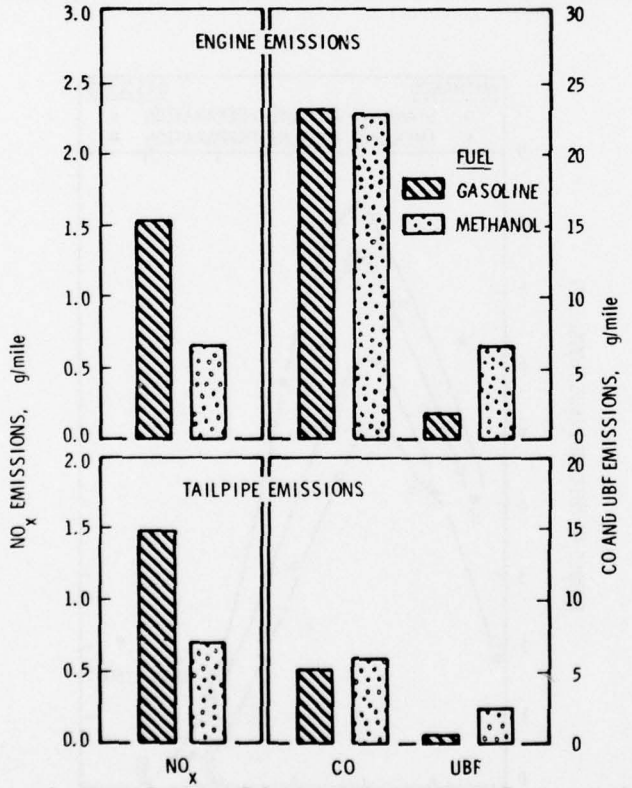


Fig. 9 Comparison of gasoline and methanol: engine and tailpipe exhaust emissions. Catalyst-equipped Electronic Fuel Injection car with production spark timing and ϕ_a = 0.96 (1975 Federal Test Procedure).[41]

mixture is such that homogeneity is approached (Fig. 11). Brinkman's vehicle tests (Fig. 9), however, show higher UBF emissions with methanol than with gasoline.[40] This finding does not disagree with Hilden and Parks,[40] who stated "fueling automobiles with methanol instead of gasoline would be expected to produce equal or greater levels of UBF emissions." They based this statement on their belief that the homogeneity of the air-fuel charge to their single-cylinder engine would be greater than that possible in vehicles.

Since methanol can be oxidized easily to formaldehyde, aldehyde emissions from methanol-fueled engines are expected to be higher than those from gasoline-fueled engines. Hilden and Parks[40] found this to be the case, as did several other investigators referenced by Hilden and Parks.[42] A recent paper by Bernhardt and co-workers[42] further confirms these findings.

Bernhardt and co-workers have published some confusing data concerning the effect of compression ratio on NO_x emissions from methanol combustion.[42,43] They have shown no

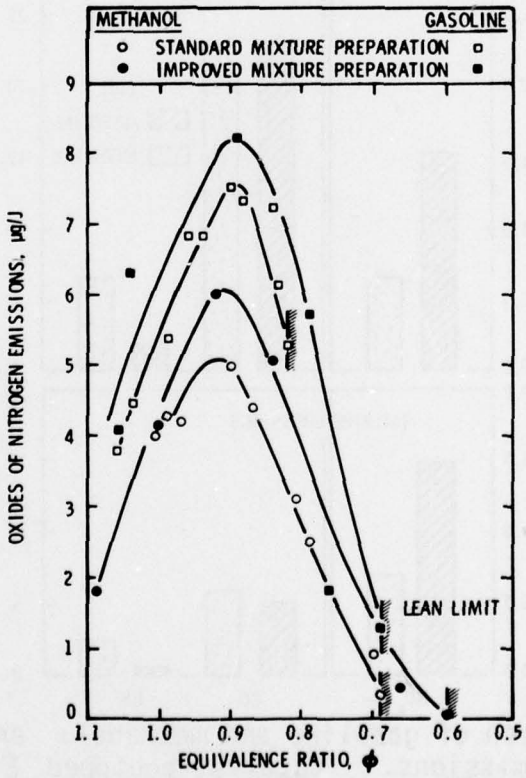


Fig. 10 Mixture preparation effects on NO_x exhaust emissions with methanol and gasoline fuels: single-cylinder engine.[40]

change[42] and a decrease[43] in NO_x emissions with increasing compression ratio, whereas an increase would be expected. Recent single-cylinder engine tests by Brinkman[44] show that emissions of NO_x increase as compression ratio increases (Fig. 12) but that a preselected level (3 g/J) of NO_x can be maintained as compression ratio is increased if the spark timing is retarded from the minimum for best torque (MBT) value. This scheme allows control of NO_x while the thermal efficiency of the engine is improved (Fig. 13). Unfortunately, Brinkman also found that UBF emissions increase with compression ratio and cannot be reduced significantly by retarding spark timing.[44]

These tradeoffs between exhaust emissions and fuel economy have been investigated over a wide range of equivalence and compression ratios and spark timings in a single-cylinder engine[44] and in a more limited fashion in a car.[41] In vehicle studies with a fuel-injected car, the compression ratio was not varied. However, the ability of methanol to burn at leaner equivalence ratios than gasoline (Fig. 11) and the effectiveness of spark retardation for control of NO_x emissions were exploited. Results from tests with the fuel-injected vehicle shown in Fig. 14 suggest that, with a complement of emission controls including spark retardation, exhaust gas recirculation, and catalytic converters, a methanol fuel-injected vehicle can have low emissions and reasonable energy-based fuel economy. Whether such a vehicle could meet

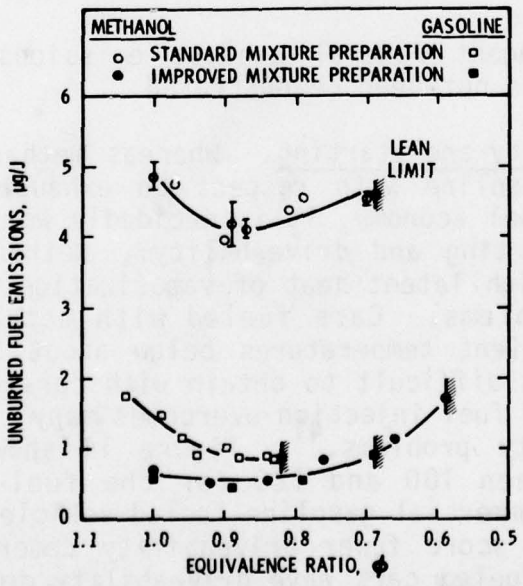


Fig. 11 Mixture preparation effects on UBF exhaust emissions with methanol and gasoline fuels: single-cylinder engine.[40]

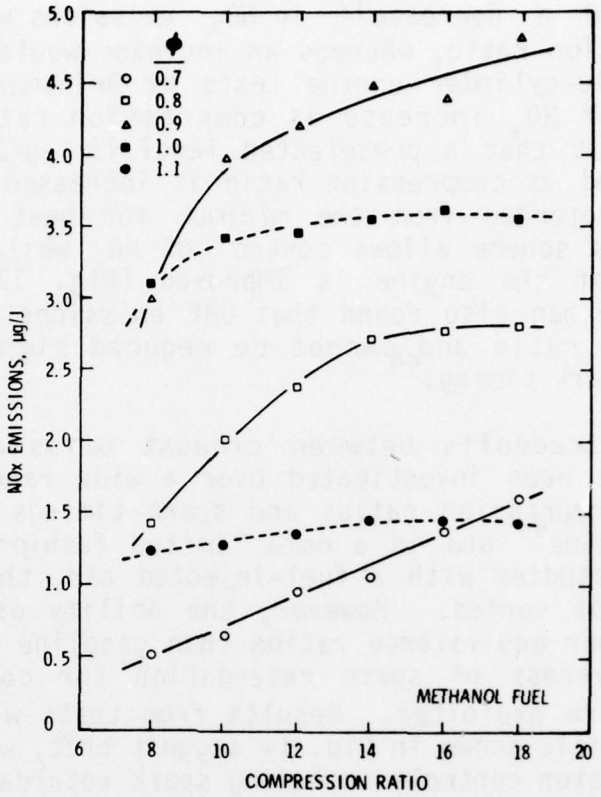


Fig. 12 Effects of compression ratio and equivalence ratio on NO_x[44] emissions at MBT spark timing: single-cylinder engine.

the most stringent Federal exhaust emissions standards for 50,000 miles has not been demonstrated.

Driveability and starting. Whereas methanol is somewhat better than gasoline with respect to exhaust emissions and energy-based fuel economy, it is decidedly worse in the areas of vehicle starting and driveability. Methanol's low vapor pressure and high latent heat of vaporization are responsible for these problems. Cars fueled with methanol cannot be started at ambient temperatures below about 5°C; acceptable driveability is difficult to obtain with cars equipped with a carburetor; and fuel injection overcomes many, but not all, of the driveability problems.[41] Figure 14 shows driveability demerits between 100 and 120 for the fuel-injected car, whereas most commercial gasoline-fueled vehicles tested on the same procedure score fewer driveability demerits. However, some gasoline-fueled cars have driveability demerits equal to or greater than those found for this methanol-fuel-injection car.

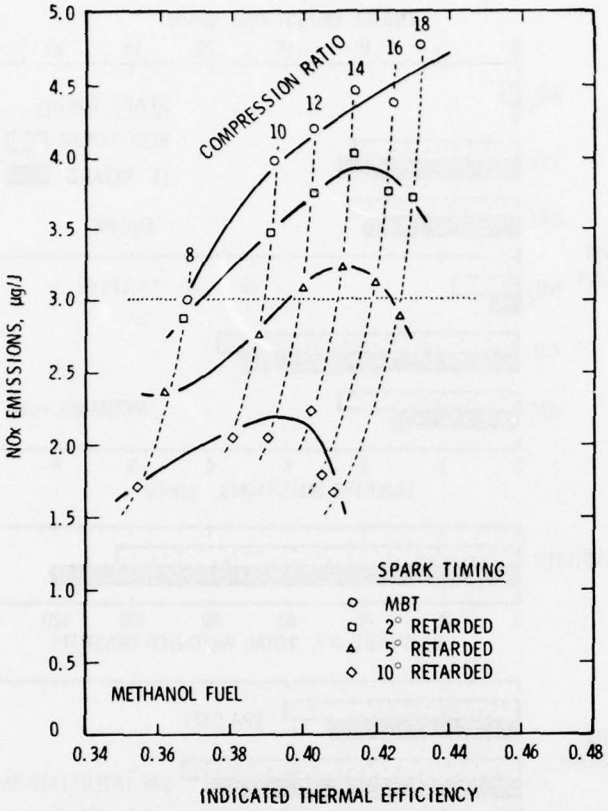


Fig. 13 Tradeoffs between NO_x emissions and thermal efficiency at $\phi = 0.9$: single-cylinder engine.[44]

Distribution, storage, and other concerns. Methanol is generally compatible with the distribution and storage systems now used for hydrocarbon liquids. However, the low volumetric energy density of methanol would require expansion of storage facilities and would cause either vehicle range to be reduced, or size and weight to be increased (Table 2). In addition, methanol is not compatible with all metallic and elastomeric materials now used in fuel systems. Therefore, materials susceptible to methanol attack will have to be avoided in new designs and replaced with appropriate substitutes in existing systems.[37]

Fire and toxicity hazards with methanol may be somewhat greater than those with gasoline.[37] The main reason for the fire hazard is that the saturated vapor over liquid methanol stored in a tank is within the flammable range, whereas gasoline vapors under similar conditions are too rich to ignite.[37] The toxicity of methanol presents greater problems than gasoline mainly because uninformed people may drink it.

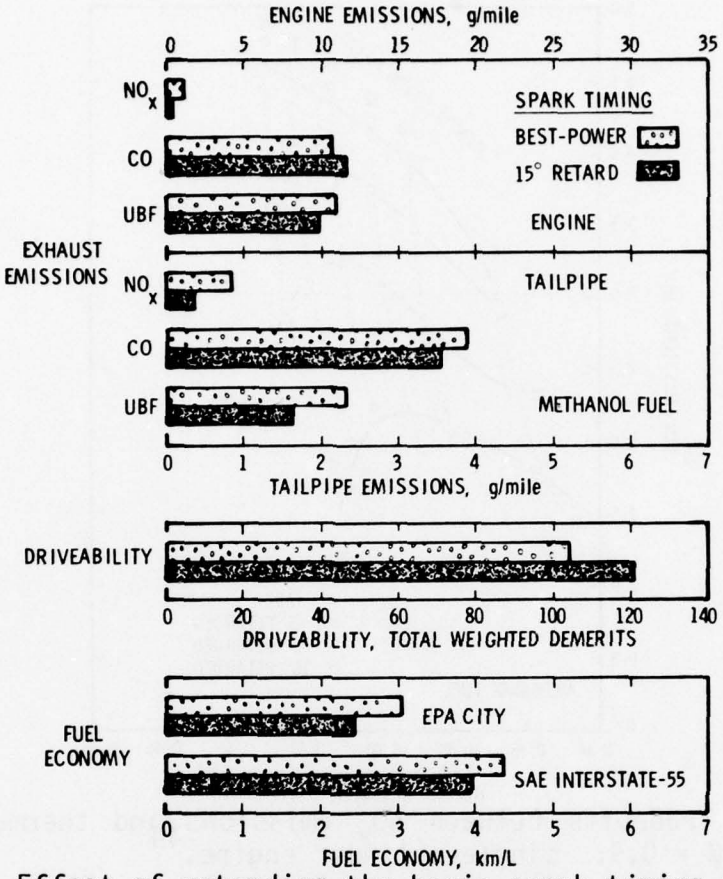


Fig. 14 Effect of retarding the basic spark timing on exhaust emissions, driveability, and fuel economy: Electronic Fuel Injection car, $\emptyset_a = 0.83$.[41]

Ethanol. The viability of ethanol as an alternative automotive fuel depends on its potential for production via fermentation of carbohydrates andd not through chemical synthesis from hydrocarbons. Carbohydrates occur naturally and abundantly in some plants (sugar cane) or must be produced by chemical or enzymatic means from the starch and even the cellulose present in plants (see p. 116 of Ref. 22). Starchy materials such as corn and potatoes are good sources of ethanol because they yield carbohydrates readily. Cellulosic material such as wood chips and agricultural wastes, on the other hand, require more severe processing (strong mineral acid hydrolysis) for conversion to carbohydrates. Recently, successful experiments in the enzymatic hydrolysis of cellulose have been reported.[45] Development of this process could make ethanol production from cellulose competitive. However, it generally is recognized even by the proponents of ethanol that, with present technology and sources, not enough

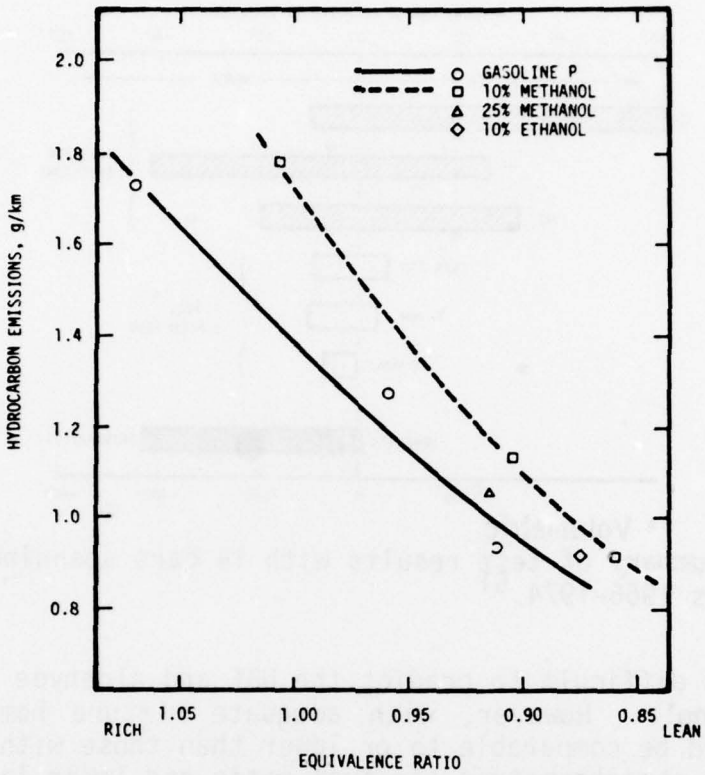


Fig. 15 Effects of alcohol and carburetion on hydrocarbon emissions: 1975 Federal Test Procedure, car X.[51]

ethanol could be made at competitive prices to be considered a viable alternative automobile fuel.[37,46] Consequently, only few, relatively old studies of neat ethanol as a fuel are found in the literature.[47]

Despite the lack of modern studies with ethanol, its combustion and emissions characteristics in spark ignition engines can be predicted qualitatively from comparisons of its properties with those of methanol. Generally, ethanol is expected to fall in between methanol and gasoline in these characteristics.

Efficiency, power, and emissions. As shown by Starkman,[48] ethanol burns somewhat less efficiently and produces less power than methanol. These differences are due to ethanol's higher combustion temperature, lower ratio of mole of products per mole of air, and lower energy density of the fuel air charge. At the same equivalence ratio, CO emissions should be largely unaffected by the change of fuel. However, the higher combustion temperature of ethanol should cause it to produce greater amounts of nitrogen oxides than methanol.

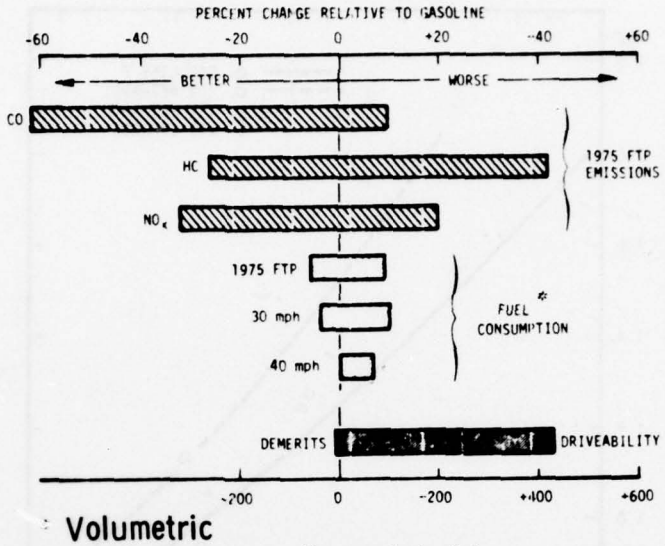


Fig. 16 Summary of test results with 14 cars spanning the model years 1966-1974.[51]

It is difficult to predict the UBF and aldehyde emissions with ethanol. However, with adequate mixture homogeneity, they should be comparable to or lower than those with methanol. The higher stoichiometric air-fuel ratio and lower latent heat of vaporization of ethanol would be responsible for any improvements over methanol.

Driveability and starting. Difficulties in this area should be comparable to those encountered with methanol. Driveability with ethanol may be somewhat better than that with methanol because of ethanol's lower latent heat of vaporization (Table 1). Starting, however, may be even more difficult because ethanol has a vapor pressure even lower than that of methanol.

Distribution, storage, and other concerns. The comments made earlier with respect to neat methanol are equally applicable to ethanol. In addition, the problem of people drinking ethanol would be much more serious than with methanol.

Alcohol-Gasoline Blends

Blends of either methanol or ethanol with gasoline have been studied. (Alcohols are not miscible with diesel fuels.) The utilization of alcohol-gasoline blends can be viewed either as a means to extend gasoline supplies, especially in case of emergencies, or as a transition phase toward a time when petroleum will be exhausted and alcohols might be the primary liquid fuel for internal combustion engines. During and immediately after the Arab Oil Embargo of 1973, the former

reason was the stimulus for much research and even greater publicity, whereas more recent and more reasoned studies have been motivated by the latter reason. Regardless of the motivation, the result has been an abundance of technical data about methanol-gasoline and, to a lesser extent, ethanol-gasoline blends. The preference for methanol over ethanol again is based on the reasons of availability previously discussed.

Another motivation for the utilization of alcohol-gasoline blends has been the increase in octane number imparted by the alcohol to the blend.[37] Although these octane number gains are real, occasionally they have been exaggerated.

Methanol-Gasoline Blends. Reference 37 reviews the literature on methanol-gasoline blends through 1975. In a recent paper, Henein and co-workers[49] give a comprehensive bibliography of the subject through 1976. Additional recent papers are those of Adt and co-workers[50] and of Bernhardt.[42]

Efficiency, power, and emissions. Methanol-gasoline blends respond to equivalence ratio, spark timing, and other engine operating changes in the manner established for either gasoline or methanol alone. When comparing methanol-gasoline blends under identical engine operating conditions (including equivalence ratio), it has been found that the effects of methanol are roughly proportional to the concentration of methanol in the blend. For example, in single-cylinder engine[43] and vehicle studies,[51] methanol addition to gasoline reduced the concentration of NO_x, as would be expected from the combustion properties of neat methanol previously reviewed. Also, volumetric fuel economy decreases with methanol addition because methanol has a lower volumetric energy density than gasoline.

However, for those measurements that are affected by the volatility of the fuel, the effects of methanol are not proportional to its concentration. This occurs because adding methanol to gasoline breaks the hydrogen bonds that give methanol its low volatility. Thus, the blend becomes much more volatile than expected based on neat methanol's properties. This disproportional increase in volatility is responsible for the increased hydrocarbon emissions from vehicles fueled with methanol-gasoline blends as opposed to gasoline alone[51]; Fig. 15 illustrates this point. In addition, more severe vapor-lock problems are encountered with methanol-gasoline blends than with gasoline alone, because of the higher volatility of the blends.[37] To combat these adverse volatility effects,

light hydrocarbons would have to be excluded from methanol-gasoline blends to compensate for methanol's effect.[37] Such an action, however, diminishes methanol's attractiveness as an extender of gasoline supplies.

Much of the original confusion about the effects of methanol addition to gasoline arose because tests were run with vehicles designed for gasoline and not modified to compensate for the leaning of the intake mixture which accompanies the addition of methanol to gasoline. This confusion now has been eliminated, and it is known that using methanol-gasoline blends in cars designed for gasoline operation will increase, decrease, or not affect exhaust emissions, fuel economy, and driveability depending on the original calibration of the carburetor. The results of a 14-car study shown in Fig. 16 illustrate this point.[51]

Although adding methanol to gasoline increases the octane number of the blend, the effect at times has been overstated. A systematic study has shown that adding methanol to gasoline increases the research octane number considerably more than the motor octane number.[51] Thus, for certain cars, improvements in the road octane number of the blend can be small. In fact, under certain conditions and at high methanol concentrations, the road octane number of the blend was less than that of the base gasoline.[51]

Distribution, storage, and other concerns. The main distribution and storage problem of methanol-gasoline blends stems from the separation of the blend into gasoline and a methanol-water phase, which is caused by even small amounts of water (as small as 0.05% water for a 10% methanol-gasoline blend).[37] Another problem is that of the limited solubility of methanol in gasolines, especially those with low concentrations of aromatics.[37]

Considering these distribution and storage disadvantages, the variable effects on emissions, fuel economy, and driveability of the existing car population, and the inability to take full advantage of methanol's good properties when using it in blends with gasoline, it seems prudent to explore all practical alternative uses of methanol before deciding to blend it with gasoline. Some alternative uses are in turbines for electricity generation and in vehicle fleets fueled from a central depot.

Ethanol-Gasoline Blends. For the reasons previously stated in connection with neat ethanol, ethanol-gasoline blends have not been studied as extensively as methanol-

gasoline blends. Reference 37 and 47 contain fairly complete bibliographies of this subject.

Ethanol-gasoline blends have been used or tested in cars, primarily in connection with efforts to utilize ethanol derived from surplus agricultural products. The state of Nebraska has supported the Gasohol project[46] because of occasional grain surpluses. In Brazil, ethanol from surplus sugar cane has been blended with gasoline for many years.

The effects of adding ethanol to gasoline follow the same rules already discussed in connection with methanol-gasoline blends. Thus, a detailed discussion of ethanol-gasoline blends, which behave essentially the same as methanol-gasoline blends, is not necessary. However, the magnitude of the effects is not the same because ethanol's properties (stoichiometric air-fuel ratio, heat of combustion, etc.) differ from those of methanol. Recently, Furey[52] published a paper on ethanol-gasoline blends in which both exhaust and evaporative emissions are discussed thoroughly. Furey found that, for his test car, which was designed to operate with rich air-fuel mixtures, addition of up to 20% ethanol to gasoline reduced exhaust hydrocarbon and carbon monoxide emissions but increased exhaust aldehyde and nitrogen oxide emissions. The leaning of the air-fuel mixture, due to ethanol addition, was the primary cause of the exhaust emission changes. Evaporative emissions were slightly higher with 10% ethanol in gasoline than with gasoline alone.

The Future in Alternative Fuels

If nothing else, this review has demonstrated that much research has been done with alternative fuels, especially those that are individual chemical compounds such as hydrogen and the alcohols. In addition, the review has identified either explicitly, or by inference, several areas that require either additional or a different kind of attention. Another conclusion from this review is that this first phase of alternative fuels research has been all-inclusive rather than selective. Perhaps the time has come to reflect on the past and plan future steps carefully. To do this, we need first to identify the fuels with potential at different points in the future, and second to increase the level of sophistication and the depth of research projects with each individual fuel. Finally, we must start looking at fuels and engines as a system that has its origin at resources in the ground and its end at car wheels on the ground.

Alternative Fuels with Potential

Prophesy is a risky business, as biblical stories demonstrate. The risk is diminished when Delphic ambiguities are substituted for prophesy, but then the usefulness of the prognosis is destroyed. Technological forecasting relies on hard data and logic but also contains both Delphic and prophetic elements; therefore, it can be both risky and useless. Nonetheless, technological forecasting is necessary in order to identify alternative fuels with potential.

The Institute of Gas Technology (IGT)[22] and Exxon Research and Engineering Company,[34] under the sponsorship of the Environmental Protection Agency, studied the feasibility of many alternative fuels for automotive transportation. These studies were comprehensive in that they considered the availability of resources, the technologies for converting resources to fuels, fuel-engine compatibility, distribution and storage, environmental impacts, and economics. Both studies concluded that the most feasible alternative fuels up to the year 2000 are liquid hydrocarbons from coal and oil shale, and methanol from coal; and after the year 2000, hydrogen based on a strong nuclear power generation industry may be added to the list of feasible alternative fuels, assuming that the hydrogen storage problem can be solved. A more recent study (see pp. 4 and 266 of Ref. 3) sponsored by the Massachusetts Institute of Technology identifies coal as the major source of liquid fuels for automotive and other applications, and oil shale as a lesser contributor. Other, less comprehensive studies[5,53] usually come to the same conclusions concerning hydrogen and liquids derived from coal and oil shale. However, a massive and sobering study by the Stanford Research Institute (SRI) clearly outlines the severe social, economic, and environmental impacts and limitations associated with the development of a liquid fuels industry based on coal and oil shale.[54,55] According to the SRI study, the financial risks of a synthetic fuels industry are too great to be assumed by the private sector without either dramatic increases in fuel prices or government support. Among the environmental problems, the SRI study identified the lack of water availability in the West and the difficulties of reclaiming strip mines as the most important. The most important social problem discussed in the SRI study is the creation of boom towns in the rural West.

Research Needs

Assuming that these technological forecasts are correct, future short-term research efforts should concentrate on

liquid hydrocarbons derived from coal and oil shale and on methanol. Longer-range research probably should encompass hydrogen, with emphasis on solving the storage problems and on designing engines best suited to hydrogen's properties.

As already demonstrated in this review, research with coal- and oil shale-derived hydrocarbon fuels has been limited severely because of the unavailability of fuels in sufficient quantities and with relatively firm properties. This situation will not change in the near future. Paradoxically, this is not a problem but an opportunity.

If samples of fuels from various sources and processes were readily available, the temptation to conduct empirical research with whatever sample was at hand would be great and would inhibit efforts to develop fundamental knowledge about the relationships between fuel properties and composition on the one hand, and engine characteristics on the other. Without fuel samples ready for immediate testing, there is an opportunity to plan studies that will yield knowledge applicable to fuels in general, rather than to a fuel with a specific source and processing history. A few specific examples of research to be done are as follows:

1) Determine flame speeds, ignition delay, and other combustion properties of fuel components and their mixtures. Such properties are essential in modeling combustion and exhaust emissions; engine design; fuel design; and mutual adaptation of engines and fuels.

2) Define fundamental relationships between fuel vaporization characteristics and engine performance and exhaust emissions, in order to improve utilization of heavy fuels by appropriate engine and fuel modifications.

3) Determine the contribution of specific nitrogen and sulfur compounds to exhaust emissions and engine durability, and define the highest allowable level for these impurities. These determinations should be based on fundamental studies of the chemistry involved in the burning of these compounds and in the reactions between these compounds and engine materials.

4) Devise replacements, based on fundamentals, for the octane and cetane number scales that no longer may be applicable to alternative fuels and redesigned engines.

5) Define fuel and engine properties that control the formation of particulate matter in order to devise means to utilize low hydrogen-carbon ratio fuels.

An explicit objective of these fundamental studies would be the accumulation of information that would allow the development of fuel-engine systems of maximum overall energy efficiency. This concept has been explored in detail by Stebar.[35] In its broadest application, it requires that all potential fuels and engines be examined and the best matches determined on the basis of the highest numerical product of the efficiencies of resource acquisition, resource conversion, fuel distribution, and fuel utilization. In the more narrow context of this review, the engine choice would be limited to reciprocating internal combustion engines. Naturally, maximum overall energy efficiency cannot be the only selection criterion for fuel-engine systems. Performance, durability, economic, social, and environmental concerns must be factored into the selection process.

To implement the concept of maximum overall energy efficiency in the development of future fuel-engine combinations will require a hitherto unparalleled level of cooperation among the energy companies, the automotive industry, and government. This is a consequence of the stepwise, iterative nature of the system optimization procedure. At each step of the procedure, fuel processing severity andd engine design will be adapted mutually to yield fuel-engine combinations of progressively higher overall energy efficiency. Thus neither the fuel processor nor the engine designer can do the job alone. And to work together, they will require the involvement of the government to remove institutional, legal, and commercial barriers that normally inhibit this type of cooperation. One method by which this type of cooperation can be achieved is through contracts awarded by the government to teams representing several interested industries.

Acknowledgment

Without the work of alternative fuels researchers at the General Motors Research Laboratories, this review could not have been written.

References

[1] "Weekly Statistical Bulletin," American Petroleum Inst., Statistics Dept., Washington, D.C., Dec. 31, 1970 and 1976.

[2] "World Energy Outlook," Public Affairs Dept., Exxon Corp., New York, 1977.

[3] Wilson, C. L. (ed.), Energy: Global Prospects, 1985-2000, McGraw-Hill, New York, 1977, pp. 3-5.

[4] "Energy and Climate," National Academy of Sciences, Washington, D.C., July 1977.

[5] Salzano, F. J. and Braun, C., "Hydrogen Energy Assessment," National Center for Analysis of Energy Systems, Brookhaven National lab., Upton, N. Y., March 1977.

[6] Escher, W. J. D., "Hydrogen-Fueled Internal Combustion Engine, A Technical Survey of Contemporary U.S. Projects," Escher, Technology Associates, St. Johns, Mich., TEC-75/605, Sept. 1975.

[7] Cole, R. B., "The Performance of Hydrogen-Fueled Reciprocating Engines," Proceedings of the Fourth International Symposium on Automotive Propulsion Systems, NATO/CCMS, Vol. 2, 1977, Session 6.

[8] McLean, W. J., deBoer, P. C. T., Homan, H. S., and Fagelson, J. J., "Hydrogen as a Reciprocating Engine Fuel," Future Automotive Fuels, Plenum Press, New York, 1977, pp. 297-317.

[9] Stebar, R. F. and Parks, F. B., "Emission Control with Lean Operation Using Hydrogen-Supplemented Fuel," Transactions of the Society of Automotive Engineers, Vol. 83, Sec. 1, 1974, pp. 821-836.

[10] Simpson, F. B., Lofthouse, J. H., and Swope, D. R., "Modification Techniques and Performance Characteristics of Hydrogen-Powered IC Engines -- State of the Art, 1975," Proceedings of the First World Hydrogen Energy Conference, Univ. of Miami, Vol. 3, 1976, pp. 6C/75-6C/95.

[11] Bowen, T. L. and Taylor, D. W., "Hazards Associated with Hydrogen Fuel," Proceedings of the Eleventh Intersociety Energy Conversion Engineering Conference, Vol. 1, 1976, pp. 997-1002.

[12] Buchner, H. and Saufferer, H., "Results of Hydride Research and the Consequences for the Development of Hydride Vehicles," Proceedings of the Fourth International Symposium on Automotive Propulsion Systems, NATO/CCMS, Vol. 2, 1977, Session 6.

[13] Breshears, R., Cotrill, H., and Rupe, J., "Hydrogen Injection for Internal Combustion Engines," Council on Environmental Quality Advisory Committee on Alternative Automotive Power Systems, Ann Arbor, Mich., June 13-14, 1974.

14 MacDonald, J. S., "Evaluation of the Hydrogen-Supplemented Fuel Concept with an Experimental Multicylinder Engine," Automotive Congress and Exposition, Detroit, Mich., Society of Automotive Engineers, Paper 760101, Feb. 1976.

15 Noguchi, M., Bunda, T., and Sumiyoshi, M., "A Study on Reformed Fuel for an Automotive Gasoline Engine," Proceedings of the Fourth International Symposium on Automotive Propulsion Systems, NATO/CCMS, Vol. 2, 1977, Session 6.

16 Hodgson, J. W., "Alternate Fuels for Transportaiton, Part 3: Ammonia for the Automobile," Mechanical Engineering, Vol. 96, July 1974, pp. 22-25.

17 Energy Depot Concept, Society of Automotive Engineers, Warrendale, Pa., SP 263, 1965.

18 Starkman, E. S., Newhall, H. K., Sutton, R., Maguire, T., and Farbar, L., "Ammonia as a Spark Ignition Engine Fuel: Theory and Application," Society of Automotive Engineers, Warrendale, Pa., Paper 660155, Jan. 1966.

19 Gray, J. T., Dimitroff, E., Meckel, N. T., and Quillan, R. D., Jr., "Ammonia Fuel-Engine Compatibility and Combustion," Society of Automotive Engineers, Warrendale, Pa., Paper 660156, Jan. 1966.

20 Schmidt, E. W., "Hydronitrogens as Future Automotive Fuels," Future Automotive Fuels, Plenum Press, New York, 1977, pp. 320-339.

21 Cornelius, W., Huellmantel, L. W., and Mitchell, H. R., "Ammonia as an Engine Fuel," Transactions of the Society of Automotive Engineers, Vol. 74, 1966, pp. 300-315.

22 Pangborn, J. and Gillis, J., "Alternative Fuels for Transportation - A Feasibility Study," Inst. of Gas Technology, Chicago, Ill., EPA-460/3-74-012-b, Vol. 2, July 1974, pp. 131-132.

23 Calvin, N., "Hydrocarbons Via Photosynthesis," Lawrence Berkeley Lab., Univ. of California, Berkeley, Calif., LBL-5387, Sept. 1976.

24 Gary, J. H., "Motor Fuels from Oil Shale - Production and Properties," Future Automotive Fuels, Plenum Press, New York, 1977, pp. 136-146.

[25] Clark, E. L., "Coal as a Source of Automotive Fuels," Future Automotive Fuels, Plenum Press, New York, 1977, pp. 125-134.

[26] Raymond, R. J., Morgan, D. T., Appleton, J. P., and Davis, J. P., "Cost and Application of Coal Burning Diesel Power Plants - A Preliminary Assessment," Thermo Electron Corp., Waltham, Mass., TE2557-110, 1975.

[27] Lee, R. C. and Wimmer, D. B., "Exhaust Emission Abatement by Fuel Variations to Produce Lean Combustion," Transactions of the Society of Automotive Engineers, Vol. 77, Sec. 4, 1968, pp. 3025-3042.

[28] Fleming, R. D. and Allsup, J. R., "Natural Gas as an Automotive Fuel, An Experimental Study," Bureau of Mines, U.S. Dept. of the Interior, Rept. of Investigations 7806, 1973.

[29] Scott, W. M., "Alternative Fuels for Automotive Diesel Engines," Future Automotive Fuels, Plenum Press, New York, 1977, pp. 263-290.

[30] Hilden, D. L. and Stebar, R. F., "Evaluation of Acetylene as a Spark Ignition Engine Fuel," Proceedings of the Fourth International Symposium on Automotive Propulsion Systems, NATO/CCMS, Vol. 2, 1977, Session 6.

[31] Hurn, R. W., "Characteristics of Conventional Fuels from Non-Petroleum Sources - An Experimental Study," Future Automotive Fuels, Plenum Press, New York, 1977, pp. 167-174.

[32] Cottingham, P. L., "Motor Gasoline from Shale Oil," Laramie Research Center, U.S. Energy Research and Development Administration, Laramie, Wyo., Conf. 760342-5, 1976.

[33] Cottingham, P. L., "Diesel Fuels from Shale Oil," Laramie Research Center, U.S. Energy Research and Development Administration, Laramie, Wyo., Conf. 760342-3, 1976.

[34] Kant, F. H., Cahn, R. P., Cunningham, A. R., Farmer, M. H., Herbst, W., and Nanny, E. H., "Feasibility Study of Alternative Fuels for Automotive Transportation," Exxon Research and Engineering Co., Linden, N. J., EPA-460/3-74-009-b, Vol. 2, June 1974, pp. 167-174.

[35] Stebar, R. F., Daniel, W. A., Sapre, A. R., and Peters, B. D., "Matching Future Automotive Fuels and Engines for Optimum Energy Efficiency," Future Automotive Fuels, Plenum Press, New York, 1977, pp. 96-116.

[36] Reynolds, R. W., Smith, J. S., and Steinmetz, I., "Methyl Ether (MTBE) Scores Well as High-Octane Gasoline Component," The Oil and Gas Journal, Vol. 73, June 1975, pp. 50-52.

[37] "Alcohols - A Technical Assessment of Their Application as Fuels," American Petroleum Inst., Washington, D.C., Publ. 4261, July 1976.

[38] Thomas, C. O., Hodgson, J. W., Carroll, S. L., Hardin, T. C., and Munoz-Candelario, R., "Methanol From Coal - Fuel and Other Applications," Inst. for Energy Analysis, Oakridge Associated Univ., Oakridge, Tenn., ORAU-126, Feb. 1976.

[39] Klass, D. L., "Wastes and Biomass as Energy Resources: An Overview," Proceedings of the Symposium on Clean Fuels, Inst. of Gas Technology, 1976, pp. 22-58.

[40] Hilden, D. L. and Parks, F. B., "A Single-Cylinder Engine Study of Methanol Fuel - Emphasis on Organic Emissions," Society of Automotive Engineers, Warrendale, Pa., Paper 760378, Feb. 1976.

[41] Brinkman, N. D., "Vehicle Evaluation of Neat Methanol - Compromises Among Exhaust Emissions, Fuel Economy, and Driveability," Proceedings of the Fourth International Symposium on Automotive Propulsion Systems, NATO/CCMS, Vol. 2, 1977, Session 4.

[42] Bernhardt, W. E., Koenig, A., Lee, W., and Menrad, H., "Recent Progress in Automotive Alcohol Fuel Application," Proceedings of the Fourth International Symposium on Automotive Propulsion Systems, NATO/CCMS, Vol. 2, 1977, Session 4.

[43] Koenig, A., Lee, W., and Bernhardt, W. E., "Technical and Economic Aspects of Methanol as an Automotive Fuel," Society of Automotive Engineers, Warrendale, Pa., Paper 760545, June 1976.

[44] Brinkman, N. D., "Effect of Compression Ratio on Exhaust Emissions and Performance of a Methanol-Fueled Single-Cylinder Engine," Society of Automotive Engineers, Warrendale, Pa., Paper 770791, Sept. 1977.

[45] Andren, R. K., Mandels, M. H., and Medeiros, J. E., "Production of Sugars from Waste Cellulose by Enzymatic Hydrolysis. I. Primary Evaluation of Subtrates," Applied Polymer Symposium, Wiley, New York, 1975, pp. 205-219.

[46] Scheller, W. A., "The Use of Ethanol-Gasoline Mixtures for Automotive Fuel," Proceedings of the Symposium on Clean Fuels from Biomass and Wastes, Inst. of Gas Technology, Jan. 1977, pp. 185-200.

[47] Alcohols and Hydrocarbons as Motor Fuels, Society of Automotive Engineers, Warrendale, Pa., SP-254, June 1964.

[48] Starkman, E. S., Newhall, H. K., and Sutton, R. D., "Comparative Performance of Alcohol and Hydrocarbon Fuels," Alcohol and Hydrocarbons as Motor Fuels, Society of Automotive Engineers, Warrendale, Pa., SP-254, June 1964, pp. 14-33.

[49] Henein, N. A., Singh, T., Rozanski, J., and Husak, P., "Flame Speeds, Performance, and Emissions with Methanol-Indolene Blends," Proceedings of the Fourth International Symposium on Automotive Propulsion Systems, NATO/CCMS, Vol. 2, 1977, Session 4.

[50] Adt, R. R., Chester, K. A., Pappas, J. M., Rajan, S., Swain, M. R., and Wiesner, C. K., "The Effect of Blending Methanol with Gasoline on Geometric Distribution," Proceedings of the Fourth International Symposium on Automotive Propulsion Systems, NATO/CCMS, Vol. 2, 1977, Session 4.

[51] Brinkman, N. D., Gallopoulos, N. E., and Jackson, M. W., "Exhaust Emissions, Fuel Economy and Driveability of Vehicles Fueled with Alcohol-Gasoline Blends," Transactions of the Society of the Society of Automotive Engieners, Vol. 84, Sec. 1, 1975, pp. 541-567.

[52] Furey, R. L. and Jackson, M. W., "Exhaust and Evaporative Emissions from a Brazilian Chevrolet Fueled with Ethanol-Gasoline Blends," Proceedings of the Twelfth Intersociety Energy Conversion Engineering Conference, Aug. 1977.

[53] Johnson, R. T., "Energy and Synthetic Fuels for Transportation - A Summary," Society of Automotive Engineers, Warrendale, Pa., Paper 740599, Aug. 1974.

[54] Dickson, E. M. and Hughes, E. E., "Impacts of Synthetic Liquid Fuel Development for the Automotive Market," Future Automotive Fuels, Plenum Press, New York, 1977, pp. 342-362.

[55] Dickson, E. M., Steele, R. V., Hughes, E. E., Walton, L., Zink, R. A., Miller, P. D., Ryan, J. W., Simmon, P. B., Holt, B., White, R. K., Harvey, E. C., Cooper, R., Phillips,

D. F. (consultant), Stoneman, W. C. (consultant), "Impacts of Synthetic Liquid Fuel Development - Assessment of Critical Factors," Stanford Research Inst., Menlo Park, Calif., ERDA 76-129, May 1976.

DISCUSSION

DR. I. GLASSMAN (Princeton University): What is the relative cost of making ethanol rom coal by biomass method such as fermentation. I am told by some authoritative people that the Brazilians have a strong program in this area. Some new data are available which make this process look more attractive than the conversion of coal to actual methanol. Are you familiar with this?

MR. GALLOPOULOS: I only have it second hand. First of all, I think we are talking about two different alochols. I am talking about methanol. They are talking about ethanol. Ethanol can be made by fermentation. However, that depends on whether you have material to ferment. If you have enough sugar, as they do in Brazil, that is okay. Of course, you can make methanol from vegetable matter also. But as I understand it, at least with today's technology, it is more expensive to go that route than it is to make methanol from coal.

DR. GLASSMAN: How does ethanol look as a fuel for the automobile engine?

MR. GALLOPOULOS: Ethanol has essentially the same problems as methanol as far as the engine is concerned. About the only thing that is not quite as bad with ethanol is that its energy density is higher than that of methanol.

DR. GLASSMAN: What about using ethanol in diesel engines?

MR. GALLOPOULOS: You have the same problems with ethanol in diesel engines as you do with methanol. However, ethanol could be used in Otto engines.

DR. WESTBERG (Aerospace Corp.): Hydrocarbon emissions are bad because hydrocarbons form photochemical smog, but methanol does not--or at least there is no evidence that it does. So it seems to me that unburned-fuel emissions from cars burning methanol should not be considered as undesirable as unburned-fuel emissions from cars burning gasoline.

MR. GALLOPOULOS: That is probably true. Not enough has been done to establish the photochemical effects of having

methanol in the atmosphere, but, from what we know, what you said is correct. On the other hand, methanol itself is toxic, and no one has looked at what would happen if we had all of these methanol emissions in the atmosphere. However, I think that there is a good possibility of handling the emissions from engines burning methanol. As I see it, there is no problem with methanol either in the ability of cars to use it as a fuel or in controlling the emissions from engines burning it. I believe the problem with methanol is the cost of making it (from coal, vegetation, or garbage) and the necessity of a distribution system alongside that now used for petroleum products.

DR. J. P. LONGWELL (M.I.T.): One of the trends both with methanol and with coal- and shale-derived liquids would be gasoline of lower volatility. In fact, you might even make a good case for cutting the front end entirely out of gasoline and have something between gasoline and kerosene. I wonder if you feel that there is any technical possibility of developing a fuel-injection or carburetion system that could handle something like that.

MR. GALLOPOULOS: I think the fuel injection system can handle many of those problems. This is why we used it with methanol. It does not solve them all. Of course, the fuel-injection system is more expensive than a carburetor.

The problem with methanol which fuel injection does not overcome is that of starting. You need to devise some other means of doing that, and it is a somewhat more difficult problem to solve. It takes money and is more complex.

MR. R. W. HURN (Department of Energy, Bartlesville): I think you have done a great job in your presentation. In an endorsement I would like to emphasize two points. First of all, we need to emphasize and focus research upon the basic properties of fuels and the relationship of those properties to fuel performance in specific systems. Alternative fuels is a "buzz" word in government, and I regret to say that I believe I see the same trend in industry. The fact is, there are no alternative fuels as of this moment and, except for limited quantities of experimental materials, there will be no production of alternative fuels for up to ten years to come. Yet people are obtaining nonpetroleum fuels by whatever means they can--simple distillation or whatever--calling them alternative fuels and experimenting with those fuels. It is absolute nonsense to work with such materials. I would strongly emphasize, therefore, that the principal focus of research effort be upon the basics of fuel properties and

combustion processes. If work is to be done in the area of adapting engines and synfuels options, there should be logic and technical relevance in the choice and manufacture of materials that represent synfuels or reflect some probable characteristics of synfuels to come.

The second point that you made was a plea to award contracts to people who have expertise both in fuels and in engines. In this you touch upon a point that can be vitally important in experimental programs that are being supported by the government agencies. We have problems in DOE, in that program managers try to compartmentalize fuels research. Even in my own organization, sponsors of research in fossil energy are saying, "Dick Hurn, you cannot do that because what you propose is engine research and you are to be concerned with fuel research." This overly narrow compartmentalization is widely--although erroneously--perceived as efficient specialization in research and is a difficult problem to correct. I would ask, therefore, for support from those of you in industry who are directly involved in fuels and engine study; go back home and from there approach the government agencies or whoever is influencing research and say, "Let's put this all together and have some integrated programs." Lack of adequately integrated research in alternative fuels development is a very serious matter--very serious indeed.

Beyond this emphasis on program I would like also to remark about something that concerns me greatly. I do not know how you can translate this concern of mine into action or influence in your own programs, but let me share it with you nonetheless. I refer to the problem with inflation and its relationship to and impact upon the research effort. This past week, I was talking with managers who are prominent in the design of experimental program and policy matters having to do with alternative fuels--the discussion was about coal gasification and the immediacy of any alternative that might result in coal gasification. In this discussion it was pointed out that the inroads of 1 or 2 years of inflation totally wipe out the process efficiency gain that we can hope to get from continued research on coal gasification in the next 10 years. Put another way: two years of inflation effect will more than wipe out the total of any gain that we can foresee in coal gasification efficiency over the old Lurgi process that was known 40 years ago. The point is, as Gene Ecklund expressed it recently, "The cheapest alternative fuel that we can see ahead is the fuel that will be made today." This appears to be true and I think it is <u>most</u> important. I would like therefore to emphasize that, somehow, we must move ahead and do what can be done today.

DR. C. T. BOWMAN (Stanford University): Can you see some specific fundamental combustion and chemical kinetic studies that would be useful in the adapting of the internal combustion engine to the use of alternative fuels? You mentioned the words "flame speed" and "ignition delay". If someone correlated turbulent flame speed with fuel properties, would that be useful to you?

MR. GALLOPOULOS: Yes, certainly, that would be useful. Another area that we are not very knowledgable about is the relationships between fuel volatility and engines. For example, we do not know how low fuel volatility can be for engines modified to accept low volatility fuels, but that is not a kinetics problem. Chemical kinetics problems are the effect of fuel nitrogen on emissions and the reactions which take place between nitrogen compounds in the fuel and engine materials or fuel system materials. Also related to kinetics are investigations of methods for stopping those reactions, perhaps by not removing the nitrogen compounds, but by modifications either of engine and fuel system materials, or of the fuel with additives. Results of these investigations would be very useful because it takes a great deal of energy and money to remove nitrogenous compounds from the fuel. The problem of hydrocarbon emissions is still with us. We really do not understand exactly where they come from. This is, to a large degree, a kinetics problem. A lot of work is being done, but I do not think there is an answer yet. More work, and perhaps more sophisticated work, is needed.

The problem of soot formation is one which needs much more work, especially as far as the diesel (also the Otto engine) is concerned. In the future, fuels may have low hydrogen content, which will make soot formation an even more serious problem. Also, soot formation may be one of the factors which could limit the penetration of diesel engines into the transportation system.

USE OF ALTERNATIVE FUELS IN STATIONARY COMBUSTORS

M. P. Heap*
Energy and Environmental Research Corporation, Irvine, Cal.

Abstract

Stationary combustion sources traditionally have utilized a wide range of fuels. This paper summarizes information available on the pollutant emission potential and combustion characteristics of alternative fuels suitable for use in boilers and furnaces. The fuels discussed are: coal-derived fuel gases, alcohol, and coal or shale-derived liquid fuels. The major problems in the combustion of these fuels will be associated with their potential for increased emissions of nitrogen oxide and carbonaceous particulate. Combustion modification techniques suitable for the control of nitrogen oxide emissions from conventional fuel-fired furnaces probably will prove to be applicable to alternative fuels.

Introduction

Stationary combustion sources accounted for 75% of the United States energy consumption in 1974, and 65% of this energy was consumed by one class of combustor, boilers. The other major stationary sources of energy consumption were process heaters and furnaces used in the petrochemical, metallurgical, cement, refractories, agricultural, and food industries. This paper will concentrate upon, but not be limited to, the application of alternative fuels in boilers, since it is reasonable to project that this application would have the greatest impact upon the pattern of fuel usage in the U.S. This impact would be greatest not only because of the fraction of the total fuel used by boilers and the expected increase in electrical power requirements, but also because a relatively small number of units account for a significant portion of the fuel used. Consequently, the suitability of alternative fuels for utility and large industrial boilers would increase the availability of conventional fuels for combustors with more exacting fuel requirements.

Although 92% of the energy consumed by stationary sources is provided by fossil fuels (26% coal, 44% natural gas, and

*Vice President

30% petroleum), traditionally these sources also have utilized a wide range of fuels. Wood, peat, industrial, and residential waste are forms of alternative fuels which have been used in boilers for many years. Refinery and blast furnace gases commonly are used in the petrochemical and metallurgical industries without operational problems. For the purposes of this paper, alternative fuels will be divided into three groups:

1) Coal-derived fuel gas. Various gasification schemes have been proposed to allow the use of coal in an environmentally acceptable manner. On-site gasification or limited distribution schemes in industrial complexes would allow coal-derived fuel gases to be used by boilers and process furnaces. The major impact of coal-derived fuel gases most probably will be associated with their use in combined cycles for power generation.

2) Alcohol fuels. Coal or refuse could be processed to produce alcohol fuels that might replace natural gas or petroleum-derived fuels in selected heavily populated areas. Alcohol fuels have the advantage that their pollutant emission potential is low.

3) Coal or shale-derived liquid fuels. Economic or political pressures could provide the impetus necessary to develop the U.S. shale reserves or commercialize processes to produce liquid fuels from coal. The major disadvantages associated with these fuels are their low hydrogen-to-carbon ratio and their relatively high nitrogen content, which may introduce pollutant-control problems.

With the exception of advanced gas turbines for combined cycle operation, it is most likely that alternative fuels will be burned in the same type of combustors currently burning fossil fuels. This paper presents a review of information available to date on the use of alternative fuels in stationary combustors. It was not the intent of the author to provide an exhaustive review but merely to choose examples that are sufficient to illustrate potential problem areas.

General Considerations in the Use of Alternative Fuels by Stationary Sources

Three major factors are involved in the use of alternate fuels in stationary sources: fuel preparation, combustion characteristics, and pollutant emission potential. Fuel preparation is a mechanical problem and will be specific to a particular alternate fuel. The physical properties of a fuel

may be such that it must be stored and transported under certain conditions to insure its delivery at the burner in a form suitable for burning. Certain forms of solvent-refined coal are solid at low temperatures and must be heated for transport and atomization.

Several combustion characteristics are important when considering the impact of conversion to alternate fuels. Boilers are fired by turbulent diffusion flames in which the fuel and combustion air are injected separately. Ignition stability normally is achieved by insuring feedback of heat to the base of the flame by the recirculation of hot combustion products. Several options are available to improve stability should conversion introduce problems: the fuel injection system can be modified or the strength of the recirculation increased. Changing the properties of the fuel can affect the heat release rate and the flame emissivity, which might affect the heat flux distribution to the combustor walls. If conversion involves the use of fuels with high ash contents, then fouling could become a problem, causing a loss in efficiency. Fouling problems may be alleviated by controlling the time-temperature history of the particulate to prevent the formation of adhesive particles.

The pollutant emission potential of alternate fuels is linked very strongly to their chemical properties, but to a large extent it can be controlled by modifying the combustion process. One incentive to provide alternative fuels for stationary combustors is the need to control sulfur emissions from combustion sources while utilizing reserves of high-sulfur coal. In many instances, reduction of the sulfur content of the fuel is more attractive than SO_2 removal from combustion products. Consequently, it can be assumed that the sulfur content of alternative fuels will be of such a level to allow their utilization without flue gas scrubbing. Nitrogen oxides are produced during combustion from two sources, molecular nitrogen and nitrogen that is bound chemically within the fuel. The fixation of molecular nitrogen forming thermal NO is a temperature-dependent process, and it has been shown that the emission of thermal NO can be controlled adqequately by the use of flue gas recirculation.[1] The range of bound nitrogen contents of various fuels is given in Table 1; naturally, the nitrogen content of a particular fuel will depend upon the details of the production process.

The precise mechanism by which fuel nitrogen compounds are converted to NO or N_2 is not known. It generally is recognized that the fate of fuel nitrogen depends upon two competing reaction paths. Under oxygen-deficient conditions,

one of these paths favors the formation of N_2 rather than NO. Thus the control of fuel NO normally is achieved by staging the heat-release process. Reaction first takes place in a fuel-rich primary stage before combustion is completed by the addition of second-stage air. The optimum conditions of temperature and stoichiometry for minimum residence time in this primary section have yet to be established. However, NO_x control via staged combustion techniques has been shown to be very successful for coal[2] but only moderately successful for residual fuel oils.[3] Those conditions that minimize fuel NO formation maximize the production of carbonaceous particulate, and the control of NO emissions for residual fuel oil-fired furnaces by staged combustion techniques normally is limited by an increase in particulate emissions.

The tradeoff in NO_x and particulate emissions observed with residual fuel oil-fired furnaces is likely to become more apparent with coal-derived liquid fuels. Longwell[4] has pointed out that the lower hydrogen-to-carbon ratios of coal-derived liquid fuels will greatly increase their tendency to produce soot. Indeed, under uncontrolled conditions the time available for soot burnout in conventional furnaces may be inadequate for alternative liquid fuels.

Coal-Derived Fuel Gases

Blast furnace gas, producer gas, and water gas (examples of lean fuel gases typical of those produced by air-blown gasifiers) have been utilized by industry for many years. Thus it can be concluded that there would be no insurmountable problems associated with the use of coal-derived fuel gases in stationary combustors. The Steag combined cycle plant at Lunnen, West Germany, is an example of a boiler designed specifically for coal-derived fuel gas. Fuel gas produced from Lurgi fixed-bed gasifiers is burned at 10 atm. The com-

Table 1 Nitrogen content of typical alternate fuels

Fuel	Nitrogen content, % wt
Coal-derived low-Btu gas	0.04 as ammonia
Solvent refined coal	1.9 (base coal 1.5 %)
Coal liquids	0.3 - 0.5
Coal-oil slurry	0.65 (oil 0.42, coal 0.78)
Shale-derived heavy fuel oil	1.4

Table 2 Summary of pilot scale results with simulated coal-derived fuel gases[5]

Fuel	Gross heating value, Btu/Standard Cubic Foot	Adiabatic flame temperature (3% O_2, 325°F preheated air)	Flue gas temperature, °F	Furnace efficiency	Flue NO ppm at 3% O_2
Naural gas	1035	3337	2553	28.6	65
Lurgi/oxygen	285	3164	2442	25.2	32
Winkler/oxygen	270	3329	2523	26.4	73
Koppers Totzek/ oxygen	285	3578	2554	33.1	104
Wellman Galusha/ air	159	2948	2434	19.0	15
Winkler/air	116	2579	2335	10.8	4

bustion products are expanded across an exhaust turbine after their temperature has been reduced in the boiler. There have been no reported combustion problems with this installation.

Shoffstall and Waibel[5] have described a program directed toward the identification of problems associated with retrofitting utility boilers with low-Btu gases manufactured from commercially available coal conversion processes. Data were collected to compare flame stability, flame length, flame emissivity, NO_x emissions, and heat absorption rates from five synthetically produced fuel gases and natural gas when burned in a pilot scale furnace fired by a typical boiler burner. Table 2 summarizes the properties of the gases tested and the measured furnace absorption efficiency after the furnace load had been adjusted to give an exit temperature of 2553°F with natural gas. In addition to changes in the fraction of heat absorbed in the furnace, conversion to coal-derived fuel gas may result in a change in the mass and enthalpy of the combustion products entering and convective section. This change will affect fan and heater performance and also change the distribution of heat absorbed in the various boiler components.

Based upon results obtained with blast furnace gas in a pilot scale furnace, Martin[6] concluded that NO_x emissions were unlikely to exceed those from natural gas if fuels were produced by air-blown gasifiers. Shoffstall's estimates also indicate that emissions from a retrofitted boiler would exceed New Source Performance Standards only if oxygen-blown systems producing medium-Btu gases were burned. These estimates were based upon an extrapolation of NO_x emissions at pilot scale volumetric heat-release rates to utility boiler rates, and the actual figures are open to question; however, the emissions probably rank in the correct order. As shown in Table 1, it may be expected that coal-derived fuel gases will contain bound nitrogen in the form of ammonia, some of which will be converted to NO during combustion. In addition to ammonia, the fuel gas also will contain hydrogen sulfide. Wendt et al[7] have shown that in small-scale turbulent diffusion flames the presence of sulfur can increase the emission of fuel NO. If dirty coal-derived fuel gases are to be burned in stationary combustors, then NO_x emissions will not be due solely to thermal NO, and, depending upon the amount of ammonia and nitrogen-containing tars, it is likely that some form of staged combustion system will be necessary to control NO emissions. Folsom[8] and co-workers presently are conducting bench scale tests to define minimum NO_x emissions expected from advanced combustors firing dirty low-Btu gases.

Methyl Alcohol as a Fuel for Package Boilers

Alcohol and alcohol blends have been proposed as fuels for internal combustion engines. In order to assess potential problems associated with the use of alcohol fuels in stationary sources, two package boilers, a 12,000 lb/h-of-steam firetube boiler and a 24,000 lb/h-of-steam watertube boiler, were modified to fire commercial grade methanol.[3] No practical problems were encountered in the conversion. In addition to modification to the fuel delivery system, it was necessary only to increase the size of the fuel nozzle to maintain the required heat input. Pollutant emissions and efficiency were measured for the two boilers and comparisons made between no. 5 fuel oil, natural gas, and methanol, and some of the results are presented in Figs. 1 and 2 for the watertube boiler. NO_x emissions were lower with methanol firing than with natural gas and considerably lower than those measured with fuel oil, which contained 0.12% nitrogen. However, boiler efficiencies were the lowest with methanol because of the increased enthalpy of the flue gases. Heat flux distributions were measured in an experimental furnace[3]

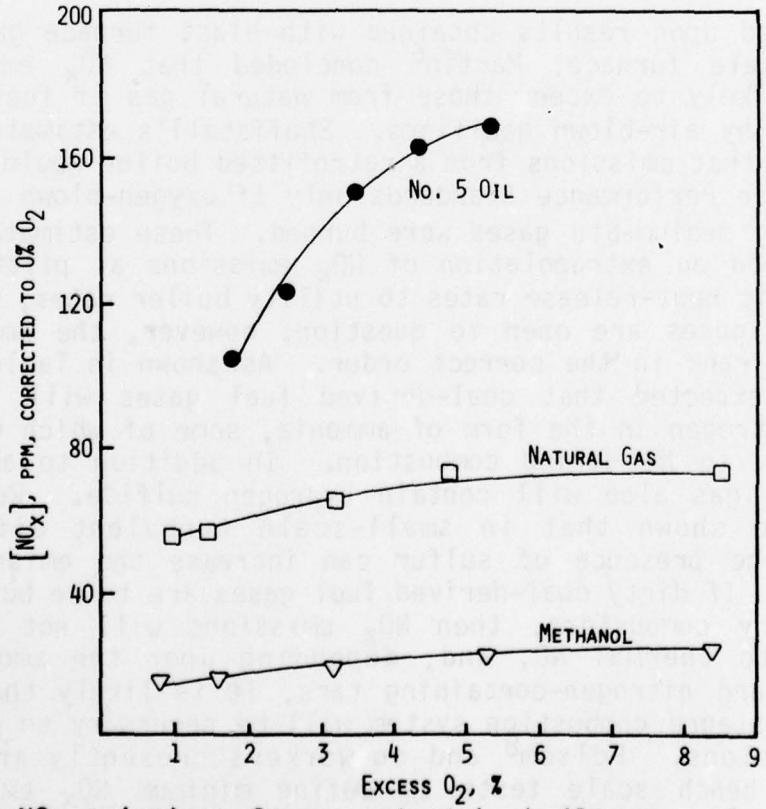


Fig. 1 NO_x emissions from a watertube boiler as a function of fuel type[3] and excess air.

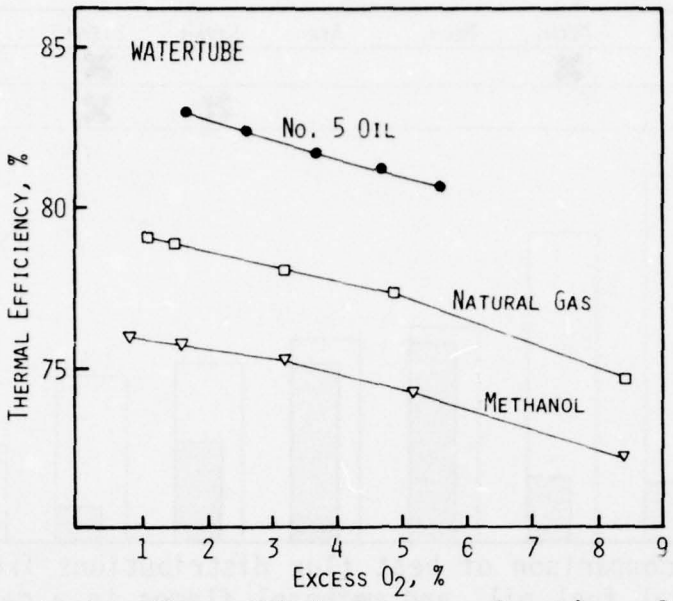


Fig. 2 Measured boiler efficiency as a function of excess air and fuel type.[3]

burning fuel oil, natural gas, and methanol. Figure 3 compares data from the three fuels by showing the coolant temperature rise across a series of cylindrical calorimetric sections for a constant fuel firing rate. It can be seen that the heat flux from the alcohol fuel is similar to that of the residual oil. If alcohol were to be produced in commercial quantities, then pollutant emissions would be reduced, but there also would be an efficiency penalty to be considered in the overall cost of energy conversion.

Coal or Shale-Derived Liquid Fuels

The nitrogen contents of both coal and shale-derived liquid fuels are higher than the corresponding grade of petroleum fuel. Haebig et al.[9] and Dzuna[10] have reported pollutant emission results obtained with a small residential furnace burning coal liquids and shale oil fuels. Figure 4 presents a plot of NO_x emissions at 3% excess oxygen for several fuels as a function of weight percentage of nitrogen in the fuel. In addition to the data reported by Haebig and Dzuna, lines are drawn representing results reported for petroleum fuels. Turner and Siegmund[11] measured NO emissions from a firetube boiler for a range of fuels with and without staged heat release. It can be seen that for the range of nitrogen contents up to 0.8% the emission levels are similar for all three types of fuel. Results also are shown in Fig. 4 for emissions from a low-NO_x burner developed for

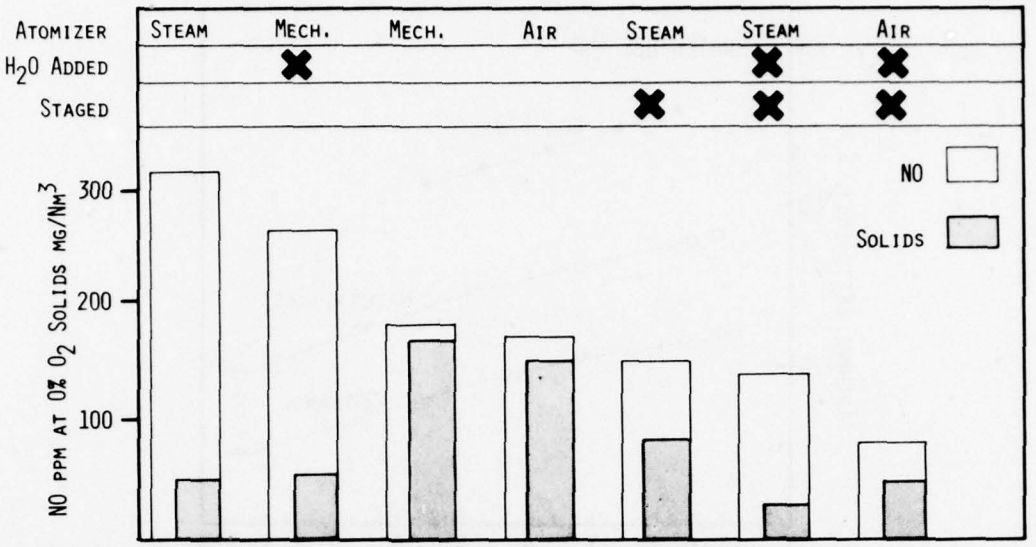


Fig. 3 A comparison of heat flux distributions from natural gas, residual fuel oil, and methanol flames in a calorimetric firetube combustor.

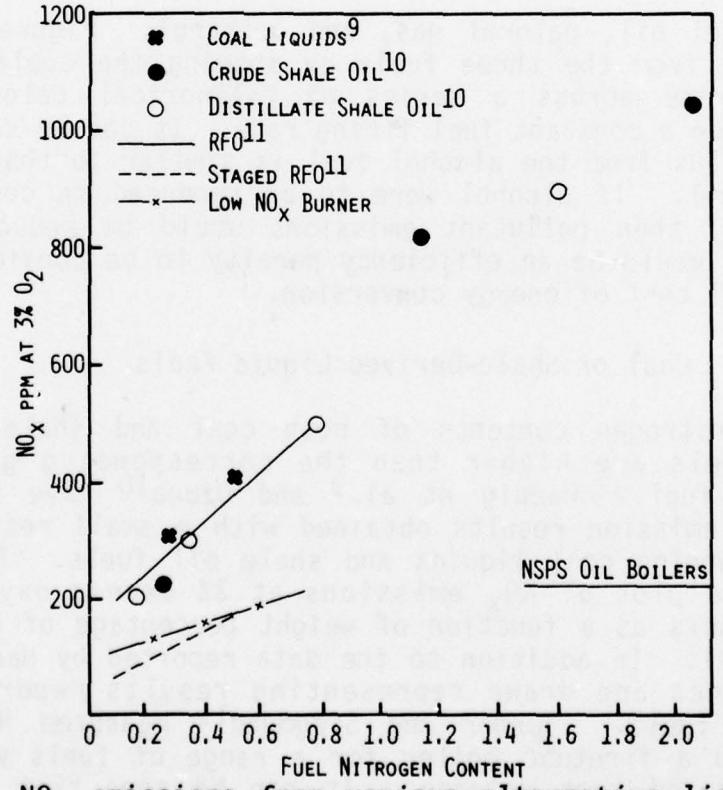


Fig. 4 NO_x emissions from various alternative liquid fuels and residual fuel oil (RFO) and the potential for control by staged combustion also shown in the new source performance standard (NSPS) for oil boilers.

firetube boilers.[3] These results suggest that burners could be designed for high-nitrogen shale oils (greater than 1%) with emission levels of the order of 300 ppm using existing technology.

Open-air burner tests[12] comparing the radiation heat flux of a shale-derived heavy fuel oil and a no. 5 fuel oil have been carried out. It is reported that the shale oil flames appeared to be cleaner and brighter than no. 5 fuel oil, and the shale fuel had a radiant heat flux approximately 0.05 Btu/ft^2-sec higher than that of petroleum-based fuels. Shale-derived heavy fuel oil also has been burned by a ship's boiler without operational problems; however, stack levels of nitrogen oxides were high.

Combustion[13] tests have been carried out in a test furnace to assess the combustion characteristics of solvent

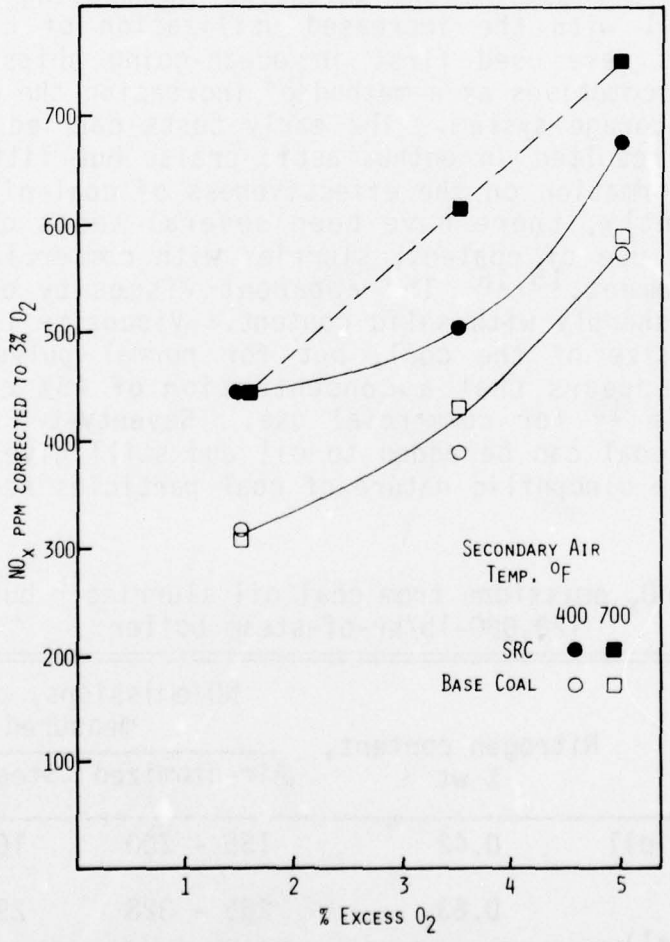


Fig. 5 A comparison of NO_x emissions from SRC and the base goal.[13]

refined coal (SRC) produced by the Southern Services Company. Although this fuel is a solid at normal temperature, it melts at relatively low temperatures and tends to stick to the fuel delivery pipe unless it is cooled, and existing units would require modification for use with SRC. Pilot scale tests indicated that NO_x emissions from SRC combustion were higher than those measured with base coals (see Fig. 5). This could be attributed to the higher nitrogen content of the SRC, 1.9% compared to a 1.5% of the base coal. However, other fuel properties may affect emissions; particle size of the SRC was less than the base coal. Also, SRC has 60% volatile content, compared to 37% for the base coal. Both of these factors will tend to increase combustion intensity. It is very probable that techniques being employed at present to control NO_x emissions from coal-fired units will be suitable for SRC.

Since 1879, sporadic attempts have been made to modify liquid fuels by the addition of pulverized coal. Suspensions of coal in oil combine the advantage of handling flexibility of fuel oil with the increased utilization of coal. Coal suspensions were used first in ocean-going ships and long-distance locomotives as a method of increasing the capacity of the fuel storage system. The early tests carried out aboard USS Gem[14] resulted in enthusiastic praise but little quantitative information on the effectiveness of coal-oil slurries. More recently, there have been several tests designed to assess the use of coal-oil slurries with commercially available equipment.[15,16] The apparent viscosity of slurries increases sharply with solid content. Viscosity is dependent upon the size of the coal, but for normal pulverized coal sizes it appears that a concentration of 45% coal should be suitable [15] for commercial use. Seventy-two percent by weight of coal can be added to oil and still give a pumpable fluid. The oleophilic nature of coal particles requires that

Table 3 NO_x emissions from coal oil slurries[16] burned in a 120,000-lb/hr-of-steam boiler

	Nitrogen content, % wt	NO emissions, ppm as measured	
		Air-atomized	Steam-atomized
No. 6 fuel oil	0.42	155 - 200	160 - 180
Slurry (35% wt coal)	0.63	265 - 328	290 - 370

an emulsifier solution be added to the slurry to maintain its stability. It has been found that lignitic coals usually are easier to blend and stabilize than bituminous coals because of their cellulosic constituents.

Combustion tests indicate that there are few problems associated with burning coal-oil slurries other than atomizer plugging. Slurries containing 50% coal have been burned satisfactorily with no effect upon boiler efficiency or any serious ash fouling problems.[16] More than 60% of the particulate emission mass is less than 20 μ . Table 3 compares NO_x emissions for slurries and fuel oil with two methods of atomization. NO_x emission are higher with the slurry, but control options suitable for coal and oil should be applicable to slurries.

Water in Fuel Emulsions

Dryer[17] has reviewed in some detail the applications of water addition to practical combustion systems and discussed in detail the fundamental aspects of combustion which are affected. The influence of water in fuel oil emulsions on boiler efficiency and pollutant efficiency has been the subject of several investigations. The use of emulsified fuels

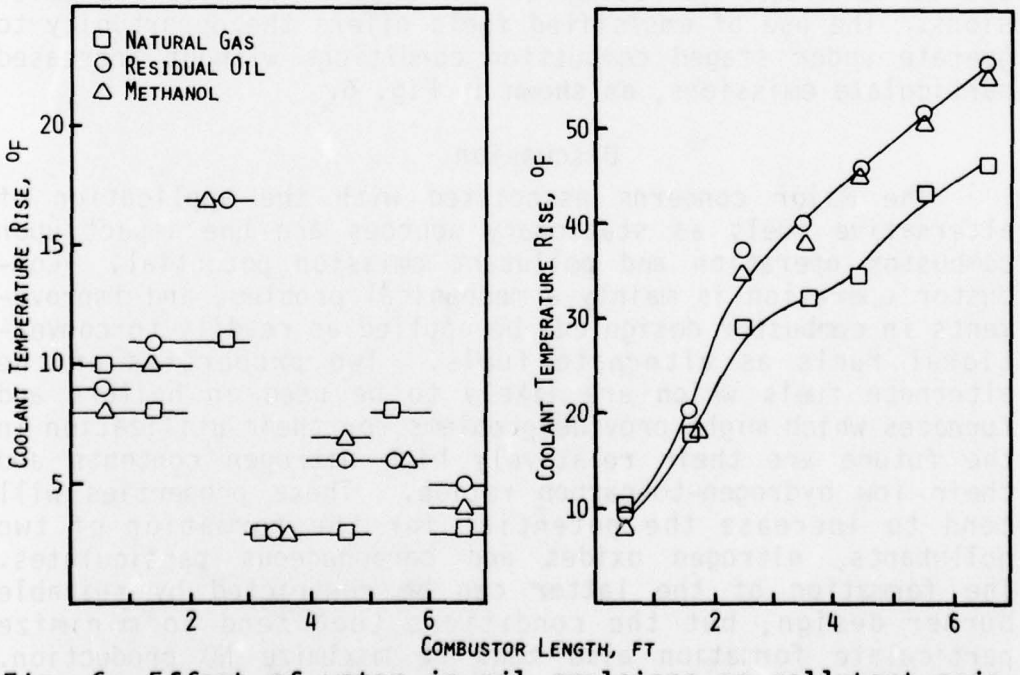


Fig. 6 Effect of water in oil emulsions on pollutant emissions from heavy fuel oil flames under staged and unstaged conditions.

generally causes a decrease in particulate mass emission. However, unless the boiler operator is willing to accept an efficiency penalty, the increased flue gas loss due to additional latent heat content must be offset by a reduction in excess air level. The operator also may be prepared to accept this penalty when burning alternative fuels since the use of water in oil emulsions might allow coal-derived liquid fuels with low hydrogen carbon ratios to be burned without increasing particulate emissions.

Figure 6 illustrates one potential application of water in fuel emulsions--simultaneous NO_x particulate control. Toussant and Heap[18] measured particulate mass and NO_x emissions in a refractory tunnel furnace for a variety of atomizers with and without water addition. The steam atomizer gave the highest NO_x emission and the lowest particulate emission for the nonemulsified fuel. NO_x emissions could be reduced by modifying the atomization method (use of mechanical or air atomizer will narrow spray angles); however, particulate emissions increased. The use of an emulsion decreased the particulate emissions but increased the NO_x emissions with the mechanical atomizer. This effect can be attributed to increased fuel nitrogen oxidation caused by the improved fuel/air mixing with the emulsified fuel. Staged combustion is an effective technique for the control of NO_x emissions, but it is often limited by an increase in particulate emissions. The use of emulsified fuels offers the opportunity to operate under staged combustion conditions without increased particulate emissions, as shown in Fig. 6.

Discussion

The major concerns associated with the application of alternative fuels as stationary sources are the impact upon combustor operation and pollutant emission potential. Combustor operation is mainly a mechanical problem, and improvements in combustor design can be applied as readily to conventional fuels as alternate fuels. Two properties of the alternate fuels which are likely to be used in boilers and furnaces which might provide problems for their utilization in the future are their relatively high nitrogen contents and their low hydrogen-to-carbon ratios. These properties will tend to increase the potential for the formation of two pollutants, nitrogen oxides and carbonaceous particulates. The formation of the latter can be restricted by suitable burner design, but the conditions that tend to minimize particulate formation also tend to maximize NO production.

Studies[1] have shown that the relaxation of the mobile source emission standards for NO_x coupled with the growth

rate of stationary sources and the increased use of nitrogen-containing fuels places increased emphasis upon stationary source NO_x control in order to maintain NO_2 air quality levels Thus the future use of alternative fuels in stationary sources may be subject to more stringent NO_x control. Consequently, a major problem associated with their use will be the control of two pollutants: nitrogen oxides and carbonaceous particulates.

Distributed air addition low-NO_x burner concepts such as those being developed for coal and oil[2] are probably suitable for application to alternate fuels. The concept is based upon three key features: 1) rapid heating of the fuel in an oxyen-deficient zone to minimize fuel NO formation; 2) fuel injection characteristics designed to prevent rapid NO formation before a fuel-rich gas-phase mixture has been achieved; and 3) distributed air addition to provide the optimum stoichiometry for rapid nitrogenous species decay and efficient burnout without contact of corrosive gases with the furnace walls. Although this concept has been used only for coal and oil, it should be applicable to alternative fuels. The distributed air addition concept might well be more successful as a means of controlling emissions while satisfying all other operational requirements because of their higher volatility.

References

[1]Mason, H. B., Shimizu, A. B., Ferrell, J. E., Poe, G. G., Waterland, L. R., and Evans, R. M., "Preliminary Environmental Assessment of Combustion Modification Techniques," Environmental Protection Agency, EPA-600-7-77-119a, Oct. 1977.

[2]Gershman, R., "Design and Scale-Up of Low Emission Burners for Industrial and Utility Boilers," Proceedings of the Second Stationary Source Combustion Symposium, Vol. V, Environmental Protection Agency, EPA 600/7-77-073, July 1977.

[3]Heap, M. P., Cichanowicz, J. E., and Tyson T. J., "Application of NO_x Control Techniques to Industrial Boilers," 69th Annual Meeting of the AIChE, Chicago, Ill., Dec. 1976.

[4]Longwell, J. P., "Synthetic Fuels and Combustion," Progress in Energy and Combustion Science, Vol. 3, No. 2, 1977, p. 127.

[5]Shoffstall, D. R. and Waibel, R. T., "Boiler Burner Design Criteria for Retrofit with Low Btu Gases," Proceedings of the Second Stationary Source Combustion Symposium, Vol. III, Environmental Protection Agency,EPA 600/7-77-073, July 1977.

[6]Martin, G. B., "Environmental Considerations in the Use of Alternate Fuels in Stationary Combustion Processes," Symposium Proceedings: Environmental Aspects of Fuel Conversion Technology, Environmental Protection Agency,EPA-650/2-74-118, NTIS PB 238-304 AS, Oct. 1974, pp. 259-276.

[7]Wendt, J. O. L., Corley, T. L., and Morcomb, J. T., "Interactions Between Sulfur Oxides and Nitrogen Oxides in Combustion Processes," Proceedings of the Second Stationary Source Combustion Symposium, Vol. IV, Environmental Protection Agency, EPA 600/7-77-073, July 1977.

[8]Folsom, B. A., "Evaluation of Combustor Design Concepts for Advanced Energy Conversion Systems," Proceedings of the Second Stationary Source Combustion Symposium, Vol. V, Environmental Protection Agency,EPA 600/7-77-073, July 1977.

[9]Haebig, J. E., Davis, B. E., and Dzuna, E. R., "Preliminary Small-Scale Combustion Tests of Coal Liquids," Environmental Science and Technology, Vol. 10, March 1976, p. 243.

[10]Dzuna, E. R., "Combustion Tests on Shale Oil Fuels," Central States Section, The Combustion Institute, April 1976.

[11]Turner, D. W. and Siegmund, C. W., "Staged Combustion and Flue Gas Recirculation: Potential for Minimizing NO_x from Fuel Oil Combustion," American Flame Research Committee Meeting, Chicago, Ill., Aug. 1972.

[12] "Compilation of Oil Shale Test Results," Applied Systems Corp., Contract N00014-76-C-0477, Office of Naval Research, April 1976.

[13]Borio, R. W., Fink Z. J., Goetz, G. J., and Haas, J. C., "An Assessment of Solvent Refined Coal," Electric Power Research Institute, Research Project 1235-26, TR 2, June 1976.

[14]Dun, J. T., Pulverized and Colloidal Fuel, Ernest Benn Ltd., London, England, 1924, p. 181.

[15]Brown, T. D., and Lee, G. K., "Liquid and Colloidal Alternatives to Conventional Liquid Fuels," IFRF 4th Members Conference, Noordwykerhout, Holland, May 1976.

[16]Brown, A., "General Motors Experience with Powdered Coal-Oil Mixtures," Fourth Annual International Conference on Coal Gasification, Liquefaction and Conversion to Electricity, Pittsburgh, Pa., Aug. 1977.

[17]Dryer, F. L., "Water Addition to Practical Combustion Systems - Concepts and Applications," Sixteenth Symposium (International) on Combustion, The Combustion Institute, 1977, p. 279.

[18]Toussant, M. and Heap, M. P., "Formation of Oxides of Nitrogen Oxides and Particulates in Flames of Water in Heavy Fuel Oil Emulsions," International Flame Research Foundation Doc. G 19/a/7, IJmuiden Holland, April 1974 (in French). Translation NERC Library, TR 75-227, Nov. 1975.

DISCUSSION

DR. B. T. WOLFSON (AFOSR): You spoke about using coal slurries. Have you tried to use, or do you know of any experiences pertaining to the use of, very small particulates in the slurries, such as graphite or another submicron particle? Would this experience indicate whether there would be any particulate problems, such as those associated with heat transfer.

DR. M. P. HEAP (Energy and Environmental Res. Corp): The slurry work that I have seen most often uses typical pulverized coal sizes, which are 75% through 200 mesh. The more you grind the fuel, the greater its cost.

DR. J. P. LONGWELL (MIT): One of the alternative fuels is pyrolysis gas and liquids. When you begin to introduce coal in new industrial and power generation installations, it is logical to pyrolize it first to recover the liquids and gas. Then you are left with a char with little volatile matter, which could be burned in pulverized or fluidized bed combustion systems. I think that you would find some rather unusual combustion problems.

DR. HEAP: I have never burned gasifier char. I have burned pulverized petroleum coke with about 11% volatile matter. In fact, it is easier to burn than anthracite. From a combustion standpoint, I believe that there would be no problems in burning char. From an NO_x control problem, I think there might very well be problems. Although inherently NO_x emissions are low from low-volatile fuels of this kind, it is very difficult to do anything from a combustion standpoint to control them. If you compare burning a char and burning a coal, you can see that you can get very wide ranges in NO_x emissions from changing burner parameters when burning coal. When burning char, very little happens to NO_x

emissions with charges in burner parameters. I think this is one area in which very little is known.

DR. F. L. DRYER (Princeton University): I would like to note at least one other synergism between some of the control techniques that you mentioned -- that of emulsion technology and coal-oil slurry combustion. Recently considerable work has been done on the suspension of these materials using water emulsion structures, particularly by General Motors. Emulsion structures have been very successful in terms of the suspending qualities of the coal dispersion. Generally, it is thought that something like 6% water addition as an emulsion in residual fuels can support as much as 45% coal at preheat temperatures of, e.g., 150° for periods of times approaching weeks.

The second part of that problem is more of a fundamental combustion problem -- namely, the possible fragmentation of the coal-oil-water slurry droplet as it enters the combustion zone. If one considers the fact that the liquid materials will vaporize (and probably pyrolize) first, one is left with a coal particle agglomerate of the small mesh size particles that were in the initial fuel droplet. The coal thus burns as a much larger particle than it would have if the small mesh particles had been uniformly distributed with combustion air. This can be an important point in terms of your argument with regard to total residence time necessary for carbon burnout of the coal.

Finally, I would like to suggest that some of the technology you have talked about certainly is relevant immediately and in fact is in current use in the gas turbine field. There is a very interesting project which has been under way now for about a year at Sea Train Lines in conjunction with Seaworthy Engine Systems on the combustion of residual oil blends in aircraft type turbines. In P&WA FT4 gas turbine systems, they have had a successful program in replacing highly refined marine distillate with blends of 70% Bunker C oil with 20% distillate and 6% water. In these systems, there is no prerefining of the residual fuel, only water washing to remove marine water contamination. There is no removal of the heavy metals. In fact, only potable water (not de-ionized) is used for emulsification. Engine testing currently exceeds 10,000 hr with about 4000 hr on a single engine. They have reported no failures of materials or increased repair costs. Sea Train Lines recently have converted their entire line of four FT4 powered container ships to operation on emulsion blends, and are currently estimating savings of roughly $4,200,000 fuel costs.

DR. HEAP: The only real advantage in using coal-oil slurries that I can see is storability. If you just wanted to replace part of the oil with coal, there is no reason why you could not do that in a burner. It is relatively easy to burn 50% oil and 50% coal by putting them into the furnace separately. In terms of the emulsion, if you can get emulsions which will operate satisfactorily with about 5% water, I can see quite a number of applications.

Chapter II - Critical Processes in Combustion of Alternative Fuels

PRECEDING PAGE NOT FILMED
BLANK

IGNITION/STABILIZATION/ATOMIZATION: ALTERNATIVE FUELS IN GAS TURBINE COMBUSTORS

Arthur H. Lefebvre,* Arthur M. Mellor,+ and James E. Peters≠
Purdue University, West Lafayette, Ind.

Abstract

Certain aspects of gas turbine performance, namely, spark ignition, lean blowoff, and spray atomization, are considered in terms of the properties of conventional and alternative fuels. Those properties are identified which appear most relevant to performance both in practical combustors and laboratory simulations. For atomization the viscosity, surface tension, and density are important, whereas for spark ignition and flame stabilization both viscosity and distillation characteristics are significant. Past research in the latter two areas tends to be apparatus specific, although some qualitative trends can be identified. A combined property that characterizes the fuel spray, rather than either the fuel or the injector, is discussed. It is found that the evaporation time for the Sauter mean diameter of the spray appears to include all of the physical properties of the fuel which are important to atomization, lean blowoff, and spark ignition, and the criterion for the ignition and blowoff limits may be expressed adequately in terms of the maximum allowable mean droplet lifetime. The relevance of a characteristic droplet evaporation time to soot formation and combustion inefficiency also is discussed. Experiments and modeling to minimize combustor development for nonspecification fuels are suggested.

Introduction

Fuel preparation, ignition, flame spreading, and stabilization are important considerations in the design of gas turbine engines. Fuel specifications for aviation combustors

---

*Professor and Head, School of Mechanical Engineering.

+Professor, Combustion Laboratory, School of Mechanical Engineering.

≠Graduate Instructor in Research, Combustion Laboratory, School of Mechanical Engineering.

PRECEDING PAGE NOT FILMED
BLANK

were chosen in part based on these factors (see, for example, Gibbons[1]) and, until very recently, remained more or less the same. Certain specifications, including maximum aromatic content, were relaxed via American Society for Testing Materials (ASTM) Emergency Specification ES-2 in 1976, and it is expected that other changes will be necessary in the future.

Longwell[2] has addressed future alternative fuels and the combustion problems he anticipates; in the following, we discuss how changes in the major properties of alternative fuels will affect atomization, ignition and flame spread, and lean blowoff in gas turbine burners.

As will be explained, it is primarily the physical properties of the fuel which influence these performance parameters. For example, viscosity, surface tension, and specific gravity affect spray Sauter mean diameter (SMD; see Table 1); and viscosity and volatility, or distillation curve, are important in ignition and flame stabilization, the topics of the next section. Chemical properties are generally similar, at least for petroleum-derived fuels, and thus represent a second-order perturbation on flame holding and ignition.

Ignition and Flame Stabilization

One method of flame stabilization is by the recirculation of burned gases to provide a continuous source of ignition to the incoming fuel/air mixture. In a gas turbine combustor, this recirculation is achieved by air swirl, sudden expansion, or penetration jet impingement.

Heat and mass transfer from the burned gases must be sufficient to induce ignition in the critical region of the

Table 1 Fuel property effects on atomization, ignition, and stabilization

Fuel properties	Of importance to		
	Atomization	Ignition	Lean blowoff
Viscosity	X	X	X
Volatility		X	X
Surface tension	X		
Specific gravity	X		

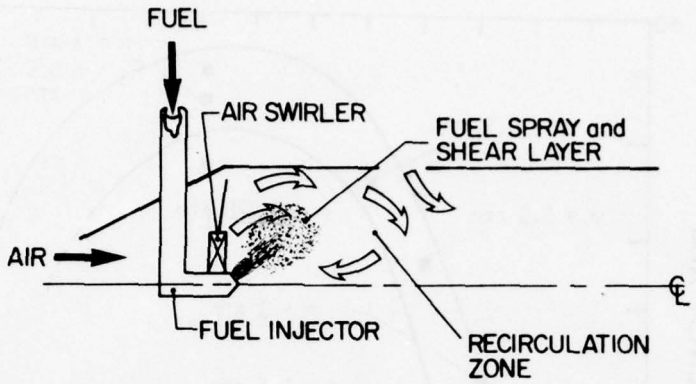


Fig. 1 Schematics of steady-state flame stabilization and ignition.

flow, i.e., the shear layer surrounding the recirculation zone (Fig. 1). The fluid mechanics of the flow then must guarantee subsequent flame spread throughout the combustor.

The present study is primarily concerned with fuel property effects. Certainly, the homogeneous induction kinetics of the fuel are important, but these are generally unknown for practical fuels, which are blends of many species. A reasonable first assumption is that ignition delay times are similar for all similar fuels.[3] By this we mean that differences between the fuels will be of the same order as that between propane and octane but not as great as that between methane and propane. For example, ignition delay time for long chain hydrocarbons can be estimated from the following rate equation derived from experimental plug flow reactor data (see also Ref. 4):

$$\frac{d(C_nH_m)}{dt} = -\frac{5.52 \times 10^8}{p^{0.825}} T (C_nH_m)^{0.5} (O_2) e^{-12,200/T} \qquad (1)$$

Here parentheses denote concentrations (moles/cm^3), t is time (sec), and p (atm) and T (K) refer to initial mixture conditions. [The pre-exponential factor and pressure exponent in Eq. (1) may be in error and will be updated by Edelman in future work.] The reaction in question is quasiglobal:

$$C_nH_m + (n/2)\, O_2 \rightarrow nCO + (m/2)_2H \qquad (2)$$

The fuels tested included propane, n-octane, and octene-1,[3] and it can be seen that Eq. (1) predicts no dependence of delay time on fuel type.

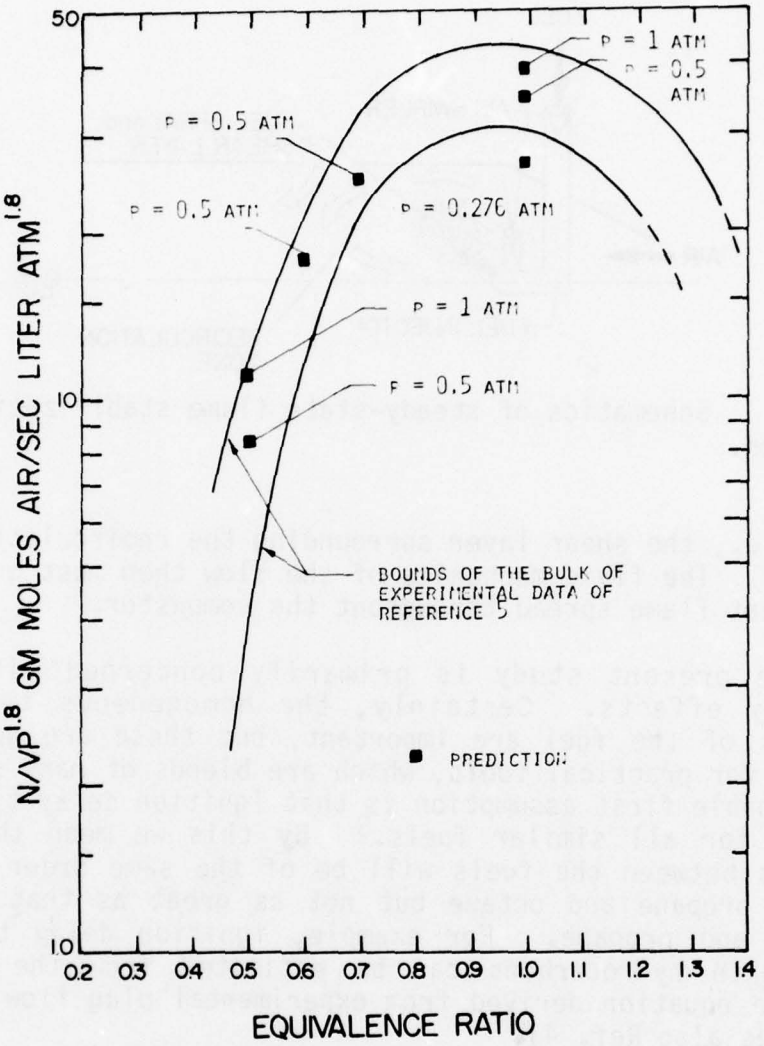


Fig. 2 Predicted[6] vs experimental values of blowoff for well-stirred reactors burning propane.

Figure 2 illustrates the use of the quasiglobal reaction (with subsequent detailed kinetics involving essentially the wet CO oxidation mechanism) to predict the blowoff limits for several well-stirred reactors burning gaseous C_3H_8/air mixtures. The experimental data bounds were compiled by Blichner,[5] and details of the analysis for the loading parameter $n/vp^{1.8}$ (where n is air molar flow rate, v the reactor volume, and p the reactor pressure) may be found in Ref. 6. The agreement for the homogeneous case is quite satisfactory, and it would appear that Eq. (1) is suitable at least for a first estimate of chemical rates for practical fuels.

In spray combustion, however, the physical properties of the fuel are important to both ignition and lean blowoff. In the critical flow regions as discussed previously, there must be sufficient fuel vapor to exceed the appropriate gas-phase lean flammability limit. Thus, both volatility and viscosity are relevant, since fuels of lower initial boiling point (increased volatility) or fuel sprays of smaller SMD (decreased viscosity) will provide a greater abundance of fuel vapor.

Ignition

Early demonstrations of the influence of fuel properties on ignition were conducted at the NACA Lewis facility during the early 1950's. These studies were directed toward altitude relight problems and defining appropriate fuel specifications, primarily volatility, with respect to ignition. Unfortunately, much of this work was apparatus dependent, and several different criteria were used to define the ignition limit (e.g., maximum relight altitude, flight Mach number, critical fuel flow, and spark energy).

Rayle and Douglas[7] investigated the ignition characteristics of three fuels at various ambient temperatures in a single J-33 combustor. Their ignition system featured an air-gap plug providing 0.016 - 0.033 J sparks at a rate of 400

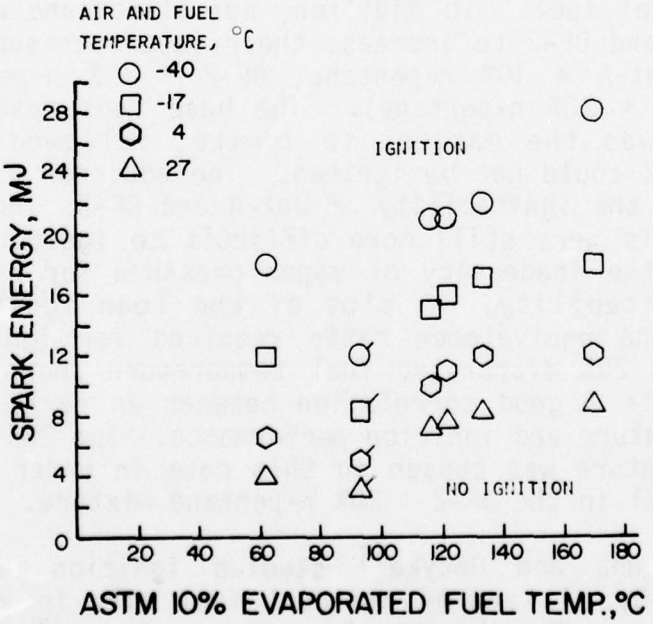


Fig. 3[9] Spark energy required for ignition vs fuel volatility.

to 800 sparks/sec.[8] The most significant result of their study was the correlation of ignition (critical fuel flow) with the ASTM 10% evaporated temperatures of the fuels. In addition to the ASTM distillation curves, Reid vapor pressure also was considered as an indicator of fuel volatility. To determine which should be used to estimate trends in ignition limits, Foster and Straight[9] studied the ignition characteristics of six fuels. Their ignition system was a variable-energy (0.008-10 J) capacitance discharge type with a standard aircraft spark plug (electrode gap, 0.15 cm) and a spark repetition rate of 8/sec. They found that Reid vapor pressure did not correlate with minimum ignition energy. However, as shown in Fig. 3, the ASTM 10% evaporated fuel temperature and minimum ignition energy were strongly related. It is of interest to note in this figure that the flagged data fall below the expected ignition energy established by the other fuels. This is due to the relative viscosities of the test fuels; the flagged data represent JP-4, which has a viscosity of 0.76 cstokes compared to a viscosity of 1 to 1.3 cstokes for the other five fuels. This is one of the earlier indications of facilitating ignition by decreasing fuel viscosity.

More recent work in the ignition field has centered upon the influence of alternate fuels on cold start and altitude relight. Moses[10] conducted ignition tests using hardware based on the Allison T-63 engine (surface gap plug, typically 0.3 J/spark and 9 sparks/sec) and three fuels: JP-4, Jet-A, and #2 diesel fuel. In addition, normal-pentane was blended with Jet-A and DF-2 to increase their vapor pressures to that of JP-4 (Jet-A + 10% n-pentane, DF-2 + 10% n-pentane) and above (DF-2 + 20% n-pentane). The base fuel results showed that JP-4 was the easiest to ignite, followed by Jet-A, whereas DF-2 could not be ignited. The addition of n-pentane did improve the ignitability of Jet-A and DF-2. However, the blended fuels were still more difficult to ignite than JP-4, indicating the inadequacy of vapor pressure for estimating a fuel's ignitability. A plot of the lean ignition limit (primary zone equivalence ratio required for ignition in 5 sec) vs the 25% evaporated fuel temperature shown in Fig. 4 again reveals a good correlation between an early evaporated fuel temperature and ignition performance. The 25% evaporated fuel temperature was chosen in this case in order to include the base fuel in the DF-2 + 20% n-pentane mixture.

Marchionna and Opdyke[11] studied ignition characteristics of JP-5, #4, and #6 residual fuel oils in an AGT 1500 configuration. Two igniter locations were employed, one in the standard dome position and the other in the wall of the

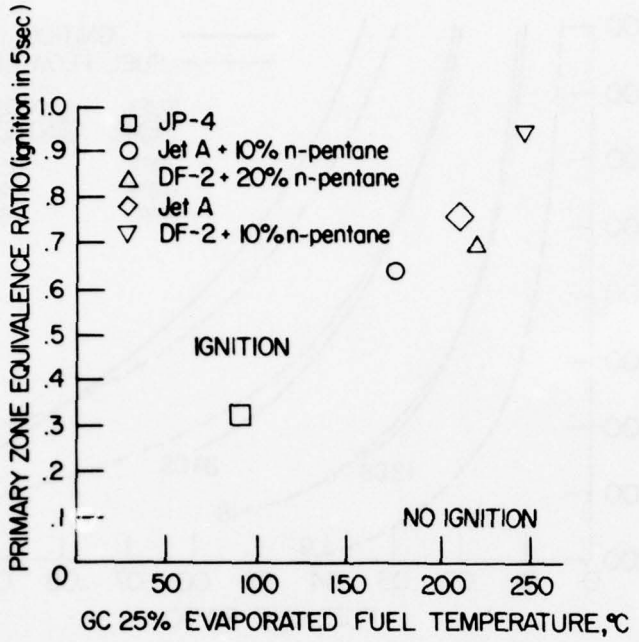


Fig. 4 Relationship between fuel volatility and lean ignition limits.[10]

combustor at an optimum site based on recirculation and entrainment theories. Each spark plug was a standard AGT 1500 air-gap discharge plug rated at 0.1 J, with a spark repetition rate of approximately 4/sec. Fuel temperatures were controlled to produce variations in viscosity for each fuel. Figure 5 (#4 residual fuel oil) is typical of the data obtained. It shows that at higher viscosities the fuel-air ratio must be increased to achieve ignition.

To determine the influence of volatility on ignition, data from each fuel must be compared at similar viscosities and airflow rates. This is done in Fig. 6, in which the fuel-air ratio required for ignition is shown plotted against the 10% evaporated fuel temperature.

The Sauter mean diameter (SMD) of a spray, defined as the diameter of a droplet whose volume-to-surface ration is the same as the volume-to-surface ratio of the entire spray, commonly is used as an indicator of atomization quality. For any given injector, increasing the viscosity of the fuel decreases the atomization quality (i.e., increases SMD). Therefore, information on SMD as related to ignition can be used to indicate viscosity effects on ignition. Rao and Lefebvre[12] demonstrated (Fig. 7) that, as the SMD of a spray increases, the equivalence ratio must increase to maintain the

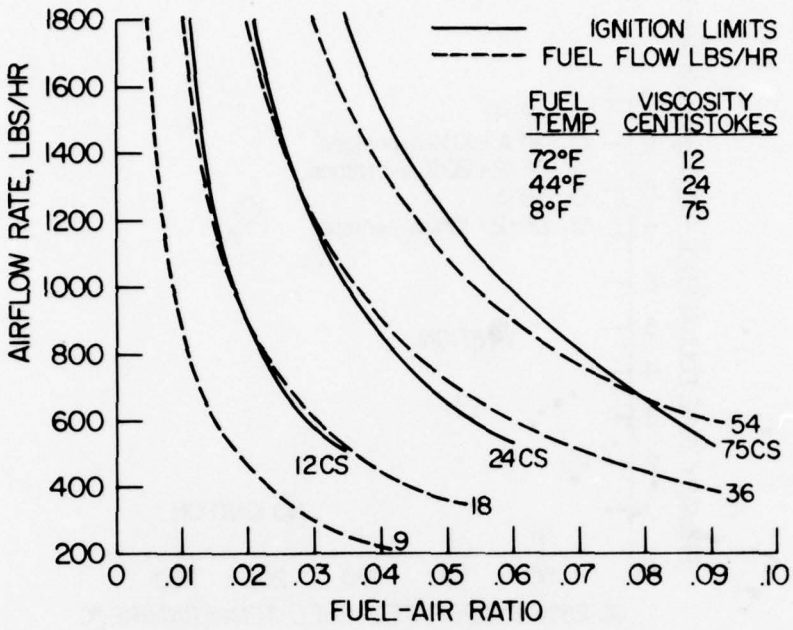


Fig. 5 [11] Influence of fuel viscosity on weak ignition limits.

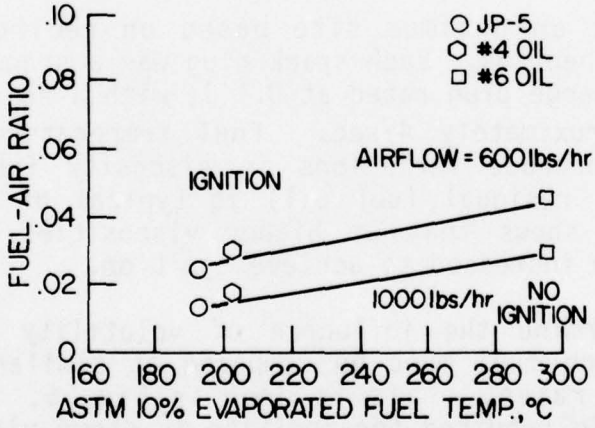


Fig. 6 [11] Influence of fuel volatility on weak extinction limits.

same minimum ignition energy, which indicates, as did the studies of Marchionna and Opdyke[11] that as viscosity (SMD) increases the lean limit for ignition is increased.

The studies just cited have shown that ignition is strongly dependent on fuel volatility and viscosity. An early evaporated fuel temperature was found to correlate well with the lean ignition limit in each case. However, this correlation is not fundamental but rather a convenient empirical

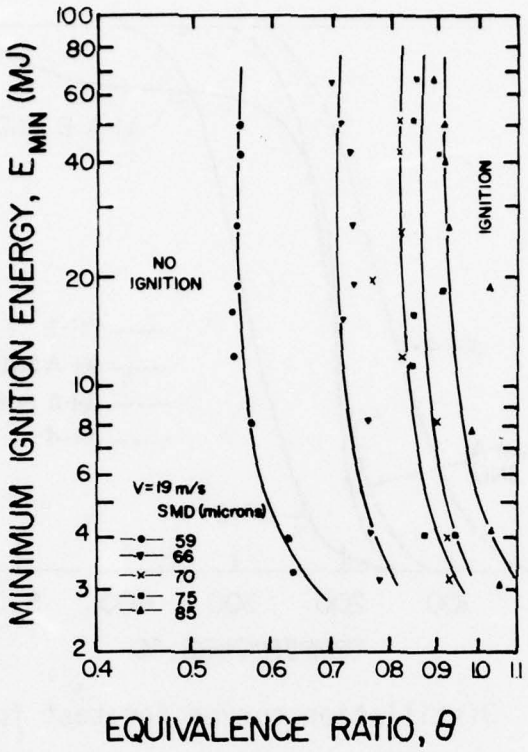


Fig. 7 Graphs illustrating the influence of atomization quality on ignition limits.[12]

relationship. Nor is it quantitative: for a given combustor and test fuels, one may estimate the ignition limit for each fuel only after experimental data have been obtained for at least two test fuels. The correlation of this early evaporated fuel temperature indicates that the limiting factor in ignition (when conditions for a stable flame are present) is the amount of fuel initially evaporated as the ignition process begins: a lean flammability limit in the vapor phase. In addition, the viscosity of a fuel also will influence the amount of fuel in the vapor phase. For example, an increase in viscosity will increase the SMD (volume-to-surface ratio), thereby reducing the surface area available for evaporation.

Lean Blowoff

Similar considerations are expected to apply to flame stabilization in heterogeneous systems. The flame stabilization zone in a conventional gas turbine combustor is the leading edge of the shear layer surrounding the centerline recirculation zone (Fig. 1), and the initial distillation curve and viscosity for a fuel must produce sufficient vapor-phase fuel in this region. Moses[10] found in the T-63 com-

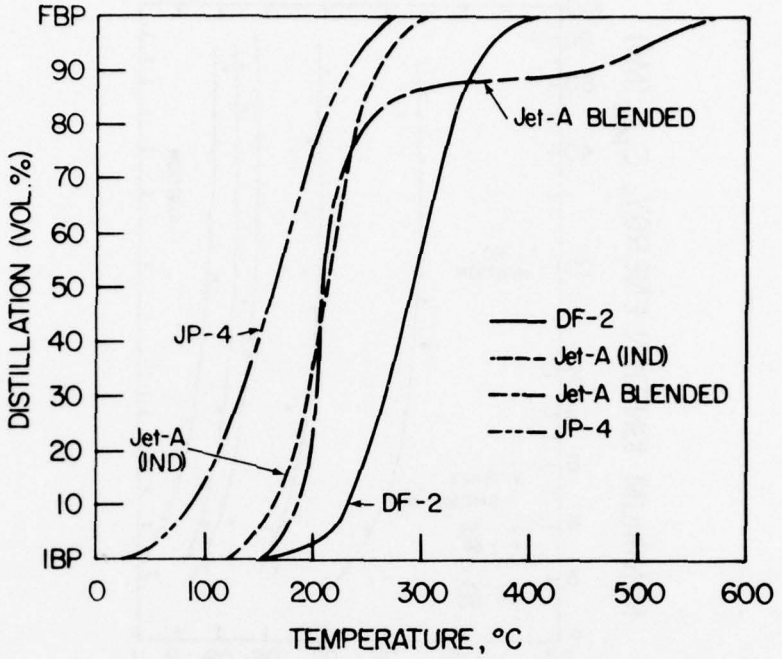


Fig. 8 Distillation curves for test fuels.[10,25]

bustor that the lean limit narrowed slightly as the fuel was varied from JP-4 to Jet-A to DF-2, which is consistent with both the increasing initial boiling points shown in Fig. 8 and the increasing viscosities (JP-4 is typically 0.67 cstokes, whereas DF-2 is 3.3 cstokes.[10]) However, addition of 10% n-pentane to the Jet-A and DF-2 fuels had little effect on the lean limit (Fig. 9), even though the viscosity and initial boiling point were decreased substantially. This suggests that under certain conditions the intervention of aerodynamic mixing and chemical reaction rates could become significant and indicates the need for a more detailed, configuration-independent study of heterogeneous combustion processes occurring near the limits of flame extinction.

In the same vein, properties that affect lean blowoff also will affect combustion inefficiency, with more stable combustors exhibiting leaner flame stabilization limits. An example is taken from Moses[10] using the T-63 combustor and a #5 fuel oil, as well as some of the fuels discussed previously. Figure 10 demonstrates the efficiency penalties to be encountered in this particular engine as fuel volatility decreases and spray atomization deteriorates. Other fuel properties, such as heating value and burning velocity, will, of course, also affect the combustion efficiency.

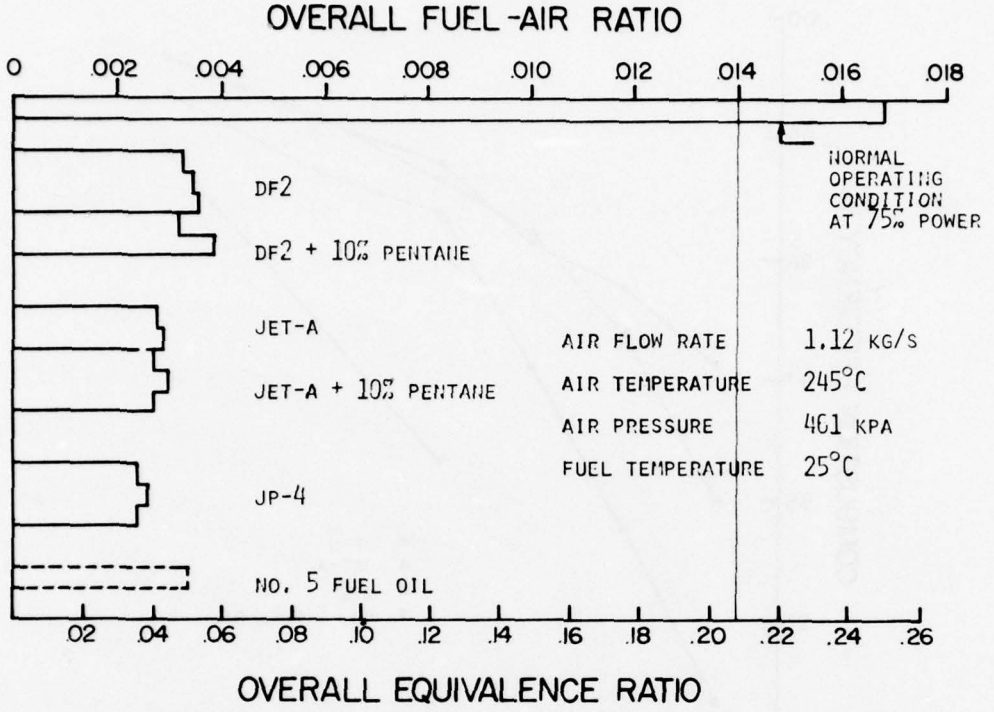


Fig. 9 T63 lean blowoff limits for alternate fuels.[10]

Atomizing Properties of Some Alternative Fuels

The discussion so far has been devoted mainly to the influence of atomization quality on ignition and lean blowoff limits. In view of the important and sometimes overriding influence of atomization quality on these key aspects of combustion performance, there is clearly a need for information on the drop sizes that are likely to be obtained with aviation fuels derived from unconventional sources such as shale oils, tar sands, and coal syncrudes.

Accordingly, drop-size estimates have been made for the two types of fuel injector most widely used in gas turbine engines, namely, the swirl chamber pressure atomizer, of simplex or dual-orifice design, and the airblast atomizer. Drop sizes for the latter, at normal atmospheric pressure, were calculated from the empirical, nondimensional relationship provided by Rizkalla and Lefebvre.[13] All of the calculations were based on an atomizing air velocity of 100 m/sec, corresponding to liner pressure drop of just over 2%, and an atomizing air-fuel ratio of 2.5. Data on fuel properties, as listed in Table 2, were obtained from Antoine and Gallagher[14] and Hendrickson.[15] In some cases, slight corrections were made to the published data in order to reduce

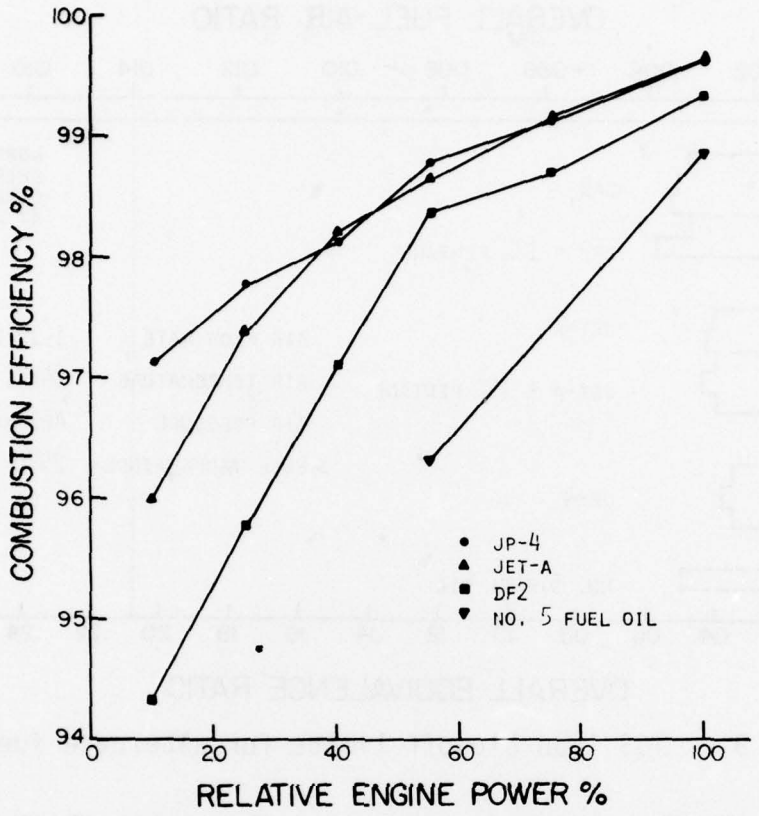


Fig. 10 T63 combustion efficiency for selected alternate fuels.[10]

the values of density and viscosity to the standard temperatures of 15° and 20°C, respectively. Unfortunately, the two main sources of fuel data contained no information on surface tension. However, Marchionna and Opdyke[11] quote values of 0.0416 and 0.0404 N/m for two shale-oil-derived JP-5 fuels, and so, based on this evidence, a mean value of 0.041 N/m was used in all calculations of SMD for alternative/synthetic fuels.

For both airblast and swirl atomizers, the constants in the equations for mean drop size were adjusted to give an SMD of unity for aviation kerosine. Thus, the numbers listed in the two right-hand columns of Table 2 represent for each fuel the ratio of its SMD to that of aviation kerosine under the same operating conditions.

Two points of interest emerge from inspection of Table 2. First of all, it is clear that for all fuels the atomization quality is markedly inferior to that of normal kerosine, indicating that problems of ignition and lean blowoff will be

Table 2 Atomizing potential of jet fuels derived from shale oils, tar sands, and coal syncrudes

Fuel	ρ at 15°C, kg/m^3	μ at 20°C, $Nsec/m^2$	SMD ratio	
			Swirl atomizer	Airblast atomizer
Aviation kerosine	800	0.00130	1.00	1.00
Shale oils				
Tosco low-yield (boiling range, 250-550K)	807	0.00547	1.73	1.38
Tosco low-yield (initial boiling point, 550K)	795	0.00376	1.61	1.30
Tosco high-yield (boiling range, 250-550K)	804	0.00565	1.75	1.38
Tosco High-yield (initial boiling point, 550K)	787	0.00341	1.59	1.28
Marine diesel produced by Paraho process to MIL-F-16884-G	801	0.00693	1.80	1.47
Jet-A/JP-5 produced by Paraho process to MIL-F-5624	805	0.00217	1.45	1.23
Green River high-grade shale	911	0.02200	2.24	2.00
Tar sands				
Alberta Shell Canada	860	0.01100	1.96	1.61
Alberta Abasand	963	0.06800	1.64	1.53
Alberta GCOS, pilot plant	837	0.00320	1.44	1.31
Alberta Sun Oil, pilot plant	900	0.00360	1.55	1.37
Alberta Sun Oil, DF #2	882	0.00544	1.70	1.44
Coal derived				
Utah A-seam	866	0.00550	1.71	1.42
Pittsburgh seam	919	0.01500	2.00	1.78

more severe. It is also apparent that the airblast atomizer is characterized by significantly lower values of SMD than the swirl atomizer, thus confirming previous observations on the reduced sensitivity of airblast atomizer performance to variations in fuel type. The superior atomizing performance of the airblast atomizer would, of course, show up to even greater advantage on engines of high pressure ratio, since SMD values for airblast nozzles diminish much more rapidly with increase in ambient gas pressure than for swirl atomizers. Thus, to a large extent the problems to be anticipated with alternative and synthetic fuels may be alleviated by the use of efficient and well-designed airblast atomizers. Where an external supply of air is available, the air-assist type of atomizer also should prove very effective.

A Single Parameter to Characterize Fuel Preparation

In the previous sections ignition, stabilization, and atomization in conventional gas turbine combustors have been discussed in terms of the physical properties of the fuel. Certain empirical or semiempirical relations have been found for a given burner/injector system, but these break down if more than one property is altered (see, for example, Fig. 3). Thus, there is a definite need for combined parameters to incorporate all variations simultaneously.

One approach would be to characterize the coupled fuel/injector combination in a particular engine, that is, to characterize the fuel spray rather than just the fuel's physical properties or the injector itself. As was demonstrated in the previous section, the latter may be accomplished via the SMD, which, with the d^2 law of Godsave,[16] yields an estimate of the evaporation time τ_{eb} for the mean-size droplet in the spray. Viscosity, surface tension, and density are introduced through the SMD relationship for a particular injector, as in Eq. (5), whereas volatility enters via the evaporation coefficient β of the d^2 law:

$$\beta = \frac{8k}{\rho_\ell c_p} \log\left(1 + \frac{c_p\,(T - T_\ell)}{L}\right) \tag{3}$$

New terms here are defined in Table 3, but T_ℓ, the droplet surface temperature, and L, the enthalpy of vaporization plus sensible enthalpy to heat the fuel to T_ℓ, are functions of the volatility.

A general model for spray combustion has been proposed elsewhere involving characteristics times.[17] Heterogeneous

fuel injector are characterized completely by τ_{eb} or, in terms of the previous discussion of spark ignition and flame stabilization, smaller droplet lifetimes widen both ignition and blowoff limits, since fuel is supplied more rapidly to the gas phase.

To illustrate the combined effects of viscosity and volatility upon droplet lifetime, τ_{eb}'s were calculated from Eqs. (3) and (4) for fictitious fuels having the properties listed in Table 3; the results are shown in Fig. 11. The SMD (microns; other units as in Table 3) of the spray was computed from the equation of Hunter et al.[21] for simplex pressure atomizing nozzles:

$$SMD = (90.5\ \nu^{0.3}\ \rho_\ell^{0.205}\ Q^{0.205})/\Delta p^{0.354} \qquad (5)$$

Rather than use the 10% evaporated fuel temperature T_{10} in the calculations for τ_{eb}, a correction for pressure was made using the Clausius-Clapeyron relationship as follows:

$$T_\ell = \left[(R \log P/\Delta H) + (1/T_{10})\right]^{-1} \qquad (6)$$

where ΔH (cal/mole) has been evaluated by Trouten's rule:

$$\Delta H = 21\ T_{10} \qquad (7)$$

The L term in Eq. (3), i.e., the sensible enthalpy change of the liquid fuel plus the latent heat of evaporation, then was evaluated using Maxwell's[22] techniques. Finally, to account for nonzero relative velocity between the fuel droplet and the ambient gas, the evaporation coefficient β was multiplied by the convective correction factor due to Frossling[23]:

$$\beta_{conv} = \beta[1 + 0.276\ Re^{1/2}\ Sc^{1/3}] \qquad (8)$$

where the Reynolds number is based on SMD and fuel injection velocity. The ambient combustor conditions listed in the table are taken as typical.

The method described previously to calculate τ_{eb} was developed to emphasize the effects of viscosity and volatility. In reality, viscosity and volatility are not unrelated, as shown for the four fuels in Fig. 11, and difficulties are encountered if one attempts to vary them independently. Also, fuel properties such as molecular weight and density will vary for different fuels. Therefore, the τ_{eb} calculations are by no means exact but rather give limited quantitative information for viscosity and volatility variations.

Table 3 Parameters for calculating τ_{eb}

Symbol	Definition	Typical value (for Fig. 11)
k	Gaseous thermal conductivity	2.35×10^{-4} cal/cm-sec-K
ρ	Density of liquid fuel at T_ℓ	820 kg/cm^3
c_p	Gaseous specific heat at constant pressure	0.241 cal/g-K
T	Temperature of ambient gas	1000 K
T_ℓ	Boiling point of liquid fuel at the local pressure	Varied
T_{10}	10% evaporated fuel temperature	Varied
L	Sensible enthalpy of the liquid fuel from the initial temperature to T_ℓ plus the latent heat of evaporation	Varied
ΔH	Latent heat of evaporation	Varied
ν	Viscosity of liquid fuel	Varied
Q	Liquid fuel flow rate	17.1 ℓ/hr
ΔP	Nozzle differential pressure	5.31 atm
R	Ideal gas constant	1.986 cal/mole-K
ρ_g	Density of ambient gas	1.41×10^{-3} g/cm^3
	Combustor pressure	4 atm
V_{inj}	Relative droplet velocity	50 m/sec
μ_g	Ambient gas viscosity	6.83×10^{-4} g/cm-sec
Sc	Schmidt number	0.7

effects (determined primarily by the physical properties of the fuel) are given by τ_{eb}:

$$\tau_{eb} = (SMD)^2/\beta \qquad (4)$$

whereas the aerodynamics of the combustor are discussed in terms of mixing times and homogeneous gas-phase chemistry in terms of kinetic times (see also Ref. 18). It will suffice to say here that at a particular gas turbine combustor operating point the mixing and kinetic times are essentially constant and thus independent of fuel/injector combination.[19] [There are slight changes in the kinetic times if fuel heating values change[20]; also, we continue to assume similar homogeneous kinetics as given, for example, by Eq. (1).] Then the importance of variations in physical properties of the fuel or the

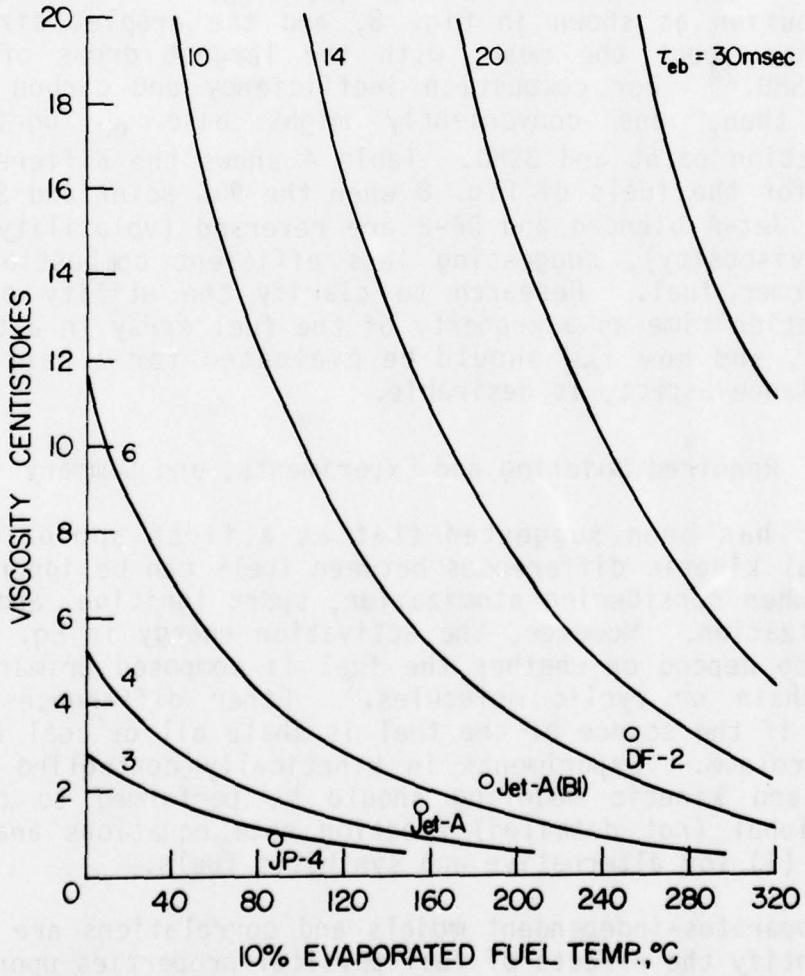


Fig. 11 Influence of fuel viscosity and volatility on droplet lifetimes.

Figure 11 indicates that, for the aviation specification fuels (JP-4 and Jet-A) at operating conditions close to the lean blowoff limit, droplet lifetimes are around 5 msec or less. Furthermore, when based on the 10% evaporation temperature, Jet-A and Jet-A blended with 15% residual rubelene have similar evaporation times. DF-2, however, has twice the lifetime of the aviation fuels and thus may exhibit some problems with both ignition and lean blowoff. As noted prviously, Moses[10] was unable to ignite DF-2 with standard T-63 hardware, which is consistent with the concept of an upper droplet lifetime for a particular engine and operating point. Thus, alternate/synthetic fuels must meet a maximum mean evaporation time to assure ignition.

Evaporation times are also very relevant to the problems of combustion inefficiency and smoke. There are actually two distributions that enter into Eq. (4) (τ_{eb}): the boiling point distribution as shown in Fig. 8, and the droplet size distribution about the mean, with the largest drops of diameter 3SMD.[24] For combustion inefficiency and carbon formation, then, one conveniently might base τ_{eb} on the 90% evaporation point and 3SMD. Table 4 shows the difference in τ_{eb}'s for the fuels of Fig. 8 when the 90% point and SMD are used: Jet-A blended and DF-2 are reversed (volatility overrides viscosity), suggesting less efficient combustion with the former fuel. Research to clarify the utility of drop evaporation time as a property of the fuel spray in a turbine engine, and how τ_{eb} should be evaluated for a particular performance aspect, is desirable.

Required Modeling and Experiments, and Summary

It has been suggested that as a first approximation chemical kinetic differences between fuels can be ignored, at least when considering atomization, spark ignition, and flame stabilization. However, the activation energy in Eq. (1) is known to depend on whether the fuel is composed primarily of long chain or cyclic molecules.[3] Other differences could emerge if the source of the fuel is shale oil or coal instead of petroleum. Experiments in kinetically controlled situations and kinetic modeling should be performed to develop quasiglobal (not detailed) reaction rate equations analogous to Eq. (1) for alternative and synthetic fuels.

Apparatus-independent models and correlations are needed to quantify the effects of fuel physical properties upon spark ignition and lean blowoff. The available data have suggested qualitatively how volatility and viscosity are important in

Table 4 Computed drop evaporation times (msec).

Fuel	10% Evaporation point	90% Evaporation point
JP-4	2.91	5.74
Jet-A	5.22	9.02
Jet-A blended	7.20	38.50
DF-2	12.10	19.50

attaining a lean flammability limit in the vapor phase at the location in the flowfield crucial to ignition and/or stabilization. Fuel droplet lifetime has been selected as a combined property to describe the quality of spray preparation rather than the fuel or injector itself; experiments to verify the validity of these concepts should continue.

Various experimental studies of atomization have yielded correlations of mean drop size for both pressure and airblast types of fuel injector. These correlations predict that jet fuels derived from shale oils, tar sands, and coal syncrudes will pose more serious problems of atomization than for similar petroleum-based fuels, thus highlighting a need for new and improved methods of fuel atomization. The only major limitation on the existing data base is that it was obtained for the most part at atmospheric pressure, and it is desirable to make similar measurements at other pressures to determine injector performance at both takeoff and altitude cruise conditions.

Acknowledgments

The authors' current research on fuel effects on gas turbine performance is supported in part by the U.S. Army Tank-Automotive Research and Development Command under Contract No. DAAE07-76-C-0063 with P. Machala and A. Jaeger as technical monitors, and in part by a grant from the Ford Motor Company, W. Wade, technical monitor.

References

[1] Gibbons, L. C., "Factors in Selecting Fuels for Gas Turbine Powered Aircraft," NACA RM E50I18, 1950.

[2] Longwell, J. P., "Synthetic Fuels and Combustion," Plenary Lecture, Sixteenth (International) Symposium on Combustion, The Combustion Institute, Pittsburgh, Pa., 1977.

[3] Edelman, R. B., Fortune, O. F., and Weilerstein, G., "Some Observations on Flows Described by Coupled Mixing and Kinetics," Emissions from Continuous Combustion Systems, Plenum Press, New York, 1972, pp. 55-91.

[4] Edelman, R. B. and Fortune, O. F., "A Quasi-Global Chemical Kinetic Model for the Finite Rate Combustion of Hydrocarbon Fuels with Application to Turbulent Burning and Mixing in Hypersonic Engines and Nozzles," AIAA Paper 69-86, New York, Jan. 20-22, 1969.

[5] Blichner, O., "A Fluid Dynamic Study of a Spherical and Cylindrical Stirred Reactor," Eighth Symposium (International) on Combustion, Williams and Wilkins, Baltimore, Md., 1960, pp. 995-1002.

[6] Edelman, R. and Weilerstein, G., "A Theoretical Study of Combustion and NO Formation in Well-Mixed Regions," General Applied Science Laboratories TR 758, 1971.

[7] Rayle, W. D. and Douglas, H. W., "Investigation of Ignition Characteristics of AN-F-32 and Two AN-F-58a Fuels in Single Can-Type Turbojet Combustor," NACA RM E50H16a, 1950.

[8] Foster, H. H., "Ignition-Energy Requirements in a Single Tubular Combustor," NACA RM E51A24, 1951.

[9] Foster, H. H. and Straight, D. M., "Effect of Fuel Volatility Characteristics on Ignition-Energy Requirements in a Turbojet Combustor," NACA RM E52J21, 1953.

[10] Moses, C. A., "Studies of Fuel Volatility Effects on Turbine Combustor Performance," Joint Meeting of WSS/CI and CSS/CI, San Antonio, Texas, 1975.

[11] Marchionna, N. and Opdyke, G., Jr., "Turbine Fuel Tolerance Study, Phase II," U.S. Army Tank-Automotive Command TR 12191, 1976.

[12] Rao, K. V. L. and Lefebvre, A. H., "Minimum Ignition Energies in Flowing Kerosine-Air Mixtures," Combustion and Flame, Vol. 27, Aug. 1976, pp. 1-20.

13 Rizkalla, A. A. and Lefebvre, A. H., "The Influence of Air and Liquid Properties on Airblast Atomization," Journal of Fluids Engineering, Vol. 97, Sept. 1975, pp. 316-320.

14 Antoine, A. C. and Gallagher, J. P., "Synthesis and Analysis of Jet Fuels from Shale Oil and Coal Syncrudes," NASA TM X-73399, 1976.

15 Hendrickson, T. A., Synthetic Fuels Data Handbook; Green River Oil Shale, U.S. Coal, Alberta Oil Sands, 1975.

16 Godsave, G. A. E., "Studies of the Combustion of Drops in a Fuel Spray - the Burning of Single Drops of Fuel," Fourth Symposium (International) on Combustion, Williams and Wilkins, Baltimore, Md., 1953, pp. 818-830.

17 Mellor, A. M., "Gas Turbine Engine Pollution," Progress in Energy and Combustion Science: Pollution Formation and Destruction in Flames, Vol. I, edited by N. A. Chigier, Pergamon Press, Oxford, England, 1976, pp. 111-133.

18 Tuttle, J. H., Colket, M. B., Bilger, R. W., and Mellor, A. M., "Characteristic Times for Combustion and Pollution Formation in Spray Combustion," Sixteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, Pa., 1977, pp. 209-219.

19 Mellor, A. M., "Characteristic Time Emissions Correlations and Sample Optimization: GT-309 Gas Turbine Combustor," Journal of Energy, Vol. 1, July-Aug. 1977, pp. 244-249.

20 Mellor, A. M., "Characteristic Time Emissions Correlations: The T-63 Helicopter Gas Turbine Engine," Journal of Energy, Vol. 1, July-Aug. 1977, pp. 257-262.

21 Hunter, S. C., Johnson, K. M., Mongia, H. C., and Wood, M. P., "Advanced, Small, High-Temperature-Rise Combustor Program. Volume I: Analytical Model Derivation and Combustor-Element Rig Tests (Phases I and II)," United States Army Air Mobility Research and Development Laboratory, TR 74-3A, 1974.

22 Maxwell, J. B., Data Book on Hydrocarbons, Van Nostrand, Princeton, N.J., 1950.

23 Ranz, W. E. and Marshall, W. R., "Evaporation from Drops," Chemical Engineering Progress, Vol. 48, March 1952, p. 173.

[24] Simmons, H. C., "Air-Blast Fuel Nozzle Spray Analysis and Drop-Size Distributions," Meeting on Multi-Fuel Capability of Gas Turbine Engines, U.S. Army Tank-Automtotive Command, Warren, Mich., July 1975.

[25] Colket, M. B., Stefucza, J. M., Peters, J. E., and Mellor, A. M., "Radiation and Smoke from Gas Turbine Flames. Part II. Fuel Effects on Performance," United States Army Tank-Automotive Command, TR 12163 Pt. II, 1977.

DISCUSSION

DR. W. S. BLAZOWSKI (Exxon Research): I think you have done an excellent job of relating viscosity and volatility to ignition and stability considerations, but I do not believe it is valid to extend those explanations of physical processes to the soot formation mechanism without consideration of chemical effects. The results that I have shown in my presentation with respect to premixed laminar flames, as well as the jet stirred reactor or backmixed flames, indicate significant differences in sooting characteristics between the fuels. These data were for totally prevaporized and premixed fuels, in which case surface tension, volatility, and viscosity played no role at all.

Secondly, it should be noted that the NASA data that were shown by Professor Longwell and the data that I presented were obtained by blending a standard fuel like a JP-4 with an aromatic stock, like xylene. The fuel physical properties that you have referred to did not change much during these tests and do not provide an explanation for the strong effects on smoke emission and combustor liner temperature. I conclude, therefore, that there are significant fuel chemistry effects in the soot formation process which occurs in gas turbine engines that need to be studied.

DR. LEFEBVRE (Purdue University): I do not disagree with anything you have said. I will just add the point that in the past all these problems have tended to be attributed almost exclusively to chemistry effects. The physical properties have been ignored. I just wanted to emphasize that one ought to take both into account.

DR. A. S. KESTEN (United Technologies Research Center): I have just one point before we argue too much about physics vs chemistry. If you look at the droplet spacing, the physics and chemistry are influenced by and influence the spacing. The environment surrounding drops, which is influential in

ignition, combustion, soot formation, and the formation of other pollutants, is defined by both physical and chemical processes. So we are really talking about everything going on around the droplets. I think perhaps you were getting to it in your suggestion that the kinds of research that should be done have to include what happens to the environment of fuel droplets as they are affected both by the oxidizing atmosphere and by other fuel droplets.

DR. LEFEBVRE: In the paper we make a plea for experimental work to be done under more controlled conditions than has been customary in the past. So often one has had to base arguments on data obtained in practical combustors where uncertainties exist as to what the conditions are. If these effects that we are discussing are important, and I think we all agree that they are, then they deserve to be thoroughly investigated. We must be able to control conditions so that we can define so many of the parameters which in the past we had to gloss over.

COMBUSTION AND CHEMICAL KINETICS PROBLEMS IN INTERNAL COMBUSTION ENGINES

F. V. Bracco*
Princeton University, Princeton, N.J.

Abstract

The engine of the automobile is the dominant internal combustion engine as far as both energy and air pollution are concerned. Combustion is examined in an automobile internal combustion engine whose configuration is general enough to include most of the controlling processes of present and future designs. Atomization, spray development, turbulent mixing, chemical kinetics, wall momentum and energy transfer, and their strong interactions are identified as the combustion-controlling processes in the most general of the engine configurations. The contributions of chemical kinetics are then examined more closely. It is concluded that the basic kinetic mechanisms of engine combustion are not known currently and that a need exists for their identification. The necessary, starting information is the pressure, temperature, and equivalence ratio of each of the many environments of chemical kinetics in engines. Such parameters are given for self-ignition, spark-ignition, liquid fuel pyrolysis, diffusion flames, premixed flames, preflame reactions, post-flame reactions, and wall quenching as they occur in engines.

Introduction

Combustion in internal combustion engines is organized differently in different engine configurations. Thus, for example, consider the state of the cylinder charge in three typical engines just prior to ignition. In the standard spark ignition engine, the charge is mostly homogeneous (gaseous) and uniform within the volume of the combustion chamber; in diesel engines (compression ignition), charge homogeneity is sought but liquid fuel is often present; and in stratified charge engines, charge homogeneity may be desirable but uniformity prior to ignition is certainly to be avoided. Accordingly, when discussing combustion in

*Associate Professor, Department of Aerospace and Mechanical Sciences.

internal combustion engines, one could consider some of the leading engine configurations one at a time, or one could select a configuration that is so general that it includes most of the processes found in all the others. The latter approach is followed here because the all-inclusive engine is also likely to be the engine of the future. This engine is introduced in the first of the following sections. The reader who is interested just in a specific engine configuration need only disregard the additional information. With the foregoing understanding, current spark ignition, diesel, and stratified charge engines are all included in this review.

After identifying the engine configuration, the next logical step is to consider the processes which control its combustion. These processes are introduced following the events experienced by a parcel of fuel on its way to being oxidized. They are just introduced, since their detailed discussion is beyond the scope of this review. However, chemical kinetics, which is only one of such processes, is then more closely reconsidered since it was emphasized in the organization of the SQUID Workshop. However, even with this restricted topic, there are several difficulties. In engine combustion, chemical kinetics is almost always strongly coupled to equally controlling transfer processes so that its isolated consideration is not easy to justify. Furthermore, few, if any, of the basic kinetic mechanisms of engine combustion have been firmly identified, in spite of the general recognition of their importance. Finally, the writer, although having some experience in engine combustion, is not a chemical kineticist. It was felt, however, that a useful purpose could be served by identifying and defining the numerous, and considerably different, environments in which chemical kinetics plays significant roles in engine combustion. The definition is achieved by giving the ranges of pressures, temperatures, and compositions of the various environments. It is hoped that the information may be useful to the chemical kineticists who are asked to investigate and identify the basic chemical kinetic paths which prevail in the various environments. Notice that, in all cases, it is information about the basic chemical kinetic paths which is needed the most from chemical kineticists and not such indirect quantities as engine ignition delays, flame speed, quench layer thicknesses, etc. Finally, it should be mentioned that selectivity, rather than comprehensiveness, was exercised in listing references. Pertinent, extensive bibliographies can be found in the quoted works which are often detailed reviews.

Engine Configuration and Fuels

In the United States, the powerplant of the automobile is by far the dominant powerplant in the transportation sector. It uses some 20% of the total energy and some 50% of the total petroleum[1] while producing about 50% of three of the major air pollutants:[2] nitrogen oxides, carbon monoxide, and unburned hydrocarbons. And these percentages are not likely to change substantially for several decades.

Thus it is reasonable to concentrate our attention on the powerplant of the automobile. A guess must then be made at which automobile engines will predominate within a reasonable future, such as the next two decades. The conclusion then is reached that the reciprocating internal combustion engine, which is by far the predominant automobile powerplant of today, is likely to remain so in that future as well. This is so mostly for economic reasons and in spite of some significant (but restricted) advantages offered by competitive alternatives such as the rotary engine, the gas turbine, the Stirling engine, and the electrical motor. The same conclusion also is reached by considering that the average life span of the American automobile is about 10 years and by estimating the length of time required for a new powerplant to be introduced to the market and to replace a signficiant number of reciprocating engines. However, the reciprocating engine of tomorrow is likely to be substantially different from its present version as far as the organization and control of its combustion processes are concerned.[3]

In the current spark ignition engine, a nearly stoichiometric, uniform mixture of air and gaseous fuel is produced by the carburetor (or by low-pressure fuel injection in the intake manifold) and introduced in the cylinder. Sometimes, after the spark, a turbulent premixed flame front is observed to move across the combustion chamber.

The preceding combustion configuration offers several disadvantages. To avoid engine knock (the sudden, rapid, and uniform reaction of the mixture ahead of the flame front), high-octane-number fuels and low compressions ratios are required. For fast and repeatable (no misfire and limited cycle-to-cycle variations) combustion, the equivalence ratio also is restricted to a narrow range (1 ± 0.15). Yet it is known that higher compression ratios (up to about 16) and lean overall mixtures (as lean as they can be used) do increase the efficiency of the engine by 20 to 40%. Furthermore, a fraction of the fuel is always adjacent to the cold walls (500-700 K), since the fuel is distributed uniformly within the entire

combustion chamber. Quenching of the flame near the walls is one of the known sources of unburned hydrocarbons.

If a small amount of fuel is injected into part of the compressed air directly in the combustion chamber and just before combustion, leaner overall mixtures and higher compression ratios can be employed. Power output then can be controlled by varying the amount of injected fuel (instead of changing the mass of the air-fuel mixture, as in the standard spark ignition engine), thus eliminating throttling losses.

If, in this overall lean, high-compression ratio engine, ignition occurs spontaneously, one recovers the diesel engine, whose greater efficiency is well known. However, the diesel engine presents some problems that can be eliminated, at least in principle, by regulating the distribution of fuel within the combustion chamber and by using a spark to provide controlled ignition. The random self-ignition of diesel combustion contributes to its noise problem, and its turbulent diffusion flames generate high nitrogen oxides emissions and slow combustion. Slow combustion undesirably limits the diesel speed range. (To improve mileage, the tendency is to go to smaller cars with smaller displacement engines operating at higher speeds.) If the fuel is premixed locally and ignition is controlled by a spark (so as to generate a premixed flame), the noise, nitrogen oxides, and speed limitations of the diesel engine can be reduced while maintaining its efficiency. Moreover, spark ignition eliminates the need for high-cetane-number fuels.

The diesel engine and the direct-injection, high-compression, spark ignition engine just described are two examples of direct-injection, stratified-charge engines. Other direct-injection, stratified-charge engines, which are currently under active development, including the PROCO engine of Ford Motor Company (Fig. 1), the TCCS engine of Texaco Inc., and the MCP engine of Mitsubishi Industries. All of these engines share similar geometrical configurations and controlling combustion processes. Moreover, and most importantly, they can be implemented through relatively minor modifications of the current spark ignition engine. Because of the indicated advantages, stratified-charge reciprocating engines are likely to become more and more common in the automobiles of the 1980's and 1990's.[3]

The same direct-injection, spark ignition, stratified-charge engine often can oprate with most of the probable future fuels, including methanol, ethanol, methane, propane, hydrogen, and petroleum- or coal-derived mixed hydrocarbon

fuels. But its emission characteristics may vary considerably. Although the ability of these engines to operate on a large variety of fuels is one of their assets, it is not likely that, in this century, the nature of the automotive

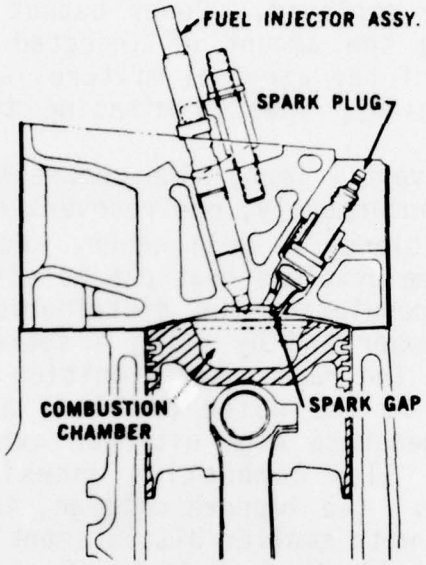


Fig. 1 351-CID PROCO engine cross section.[20]

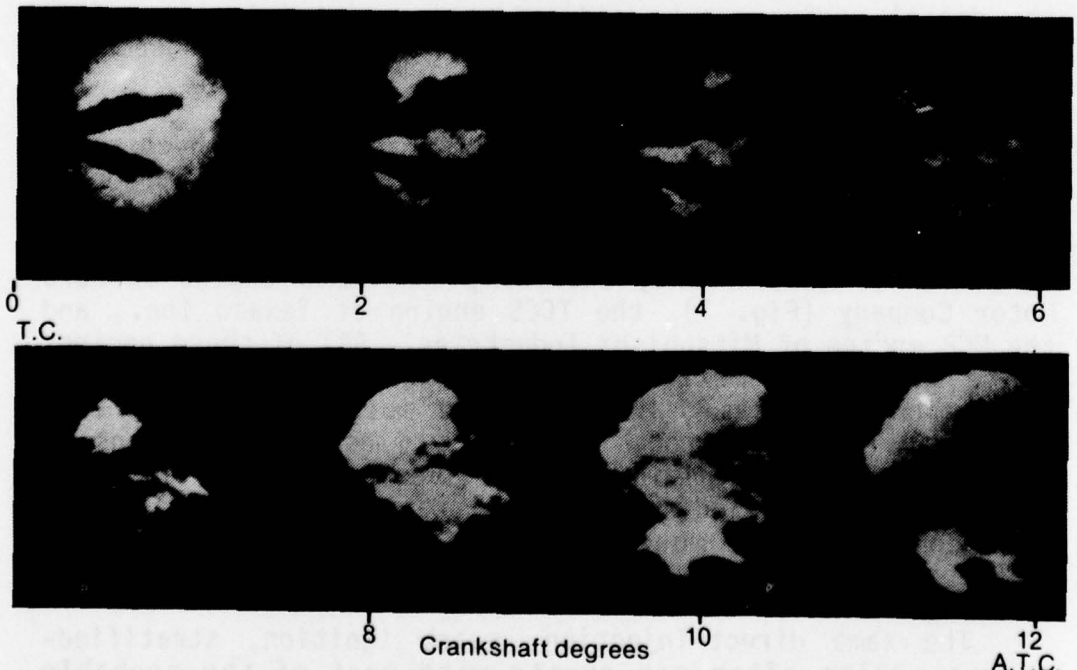


Fig. 2 Filmed spray penetration, self-ignition, and combustion in a diesel engine.[21]

fuels will change drastically except, perhaps, for some shift to lower H/C ratios.[4] This is so again both for economic reasons and for the time lag associated with building significant production capacity for any new fuel.

Controlling Combustion Processes

Having selected a powerplant and a class of fuels, the controlling combustion processes[5] now can be considered briefly. For that, it is convenient to follow the events experienced by a parcel of fuel from intake to exhaust (Fig. 2).

The purpose of the fuel-injection system is to break the fuel into small drops (generally less than 50-μ diam) and to direct it so that it reaches various regions of the combustion chamber in appropriate amounts. For that, different injectors are used (single hole, shower head, pintle, impinging jets, etc.) which produce different distribution functions of droplet radii and velocities and, ultimately, different distributions of fuel in the combustion chamber. The mechanism by which fuel jets and sheets are atomized, i.e., broken down into drops, by the injectors used in direct-injection internal combustion engines currently is poorly understood.[6] Approximate, experimental droplet radii distribution functions for specific injectors often can be found, but they generally are determined in gas conditions different from those prevailing in the engine. Since the mechanism of atomization is not known, the many scaling correlations that are used do not rest on solid ground, and large errors, even in estimating just the average drop size or the drop size distribution function, can be expected. Such errors, in turn, drastically influence our ability to predict the behavior of the spray. Thus, for example, an error by a factor of 3 in the initial size of the drop can result in an error by a factor of 10 in the lifetime of the drop (D^2 law) and a complete misjudgment of the whereabouts of the fuel in the combustion chamber. Accordingly, atomization is the first of a series of strongly coupled processes that control combustion in direct-injection, internal combustion engines.

The second controlling process is the penetration and vaporization of the spray.[7] Each drop within the spray exchanges mass and momentum (vaporization and drag) with the surrounding gas, thus influencing the local and instantaneous availability of gaseous fuel. Even though the processes of drag and vaporization of individual drops have attracted the attention of researchers for a long time, a complete understanding of them has yet to be reached, particularly for mul-

ticomponent fuels and for the thick sprays of engines. In thick sprays, the drops are so close to each other that they directly influence each other's motion and vaporization. When the interdrop distance is much greater than 10 drop diameters, the spray can be considered thin, and the motion and vaporization of each drop can be studied as if it were in an infinite, uniform gaseous medium. In this case, practically useful drag and vaporization correlations are available even though their fundamental underpinning is not very rigorous. A spray in a direct-injection engine is very thick at its core and thinner at its periphery, and appropriate ways of representing it are not available yet.

The spray penetrates into, vaporizes in, and mixes with the turbulent air of the combustion chamber. The quesiton of the degree of direct influence of the turbulent fluctuations of the gas properties on the vaporization process of the individual drops also is unresolved presently. However, turbulence has a strong indirect influence even by just diffusing and mixing the gaseous fuel generated by the spray and thus enhancing the vaporization and entrainment rates.

The nature of engine turbulence also is poorly understood.[8] For simple chamber geometries, the available experimental information indicates that, at combustion time, the amplitude of the velocity fluctuation is proportional to the engine speed. It also would appear that much of the turbulence is generated during the intake process, but the contribution of the piston motion and even the definition of turbulence in this fully unsteady flowfield are subjects of current debate.

As vaporized fuel and hot compressed air are mixed turbulently, primarily at the periphery of the spray, the local equivalence ratio increases, and conditions more favorable to the onset and support of combustion are generated. In diesel engines, self-ignition at one location (often at the edges of sprays, as at point A of Fig. 2) is followed rapidly by additional self-ignition spots (as point B of Fig. 2) at various locations.[9,10] Atomization, spray development, and turbulence have strong inputs on the location and timing of the self-ignition spots. However, chemical kinetics is the most influential of the controlling processes in the self-ignition event. This is shown by the effect of the fuel cetane number and by the temperature and pressure dependence of the self-ignition delay time.[9,10] But combustion also could be initiated, at a selected time and location, by a spark (as in the PROCO, TCCS, and MCP engines). In this case, the energy delivered by the spark is believed to be the most

relevant of the parameters, after one is assured that the equivalence ratio at the position and time of the spark (and in its vicinity) is adequate to support a flame.[9,10]

Once initiated, the flames propagate or process the air-fuel mixtures at rates that are controlled primarily by turbulent diffusion and chemical kinetics (in various degrees, depending on the nature of the flame). If drops still are present in the chamber, their vaporization rate still may influence the overall combustion rate.

All along, the convective motion of the chamber gases is influenced by the walls (wall momentum transfer), and so are the gas internal energy and its space distribution (wall heat transfer). Wall heat transfer by convection and radiation can have a significant influence on the combustion process, as evidenced, for example, by the cold-start problem of diesel engines.

In general, then, the controlling processes of combustion in direct-injection internal combustion engines are atomization, droplet drag and vaporization, turbulent mixing, chemical kinetics, and wall energy and momentum transfer.[5] Moreover, they interact strongly with each other so that isolation of their individual contributions is difficult at best. The above controlling processes are all active in a standard diesel engine, whereas only turbulent mixing, chemical kinetics, and wall energy and momentum transfer are of interest for the standard spark ignition engine.

Chemical Kinetics

Let us now concentrate on some of the roles of chemical kinetics, even though the implication that chemical effects can be considered separately from the other controlling processes would be difficult to justify in most cases. In an engine, chemical kinetics generally does not operate independently of the other controlling processes. For example, the composition and temperature of a parcel of gas changes in time not just because of chemical reactions but also because of turbulent diffusional exchanges with neighboring parcels, convective processes, and the possible addition of fuel from vaporizing drops. Indeed, in the mass, momentum, and energy conservation equations, this interdependence is shown clearly, since none of the terms are consistently negligible and all of the equations are strongly coupled.[5]

The chemical nature of the fuel influences all subsequent chemical transformations. Even assuming that mixtures of hy-

drocarbons will continue to be the primary automotive fuels, their complexity constitutes the first chemical kinetic difficulty. Indeed the chemical composition of fuels for spark and self-ignition engines is not in itself part of current fuel specifications. These specifications emphasize such overall fuel properties as octane number, volatility, deposits, and corrosion characteristics for spark ignition engines, and cetane number, volatility, flash point, viscosity, and smoke and corrosion characteristics for self-ignition engines.[9,10] Even though the properties of the fuel are determined by its composition, a large variety of mixtures of hydrocarbons of different families (paraffin, aromatic, olefin, etc.) have properties that meet the specifications.[9,10] Consequently, even different samples of fuels with similar specifications, i.e, for the same application, can exhibit significant variations in composition.[4] Possible future shifts to hydrocarbons with lower H/C ratio[4] (aromatics) would present new practical challenges on account of their different physical and emission characteristics and the lesser known nature of their oxidation kinetics but would not constitute a fundamental change, since current fuels already contain significant fractions of aromatics.

Upon injection of the fuel in the combustion chamber, fuel drops are formed by the atomization process within times

Table 1 Environments of chemical kinetics in internal combustion engines

	Pressure atm	Temperature K	Equivalence ratio
Self-ignition	>40	800-900	0(1)
Spark ignition	15-30	Plasma-600	≈ 1
Liquid fuel pyrolysis	14-70	>400	→ ∞
Diffusion flames	30-100	700-3000	0- ∞
Premixed flames	15-100	600-2800	0.6-1.4
Preflame reactions	15-100	600-1000	0-1.4
Postflame reactions	15-100	2000-3400	0.6-1.4
Wall quenching	15-100	500-1500	0-1.4

of the order of 10 μ sec, i.e., instantaneously for practical purposes. They meet compressed air at 14-50 atm and 600-800 K. These ranges are estimated considering compression ratios of 12 to 22 and fuel injection to start up to 30 crank angle degrees before top-dead-center. The vaporization process and the warming up of the gaseous fuel from its initial temperature of probably greater than 400 K will subtract some energy from the compressed air. However, whereas at the core of the spray the temperature should be close to the initial temperature of the liquid, along its edges a combustible mixture is likely to form at temperatures not much lower than the initial temperature of the air. This is because of the relatively small amount of fuel which is necessary to form a stoichiometric mixture, the small energy required for its vaporization, and the similar rates at which mass and energy are transferred. Indeed, it takes only 6% of the fuel (by mass) to form a stoichiometric fuel-air mixture; the heat of vaporization of the liquid is smaller than at atmospheric conditions (the critical pressure of many of the hydrocarbon components is in the range of 20 to 50 atm); and the turbulent Lewis number for the liquid-gas jet is likely to be of order one.

The warm combustible mixture at the edge of the spray then can self-ignite or can be set off by a spark. The diesel self-ignition process is believed to be controlled almost exclusively by chemical kinetics.[9,10] Indeed, the corresponding ignition delay time decreases slightly with increasing chamber pressure and falls exponentially with increasing chamber temperature. The same behavior is exhibited by the ignition delay of individual drops injected in streams of hot air. Such a delay shows only a slight dependence on the size of the drops. It thus would appear that the formation of small amounts of mixed gaseous fuel and air, through evaporation and mixing, is much faster than the reactions that ultimately lead to self-sustaining combustion. However, little is known about the specific kinetic steps of the self-ignition process. Since the ignition delay time is a very important parameter of diesel combustion, studies of the chemical kinetics of self-ignition are of importance. The environment of self-ignition is characterized by high pressure (>40 atm), temperatures close to the compressed air temperature (800-900 K), and, presumably, near-stoichiometric mixture ratios (Table 1). However, gas-phase pyrolysis of the fuel in the hot, oxygen-rich environment during mixing also must be important in the self-ignition process.

Following fuel injection, combustion also may be initiated by a spark for both low- and high-compression-ratio engines. Spark ignition offers the advantage that combustion

is started where and when desired; i.e., with spark ignition, the combustion process can be controlled more closely. Most engine researchers seem to think that spark ignition is controlled mostly by physical processes[9,10] (in contrast to the chemical kinetics control of self-ignition), including the local addition and diffusion of heat. Energy levels, spark duration, geometries, and structure and intensity of the local turbulence field thus are studied more closely than chemical kinetics as far as spark ignition is concerned.[11] However, the arc does generate ions and elementary species that are very active chemically. And the question has been raised of the relative efficiency of igniting a mixture by chemical vs thermal means.[12] Ultimately, of course, chemical reaction, diffusion, and convection are equally essential elements of the structure of the steady premixed flame. Accordingly, the role of chemical kinetics in spark ignition may be investigated, but it should not be uncoupled from the physical processes and should be framed within the plasma environment generated by the spark. Since spark ignition can be used in both low (8) and high (16)-compression-ratio engines, the pressure of the mixture may be between 15 and 30 atm. The temperatures of the spark plasma and of the unreacted (600-700 K) and related (2200-2400 K) mixtures all should be relevant parameters, but the local equivalence ratio will have to be near 1 if a self-sustaining premixed flame is to follow (Table 1).

Normally, fuel injection continues after self- or spark ignition (in diesel and high-compression, spark ignition engines), and so does the process of drop vaporization. The droplets at the core of the spray vaporize without combustion in a fuel-rich environment. Those at the edge of the spray vaporize in a fuel-lean environment and may be surrounded, or followed (in their wakes), by diffusion flames.

Liquid-phase pyrolysis of some of the compounds may occur in multicomponent fuel drops. Its occurrence will depend on the availability of trace species that may catalyze pyrolysis, on whether the interior of the drop achieves temperatures in excess of the boiling temperature of some of the compounds (because of the presence and vaporization of the other compounds), on whether sudden internal boiling and drop shattering then would occur, and, if not, on whether the characteristic time for pyrolysis is shorter than the residence time of the liquid at the high temperature. All of this is complicated further by a chamber pressure, which, in the range of 14 to 70 atm, is likely to exceed the critical pressure of at least some of the hydrocarbon compounds which is 20 to 50 atm for heavy to light components. (For practical compression ratios of 12 to 22, top-dead-center pressures due to compres-

sion would be 30 to 65 atm, but early injection and the possible presence of drops at the beginning of combustion broaden the range somewhat.) In any case, the internal and instantaneous liquid drop temperature would depend on the boiling temperature of the various compounds (at the indicated pressures) and on the transport rates to and within the drop.[13] All of this indicates that no single characteristic liquid temperature can be singled out; only the initial liquid temperature can be given as a lower bound (Table 1).

When sprays are present in the cylinder during combustion, diffusion flames are inevitable. They may occur at the edge of the spray, around and behind the moving drops, or at the boundaries between rich and lean pockets. Even without sprays, i.e, if one assumes quick vaporization of the injected fuel, diffusion flames are present if injection continues during combustion. The role of chemical kinetics in diffusion flames can be analyzed from the viewpoint of the structure of the flame or from that of the formation of trace species within the flame.

It has been recognized for a long time that significant amounts of nitric oxides are formed in diffusion flames. Although influenced by many factors, such formation is ultimately kinetically controlled, and therefore the knowledge of its detailed kinetic paths is important. Similarly, it is believed that the formation of engine soot also takes place in connection with diffusion flames and that chemical kinetics is again rate-controlling.

However, it is the general opinion that chemical kinetics is not controlling in the determination of the structure of the diffusion flame itself. Indeed, as its name indicates, diffusion is considered to be the controlling process, and chemical kinetics is regarded as occurring very rapidly. Significant chemical reactions are expected to take place only within a region whose thickness is much smaller than the flame thickness. Actually, significant pyrolysis and partial oxidation of the gaseous fuel have been measured in the fuel side of droplet diffusion flames.[14] Neither does the energy release of such reactions appear to be negligible with respect to the total heat of combustion. Thus it would appear that the region within which energy-releasing reactions take place is smaller than the flame thickness but not negligibly so. Moreover, pyrolysis of the gaseous fuel still would take place outside the region within which signficant energy is released. If one couples the fact that chemical kinetics may influence the structure of a diffusion flame with the recognized fact that it is the controlling agent in the formation of some of

the key pollutants within such flames, one may come to the conclusion that a complete re-examination of our current thinking of the role of chemical kinetics in engine diffusion flames is in order. The environment of such flames is characterized by pressures of 30 to 100 atm (well into the combustion process), temperature of 700 K (away from the flame and at the beginning of combustion) to 3000 K (within the flame and toward the end of combustion), and equivalence ratios approaching zero on the air side and infinity on the fuel side (Table 1).

Actually, an ideal engine should not rely on diffusion flames to carry out its combustion process at all.[3] For similar turbulence levels, they are slower and more pollutant-forming than premixed flames. Chemical kinetics is a key element of premixed flames, since the reaction rate is one of the parameters that control the structure and the speed of these flames. Of particular interest today are the reactions that take place ahead of a premixed flame and behind it. The preflame reactions are responsible for the process of engine knock and determine the nature of the unburned hydrocarbons that are emitted when the flame fails to process all of the combustible mixture ahead of it. Depending on the local equivalence ratio, the postflame reactions are important in determining nitric oxides, unburned hydrocarbons, and soot emissions.

A formidable obstacle to a study of the chemical kinetics of pre- and postflame reactions is the diverse nature of the fuel itself. However, the broad environment in which such reactions take place in an engine constitutes an added complication. The pressure may vary from the spark-time pressure to the top cylinder pressure (15-100 atm). The gas ahead of and behind the flame undergoes polytropic compressions (approximately), and its temperature can be estimated to fall in the ranges of 600-1000 K and 2000 to 3400 K, respectively. Ahead of the flame, the equivalence ratio will be near unity for carbureted engines but could be tending to zero (very lean) or exceed one for stratified charge engines. Behind the flame, the possible composition range is narrower, since the mixture processed by the flame must have been within the flammability limits (approximately $0.5 < \phi < 2$). However, fresh charge of air may be brought around the flame front and mixed with the products of the cylinder gas motion (an approach that actually may be sought to achieve further oxidation of the combustion products, for example). The temperature and composition ranges of Table 1 do not account for such back-mixing processes.

Chemical kinetics is found again as one of the controlling processes in the wall boundary-layer quenching phenomenon. For mechanical integrity, the walls are kept at relatively low temperatures, generally less than 700 K. The resulting local energy losses due to heat transfer reduce the local temperature and the reaction rates to the point that the main energy-releasing steps become too slow, and the propagation of flames along or up to the walls is prevented. This was one of the first mechanisms of products of unburned hydrocarbons to be identified, and it still is believed to be one of the major sources. However, the composition of exhaust hydrocarbons is not the same as that of the fuel. Pyrolysis and partial oxidation of the fuel near the walls have been shown to occur, but the investigation of their kinetic paths has barely been initiated. The complexity of the fuels and of the resultant exhaust hydrocarbons is considerable. Indeed, exhaust hydrocarbons have been shown to contain of the order of 100 compounds.[15] Studies of pyrolysis and oxidation mechanisms for practical fuels at 15-100 atm and 500-1500 K are needed not only for the wall quenching problems but also, as previously indicated, for an understanding of preflame reactions as well (Table 1).

In the preceding paragraphs, the established or possible roles were considered of chemical kinetics within such engine processes as ignition, spray developments, diffusion flames, premixed flames, and wall quenching. In current literature on chemical kinetics of engine combustion, a different, more specific approach often is followed in which a compound is singled out and its origin is traced back through the engine combustion processes. Such an approach, which is particularly appropriate for the discussion of air pollutants, was used in recent reviews by Heywood[16] for spark ignition engines, by Henein[17] and Greeves et al.[18] for diesel engines, and in the informative summary by Bowman[19] of the known or proposed kinetic mechanisms of formation of pollutants in combustion processes in general. Since these reviews are rather complete and readily available, there appears to be no reason for this paper to cover the same ground.

Summary

The reciprocating engine is likely to remain the dominant internal combustion engine for the next one or two decades, but its combustion probably will be organized differently from that of today's engines. Direct fuel injection and higher compression ratios, with self- or spark ignition, should become more popular because of their greater efficiency. They also can present emission advantages if proper control of the

combustion can be achieved. Moreover, combustion in such engines includes so many of the combustion processes of standard spark ignition and diesel engines that by discussing the former configurations, one also indirectly included the later ones.

Chemical kinetics is only one of several strongly coupled processes which control combustion in direct-injection engines. Yet the complexity of the total combustion event forces one to study its components individually. In isolating chemical kinetics, it is advisable to try to preserve the actual temperature, pressure, and stoichiometry of the engine, since different kinetic paths often prevail in different ranges of those parameters.

Accordingly, the different environments in which chemical kinetics is known, or suspected, to play a role, within the heterogeneous combustion of a direct-injection engine, have been described, and temperature, pressure, and stoichiometric ranges have been listed. They include the engine environments of self-ignition, spark ignition, liquid fuel pyrolysis, diffusion flames, wall quenching, and of the regions ahead, behind, and within premixed flames. It is hoped that the information may be helpful to researchers with experience in chemical kinetics but unfamiliar with the heterogeneous combustion of direct-injection engines.

Acknowledgment

This paper was prepared as part of a research program on combustion in direct-injection stratified charge engines which is sponsored by the Department of Energy under Contract EC-77-S-02-4191, Dr. Jørgen W. Birkeland, Program Monitor.

References

1 Schurr, S. H., "Energy Research Needs," Resources for the Future Inc., Rept. PB-207516, 1971.

2 "Control Techniques for Carbon Monoxide, Nitrogen Oxide, and Hydrocarbon Emissions from Mobile Sources," U.S. Dept. Of Health, Education and Welfare, Rept. AP-66, 1970.

3 Bracco, F. V., "Toward an Optimal Automobile Power Plant," Combustion Science and Technology, Vol. 12, 1976, pp. 1-10.

4 Longwell, J. P., "Synthetic Fuels and Combustion," 16th Symposium on Combustion, The Combustion Institute, Pittsburgh, Pa. 1977.

[5] Bracco, F. V., "Introducing a New Generation of More Detailed and Informative Combustion Models," Society of Automotive Engineers Transactions, Vol. 84, 1975, pp. 3317-3340.

[6] Reitz, R. D. and Bracco, F. V., "Breakup Regimes of a Single Liquid Jet," Combustion Institute Eastern States Section Fall Meeting, Philadelphia, Pa., Nov. 1976.

[7] Faeth, G. M., "Current Status of Droplet and Liquid Combustion," Combustion Institute Central States Section Spring Meeting, Cleveland, Ohio, March 1977.

[8] Tabaczynski, R. J., "Turbulence and Turbulent Combustion in Spark-Ignition Engines," Progress in Energy and Combustion Science, Vol. 2, March 1976, pp. 143-166.

[9] Obert, E. F., Internal Combustion Engines, International Textbook Co., Scranton, Pa., 1973.

[10] Taylor, C. F., The Internal Combustion Engine, The M.I.T. Press, Cambridge, Mass., 1977.

[11] Lewis, B. and von Elbe, G., Combustion, Flames, and Explosions of Gases, Academic Press, New York, 1961.

[12] Dixon-Lewis, G. and Shepherd, I. G., "Some Aspects of Ignition by Localized Sources, and of Cylindrical and Spherical Flames," 15th Symposium on Combustion, The Combustion Institute, Pittsburgh, Pa., 1975.

[13] Sirignano, W. A., "Theory of Multicomponent Fuel Droplet Vaporization," Proceedings of the International Symposium on Combustion Processes, Krakow, Poland, Sept. 1977.

[14] Ludwig, D. E., Bracco, F. V., and Harrje, D. T., "Nitric Oxide and Composition Measurements within Diffusion Flames around Simulated Ethanol and Ethanol-Pyridine Droplets," Combustion and Flame, Vol. 25, Jan. 1975, pp. 107-120.

[15] Black, F. M. and High, L. E., "Automotive Hydrocarbon Emissions Patterns in the Measurement of Non-methane Hydrocarbon Emission Rates," SAE Congress, Society of Automotive Engineers, Paper 770144, Detroit, Mich., Feb. 1977.

[16] Heywood, J. B., "Pollutant Formation and Control in Spark-Ignition Engines," Progress in Energy and Combustion Science, Vol. 1, April 1976, pp. 135-164.

17 Henein, N. A., "Analysis of Pollutant Formation and Control and Fuel Economy in Diesel Engines," Progress in Energy and Combustion Science, Vol. 1, April 1976, pp. 165-207.

18 Greeves, G., Khan, I. M., Wang, C. H. T., and Fenne, I., "Origins of Hydrocarbon Emissions from Diesel Engines," SAE Congress, Society of Automotive Engineers, Paper 770259, Detroit, Mich., Feb. 1977.

19 Bowman, C. T., "Kinetics of Pollutant Formation and Destruction in Combustion," Progress in Energy and Combustion Science, Vol. 1, Jan. 1975, pp. 34-45.

20 Simko, A., Choma, M. A., and Repko, L. L., "Exhaust Emission Control by the FORD Programmed Combustion Process--PROCO," SAE Congress, Society of Automotive Engineers, Paper 720052, Detroit, Mich., Jan. 1972.

21 Rothrock, A. M. and Waldron, C. D., "Some Effects of Injection Advance Angle, Engine-Jacket Temperature, and Speed on Combustion in a Compression-Ignition Engine," NACA TR 525, 1934.

DISCUSSION

DR. B. T. WOLFSON (AFOSR): I want to bring up an issue which you have not touched on. It pertains to how these systems and other systems actually burn. Do they burn in droplet form with the vapor surrounding the droplet, or do they burn with coupling between droplets and burn in the form of a vapor cloud?

In your investigation it looked as though a single liquid droplet was being investigated. I do not think that is the real situation.

DR. BRACCO (Princeton University): I fully agree that single droplet combustion is not the only controlling process. The controlling processes are: atomization, spray drag and vaporization, turbulent mixing, chemical kinetics, and wall effects. Moreover, the processes are strongly coupled so that it is difficult to isolate their individual contributions. In particular, the fraction of drops which vaporizes with envelope or wake flames, if any, will be a function of the engine design and operating conditions.

DR. A. H. LEFEBVRE (Purdue University): I am interested in the figure illustrating the flame propagating around the

cylinder head, with a pocket of unburned gas ahead of it. I would have thought that under those conditions, and bearing in mind that we are discussing a high-compression ratio engine, you would have all the basic ingredients required for knock. In other words, I would expect knocking combustion to be a severe problem.

On another figure listing what you thought were the key factors governing the process, you included turbulence. I do not think you referred to it again. It seems to me that turbulence could have rather interesting and, in some ways, opposing effects. For the fuel that is evaporating and burning as a conventional flame front, I would expect turbulence to improve the rate of flame spread, as it is well-known to do. However, for that fraction of the fuel which burns as droplets, I would expect turbulence to have a quenching effect.

DR. BRACCO: The picture of the flame propagation in a carbureted engine was used in the presentation to illustrate combustion in a standard, low-compression-ratio, spark-ignition engine. Dr. Lefebvre is right: had the engine been a high-compression-ratio one, knock would have been practically inevitable. Indeed, this is one of the reasons for using fuel injection directly into the cylinder and just prior to ignition in the high-compression, spark-ignition engine.

There is no question that turbulence is one of the controlling processes. In my presentation, and in its written version, I chose to concentrate on some aspects of chemical kinetics because it would have been too laborious to discuss all controlling processes to the same extent. In any case, it is definitely true that turbulence increases the speed at which the gaseous flames process the fuel, but I do not know whether turbulence would have a quenching effect in droplet combustion or not.

DR. H. F. CALCOTE (Aero Chem Research): If I understood you correctly, you said that spark ignition was independent of chemical kinetics.

DR. BRACCO: My oral presentation of the role of chemical kinetics in spark ignition and my oral discussion of it generated considerable confusion. A premixed flame is controlled both by chemical kinetics and by transport processes and so is ignition. Indeed, Dixon-Lewis and Shepherd (the 15th Symposium on Combustion, The Combustion Institute, Pittsburgh, Pa., 1974, pp. 1483-1491), for example, clearly showed that hydrogen-air mixtures can be ignited both by starting with an

unreacted composition and raising the local temperature and by starting with a uniformly low temperature and raising the local concentration of hydrogen atoms. The self-ignition process of diesel combustion is another clear example of the importance of chemical kinetics in ignition.

What I meant to say is that an engine designer thinks of spark ignition in terms of the energy that he has to supply and of self-ignition in terms of the properties of the fuel and the chamber temperature. Another way of putting it is that a designer of spark ignition engines would not put at the top of his priorities the study of the chemical kinetics of spark ignition (bcause he knows he can generate ignition by raising the energy of the spark and changing the spark configuration), whereas a designer of compression ignition engines would.

DR. CALCOTE: I would propose that chemical kinetics are a very important part of ignition, and I agree with you that the basic phenomena involved balancing the rate of heat generation and the rate of heat loss. During the time the spark ignition kernels decide whether they are to grow or die, the temperatures that you have listed here as plasma temperatures have become quite low. The rate at which heat is generated in the kernel is then due to the rate of chemical reaction.

The importance of chemistry is easily demonsrated by comparing the spark ignition energy of normal hydrocarbons, acetylene, which has a very low ignition energy, carbon disulfide, which has an extremely low ignition energy, and hydrogen. Just the fact that these very different fuels have extremely different ignition energies demonstrates the importance of chemistry.

As long as you continue to look at one series of hydrocarbons, all alkanes, you can correlate anything you wish with anything. That, I think, is part of the problem that we have in this business of combustion. Someone does a study on a whole series of alkanes, in which they correlate the results with the HC ratio. They could just as well have correlated the results with the boiling point, the melting point, or most any other property. No one ever correlates against melting point, but if you are just making a correlation, the melting point turns out to be quite good. You cannot pull the chemistry out of a correlation when you are dealing with a system where the chemistry is all the same.

DR. LEFEBVRE: All expressions for ignition energy contain reaction kinetic parameters, including those of Lewis

and Von Elbe. Usually, they are expressed in the form of flame speed. Certainly, ignition depends on a balance between heat release and heat loss, but heat release is generated by chemical reactions. In fact, for a wide range of mixtures, minimum ignition energy is inversely proportional to laminar flame speed cubed. Thus, reaction kinetics is always there; it is an integral part.

DR. BRACCO: In the opinion of Professor Lefebvre, chemical kinetics is recognized as being an essential element of spark ignition. He quotes the fact that one correlates the minimum ignition energy with the flame thickness or flame speed. So one brings chemical kinetics into the heat for ignition. Professor Lefebvre's point is well made: chemical kinetics is important in ignition.

DR. CALCOTE: You and other people have referred to the pyrolysis of liquid droplets in the liquid phase to produce soot and carbon. I find this a little difficult to understand for two reasons. First, the heat of vaporization, or the activation energy for vaporization, must be very much lower than the activation energy for chemical reactions. Thus, I would expect the droplet to evaporate long before it actually cracks in the liquid phase to produce carbon. Further, most of the liquids that we are dealing with in processed fuels were produced by distillation in which the fuel was heated, evaporated, and then condensed. If it did not crack during that process, why should it crack in the liquid phase during the short period of time that it is heated in a reactor?

DR. BRACCO: For the reasons given in my write-up, the question of whether or not liquid phase pyrolysis takes place in a multicomponent fuel drop has not yet been settled. I am neither in favor nor against the proposition; the problem is too complex for me to guess its solution. I simply listed it as one of the current questions.

AD-A061 050 PURDUE UNIV LAFAYETTE IND PROJECT SQUID HEADQUARTERS F/G 21/4
ALTERNATIVE HYDROCARBON FUELS: COMBUSTION AND CHEMICAL KINETICS--ETC(U)
OCT 78 C T BOWMAN, J BIRKELAND N00014-75-C-1143
UNCLASSIFIED SQUID-PU-R2-78 NL

3 OF 5
AD A061050



COMBUSTION OF DROPLETS AND SPRAYS OF SOME ALTERNATIVE FUELS

J.B. Jordan* and Alan Williams+
The University of Leeds, Leeds, England

Abstract

The paper describes a method of studying the rate of combustion of suspended single droplets of liquid fuels by means of continuously recording microbalance. The technique has been applied to a range of alternative liquid fuel combinations and to coal/oil mixtures. Experimental data are presented on the continuous variation of diameter and mass of burning droplets as a function of time for the various fuel combination burning in air at 850°C. The results are analyzed in terms of D^2 rate constants and mass burning rate constants. The influence of fuel composition and, in particular, of the asphaltene content, coal content in the coal/oil mixtures, and the influence of water emulsification are analyzed. In addition, some data are given on ignition delay times.

Introduction

The combustion of sprays of alternative liquid fuels can present a number of interesting technical problems. In the case of hydrocarbon-based fuels, the major synthetic routes presently available generally result in products containing aromatic compounds which are frequently of high molecular weight. The carbon/hydrogen ratios are generally higher than those in fuels currently in use today, particularly in the case of engine fuels. Consequently, there is considerable interest in the combustion of liquid fuels of this type because of the economic advantages in their use rather than more highly hydrogenated products. Secondly, there is an interest in using heavier crude oil fractions with minimal processing or blending as a substitute light fuel, e.g., for engine application fractions. One solution here is the use of "dumbbell" mixtures of the heavier fraction with a low boiling component. One special case of dumbbell mixtures which has attracted considerable attention is that of water-oil emulsions.

*Research Fellow, Department of Fuel and Combustion Science.
+Livesey Professor, Department of Fuel and Combustion Science.

One of the major problems is the emission of particulate material, especially in the case of the higher-molecular-weight fuels containing asphaltic material. Although the larger particulates, including cenospheres, are produced from the liquid-phase thermal cracking of the unstable components of the fuel, little is known of the mechanism, particularly in the case of multicomponent fuels, in which asphaltenes form one of the components.[1-4] Detailed investigations of a number of alternative fuels are being undertaken in this laboratory as an extension of our earlier studies.[5-7] This paper presents results on the single suspended droplet combustion of a number of fuel combinations suitable for engine and boiler use.

The fuel systems studied in this investigation are: 1) coal-derived liquid fuels; 2) mixtures of residual fuel oil with either methanol, n-pentane, or n-heptane (dumbbell

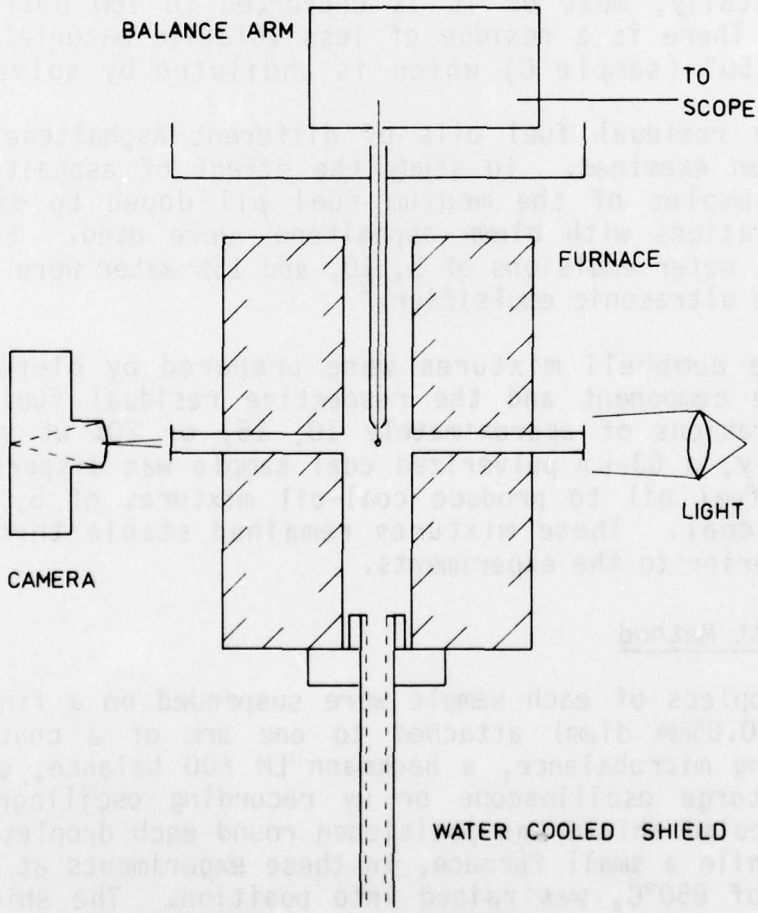


Fig. 1 Diagram of experimental apparatus.

mixtures); 3) residual fuel oil/asphaltene-water emulsions; and 4) coal/oil mixtures. These combinations have been chosen to demonstrate the basic features of dumbbell mixtures and coal-derived fuels, together with the influence of asphaltene content. The coal-oil mixtures are considered to be a further example of a dumbbell fuel. Whilst a number of practical experiments have previously been undertaken with such mixtures no fundamental studies have been made so far.

Experimental Method

A. Sample Preparation

The coal-derived liquid samples studied here were obtained by a process developed by the National Coal Board. Solvent extraction and filtration yields a "coal solution" (sample A) containing all of the solvent oil. Removal by distillation of most of this solvent gives a more concentrated extract (sample B). When the coal solution is hydrogenated catalytically, most of it is converted to low boiling products. There is a residue of less volatile material boiling above 550° (sample C) which is undiluted by solvent oil.

Two residual fuel oils of different asphaltene content have been examined. To study the effect of asphaltene content, samples of the medium fuel oil doped to different concentrations with blown asphaltene were used. From such samples, water emulsions of 5, 10, and 15% water were prepared using an ultrasonic emulsifier.[6]

The dumbbell mixtures were prepared by blending the volatile component and the respective residual fuel oil to concentrations of approximately 10, 15, or 20% wt volatile. Similarly, a 63-μm pulverized coal sample was dispersed in a medium fuel oil to produce coal-oil mixtures of 5, 10, and 20% wt coal. These mixtures remained stable through the period prior to the experiments.

B. Test Method

Droplets of each sample were suspended on a fine quartz fiber (0.05mm diam) attached to one arm of a continuously recording microbalance, a Beckmann LM 600 balance, connected to a storge oscilloscope or uv recording oscillograph. A water-cooled shield was positioned round each droplet (ca 1mm diam) while a small furnace, in these experiments at a temperature of 850°C, was raised into position. The shield then was removed, exposing the drop to the hot furnace environemnt. Two narrow horizontal tubes, arranged coaxially on opposite

Table 1 Average data for medium fuel oil-coal mixtures[a]

Sample	$(M_o-M_i)/M_o$	T_i/D_o, sec/mm	K_p, mm^2/sec	K_o, mm^2/sec	Mass burning rate, sec^{-1}
Medium fuel oil	0.256 (0.036)	1.33 (0.002)	0.458 (0.002)	0.556 (0.012)	1.144 (0.027)
+ 5% coal	0.302 (0.050)	0.994 (0.002)	0.518 (0.015)	0.606 (0.018)	1.137 (0.083)
+ 10% coal	0.287 (0.039)	0.928 (0.048)	0.544 (0.036)	0.546 (0.021)	1.260 (0.040)
+ 20% coal	0.227 (0.011)	0.870 (0.041)	0.524 (0.019)	0.433 (0.071)	1.162 (0.036)

[a]The standard deviations of individuals about the mean are shown in parentheses.

sides of the furnace center, allowed the droplet to be filmed by a cine camera at 64 fps using background illumination, as shown in Fig. 1. The effects of convection currents have, as far as possible, been minimized, and the slight disturbance created by the withdrawal of the water-cooled shield appears to occur in a reproducible fashion. The accumulation of deposited soot or carbon on the quartz fiber above burning droplets of asphaltic samples toward the end of their lifetime tends to impair the accuracy of the weight-time data during

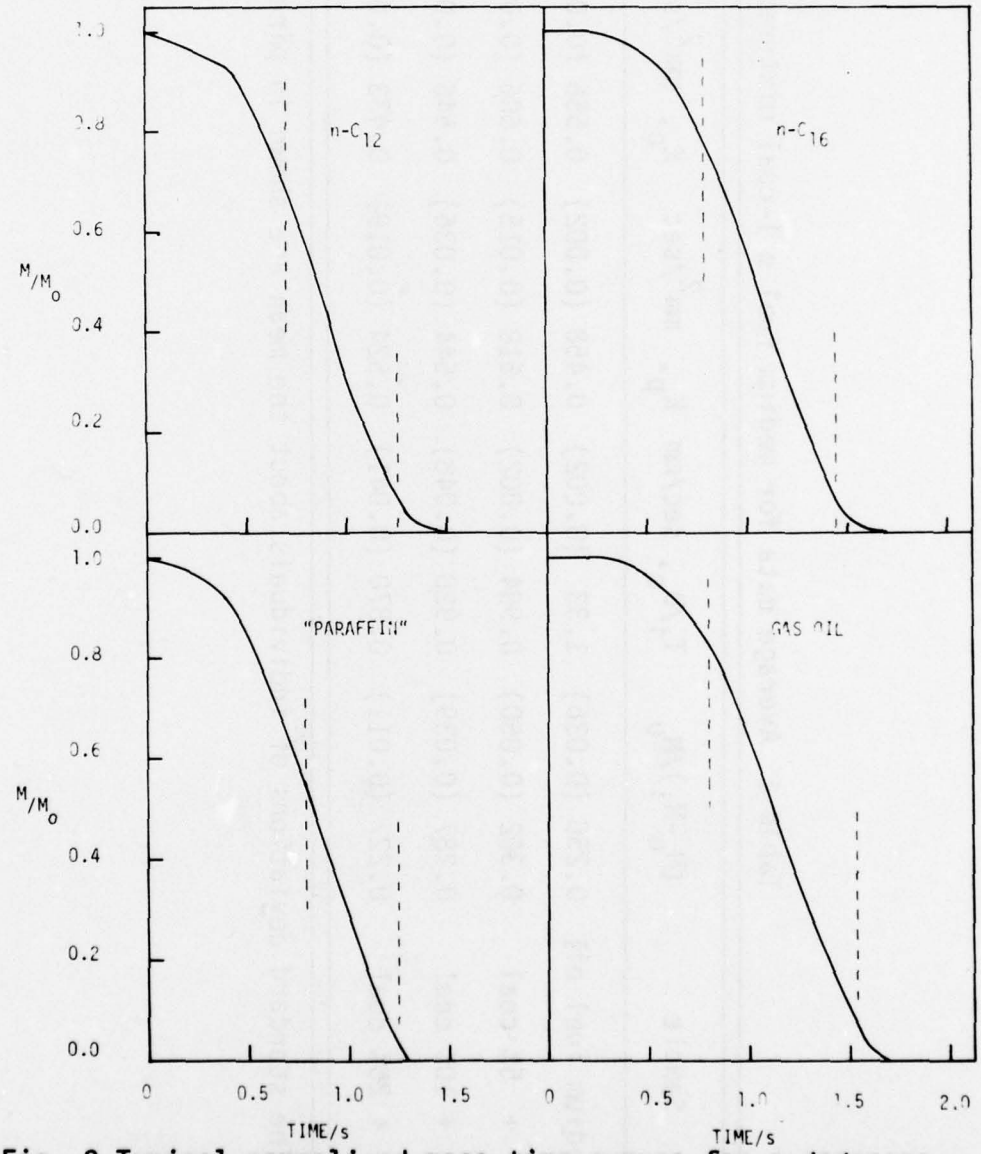


Fig. 2 Typical normalized mass-time curves for n-dodecane, n-Hexadecane, a commercial "paraffin," and a gas oil. (For each curve, the duration of the diffusion flame is bounded by vertical dashed lines; the furnace temperature is 850°C.)

Table 2 Average data for oils of different asphaltene contents[a]

Sample	$(M_o-M_i)/M_o$	T_i/D_o, sec/mm	K_p, mm^2/sec	K_o, mm^2/sec	Mass burning rate, sec^{-1}
0.36% asph.	0.064 (0.021)	0.759 (0.026)	0.709 (0.039)	0.655 (0.086)	0.828 (0.009)
2.5% asph.	0.068 (0.002)	0.743 (0.012)	0.747 (0.020)	0.719 (0.097)	0.935 (0.031)
5.0% asph.	0.035 (0.003)	0.650 (0.102)	0.839 (0.097)	0.743 (0.179)	1.050 (0.016)
6.8% asph.	0.044 (0.007)	0.573 (0.008)	0.877 (0.020)	0.684 (0.035)	1.010 (0.020)

[a]The standard deviations of individuals about the mean are shown in parentheses.

Table 3 Average data for oil-water emulsions of different asphaltene contents[a]

Sample %wt asph.	%wt water	$(M_o-M_i)/M_o$	T_i/D_o, sec/mm	K_p, mm^2/sec	Mass burning rate, sec^{-1}
0.36	0	0.150 (...)	0.937 (0.106)	0.595 (0.048)	0.557 (0.015)
0.36	10	0.275 (0.013)	1.136 (0.227)	0.597 (0.071)	0.608 (0.015)
0.36	15	0.300 (0.016)	1.388 (0.067)	0.537 (0.035)	0.688 (0.012)
5.0	0	0.112 (0.004)	0.991 (0.073)	0.615 (0.010)	0.823 (0.024)
10	0	0.043 (0.033)	0.921 (0.101)	0.668 (0.042)	0.800 (0.106)
5.0	10	0.472 (0.099)	1.298 (0.034)	0.608 (0.063)	0.537 (0.122)
5.0	15	0.465 (0.106)	1.217 (0.208)	0.611 (0.032)	0.621 (0.102)
2.4	5	0.376 (0.098)	1.225 (0.185)	0.567 (0.021)	0.710 (0.019)
4.75	5	0.286 (0.093)	1.303 (0.063)	0.570 (0.011)	0.733 (0.058)
8.1	5	0.240 (0.028)	1.291 (0.005)	0.532 (0.021)	0.780 (0.007)

[a] The standard deviations of individuals about the mean are shown in parenthesis.

this period. While the droplet is being introduced into the furnace, it heats up prior to removal of the shield, causing a loss of weight (up to 5%) because of the partial evaporation of any volatile component present. However, this can be accounted for by careful analysis of the droplet weight time history.

Experimental Results

The experimental technique provides a photographic and gravimetric record of the burning droplet. The cine film was analyzed by measuring, frame by frame, the size of the droplet which then was expressed in terms of an equivalent diameter so that curves of actual or relative diameter against time could be plotted.[5-7] The rate of droplet combustion is indicated by an over D^2 rate constant, $K_o = (D_o^2 - D_b^2)/T_b$, where D_o is the initial drop diameter. D_b the diameter of the residue at the moment of flame extinction, and T_b the time to flame extinction. Reduced ignition delay times[8] (= T_i/D_o, where T_i is the time to ignition based on flame appearance) also are calculated.

Because of convection effects inherent in the system, the record of the microbalance output first must be compared with a dummy output obtained in the absence of a fuel droplet. By comparing the mass of the droplet before and immediately after entry to the furnace, an estimate of the mass lost during introduction can be made. Initially a curve of relative droplet mass, M_t/M_o (where M_t is mass at time t, and M_o is the droplet mass on exposure to the furnace), is plotted. By linear interpolation between data points, the relative mass on ignition, M_i/M_o (where M_i is the droplet mass on ignition), is found. During the flame lifetime, the mass loss curve is approximately linear, and mass burning rates are calculated as the best straight line through data points during this period. Peterson[8] rate constants K_p are calculated from the initial droplet diameter and the time at which $M_t/M_o = (\exp)^{-1}$.

Figures 2-4 show relative mass-time curves representative of some of the fuels studied. Tables 1-6 present averaged data. Table 1 shows the effect of dispersing coal in a medium fuel oil. The increase in mass loss rate before ignition is reflected in the significant increse in K_p when coal is added, although mass burning rates show only a marginal increase. Table 2 and Fig. 5 show how the presence of asphaltene tends to accelerate the combustion process by reducing ignition delays and raising mass burning rates. Conversely, Table 3 shows that, in the presence of 5% asphaltene, the excessive mass lost before ignition due to water emulsifica-

Table 4 Average data for medium fuel oil/dumbbell mixtures[a]

Sample	$(M_o-M_i)/M_o$	T_i/D_o, sec/mm	K_p, mm^2/sec	K_o, mm^2/sec	Mass burning rate, sec^{-1}
Medium fuel oil	0.168 (0.009)	1.240 (0.084)	0.425 (0.008)	0.479 (0.028)	1.075 (0.069)
+ 10% n - C_5	0.190 (0.050)	1.253 (0.031)	0.431 (0.003)	0.488 (0.009)	1.034 (0.006)
+ 12.3% MeOH	0.156 (0.049)	1.047 (0.003)	0.521 (0.004)	0.586 (0.015)	1.144 (0.159)
+ 10% n - C_7	0.145 (0.004)	1.092 (0.062)	0.500 (0.016)	0.546 (0.018)	1.154 (0.050)

[a]The standard deviations of individuals about the mean are shown in parentheses.

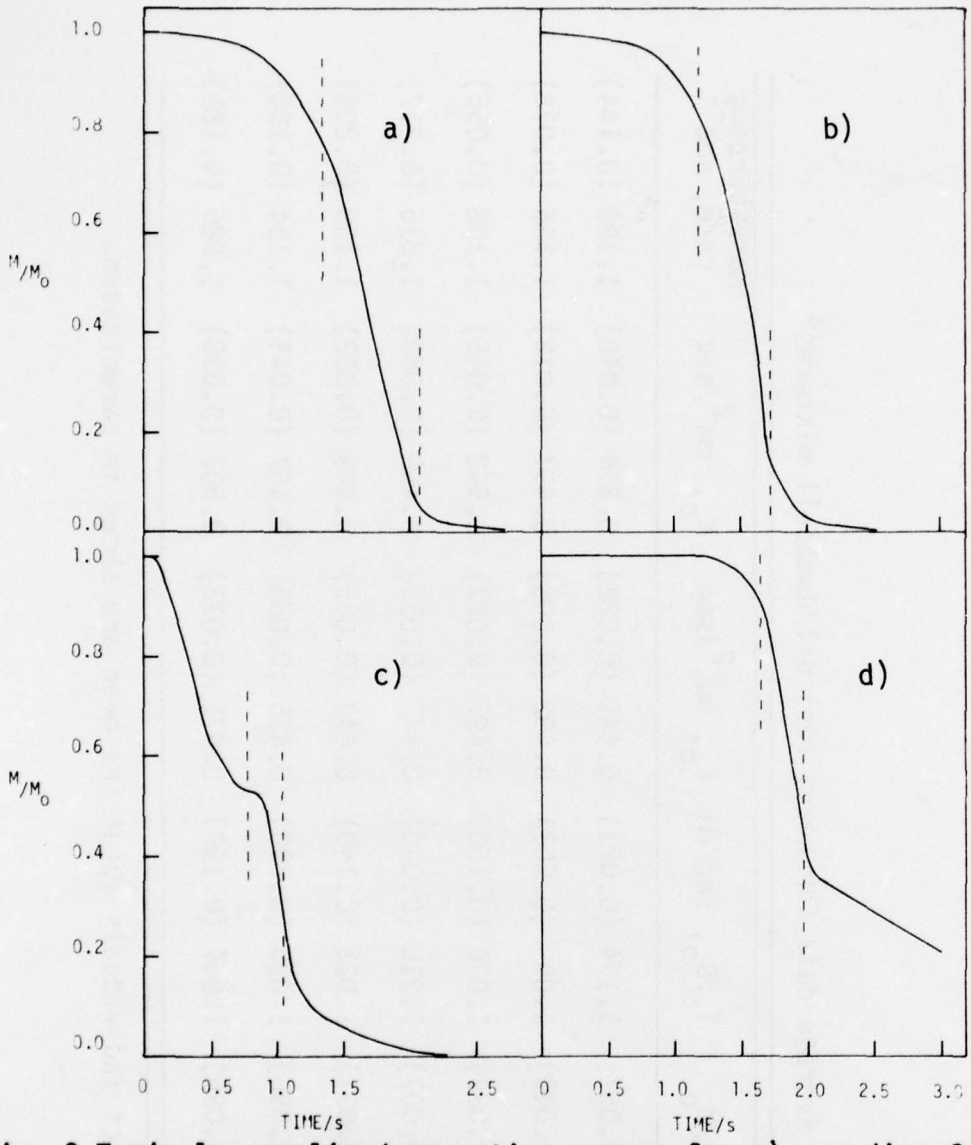


Fig. 3 Typical normalized mass-time curves for a) a medium fuel oil (0.36% asphaltene), b) a heavy fuel oil (3-4% asphaltene), c) a heavy fuel oil (~ 11% asphaltene; dumbbell mixtures of this oil have not been examined yet), and d) coal-derived liquid, sample C. (For each curve, the duration of the diffusion flame is bounded by vertical dashed lines; the furnace temperature is 850°C.)

tion is more than compensated for by increased ignition delays and lower mass burning rates. Tables 4 and 5 present the corresponding results for "dumbbell" mixtures of a medium fuel oil (0.36% asphaltene) and a heavy fuel oil (3-4% asphaltene). The spread of the data makes it difficult to discern quantitative trends. However, for the medium oil, dumbell mixtures

Table 5 Average data for heavy fuel oil/dumbbell mixtures[a]

Sample	$(M_o-M_i)/M_o$	T_i/D_o, sec/mm	K_p, mm^2/sec	K_o, mm^2/sec	Mass burning rate, sec^{-1}
Heavy fuel oil	0.195 (0.057)	1.134 (0.073)	0.441 (0.028)	0.374 (0.048)	1.198 (0.144)
+ 4.1% MeOH	0.215 (0.043)	1.09 (0.053)	0.492 (0.009)	0.497 (0.012)	1.186 (0.078)
+ 13.2% MeOH	0.328 (0.087)	1.070 (0.160)	0.497 (0.027)	0.542 (0.045)	1.108 (0.056)
+ 5.4% n - C_5	0.267 (0.007)	1.216 (0.040)	0.442 (0.033)	0.459 (0.080)	1.316 (0.212)
+ 11.3% n - C_5	0.167 (0.031)	1.023 (0.140)	0.447 (0.035)	0.449 (0.032)	1.139 (0.208)
+ 8.5% n - C_7	0.194 (0.096)	1.035 (0.290)	0.465 (0.058)	0.487 (0.045)	1.154 (0.158)
+ 16.3% n - C_7	0.230 (0.096)	1.064 (0.190)	0.471 (0.032)	0.507 (0.038)	1.086 (0.185)

[a]The standard deviations of individuals about the mean are shown in parentheses.

appear to exhibit both reduced ignition delays and increased mass burning rates. The two effects combine to produce increases in both K_D and K_Q. Ignition delay times also are reduced for the more highly asphaltic heavy oil mixtures. Increasing the volatile concentration apparently lowers ignition delays further and also reduces mass burning rates. In this case, the effects combine to raise K_D only marginally above that of the base oil. Table 6 contains similar data for the three coal-derived liquids. Relative diameters

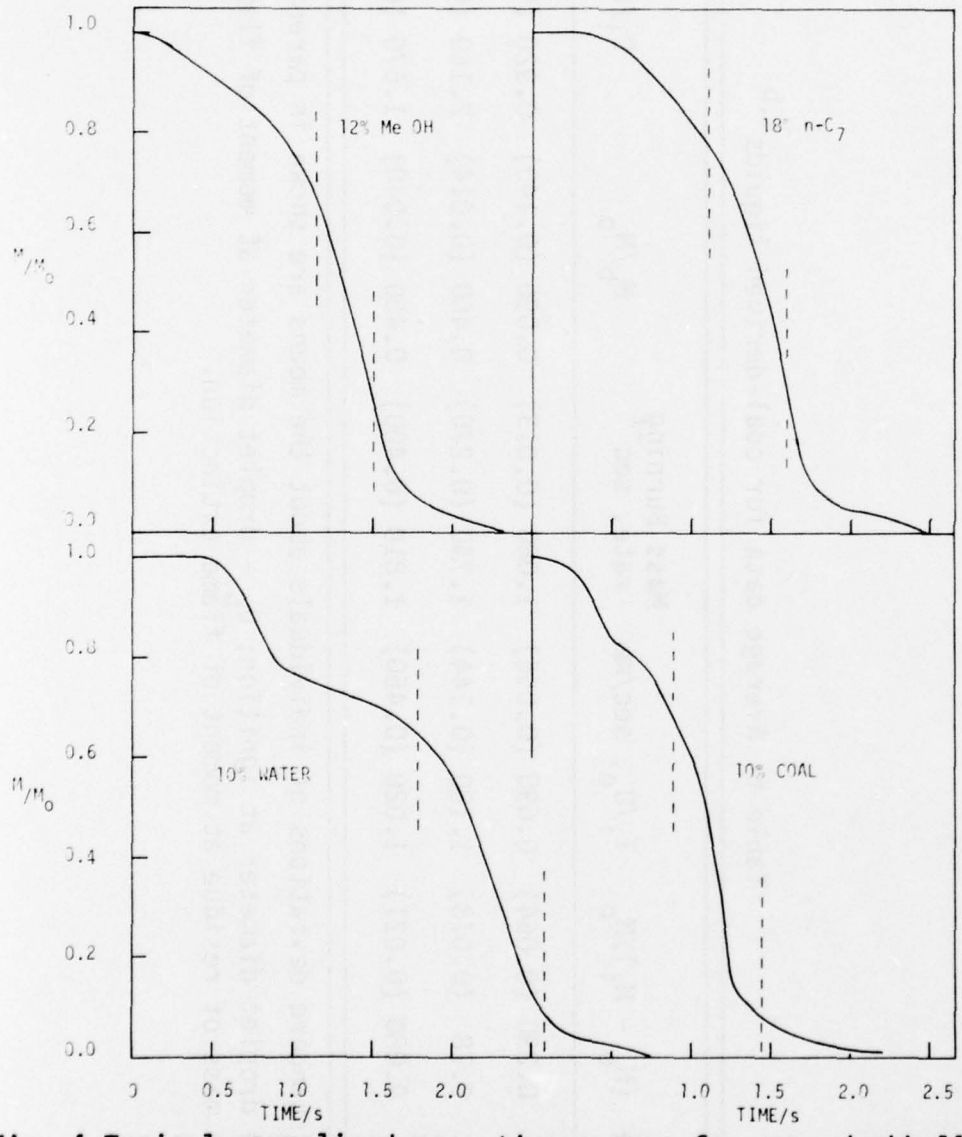


Fig. 4 Typical normalized mass-time curves for some dumbbell mixtures: 12% methyl alcohol, 18% normal heptane, 10% emulsified water, and 10% coal suspension. (For each curve, the duration of the diffusion flame is bounded by vertical dashed lines; the furnace temperature is 850°C.)

Table 6 Average data for coal-derived liquids[a,b]

Sample	$(M_o - M_i)/M_o$	T_i/D_o, sec/mm	Mass Burning rate, sec^{-1}	M_b/M_o	D_i/D_o	D_b/D_o
A	0.290 (0.064)	0.690 (0.056)	1.080 (0.013)	0.090 (0.140)	0.920 (0.001)	0.760 (0.004)
B	0.18 (0.078)	1.180 (0.144)	1.740 (0.270)	0.400 (0.014)	2.160 (0.270)	2.110 (0.230)
C	0.080 (0.021)	1.020 (0.460)	1.810 (0.400)	0.450 (0.040)	1.670 (0.110)	2.060 (0.260)

[a] The standard deviations of individuals about the means are shown in parentheses.

[b] D_i = droplet diameter at ignition; D_b = droplet diameter at moment of flame extinction; M_b = mass of residue at moment of flame extinction.

and masses at ignition and extinction of the flame are included to show their unique behavior. The high mass burning rates and the formation of a large carbonaceous residue is consistent with their highly asphaltic nature.

Discussion

Although single suspended droplet studies often are considered to have little relevance to spray combusion systems, these results indicate that it may be possible to associate the effects of fuel composition on, for example, particulate emission from sprays with the influence of composition at critical stages in the combustion of single droplets. The gravimetric technique provides a continuous mass-time history of a burning droplet. This is particularly advantageous when studying asphaltic fuels, for which the photographic technique produces only an overall, diameter-based rate constant. For example, the excessive swelling exhibited by the coal-derived liquids precludes the application of any D^2 rate-constant type of analysis.

Since droplets of the fuels examined were burnt in air, the lifetime falls into three periods: preignition, combustion, and residue burnout. Within the limitations of the present method, interest centers on first the preignition phenomena and the preignition duration and second the rate of combustion. Figure 2 and the data presented on the different base oils used show the dependence of behavior on composition. Apart from residue burnout, combustion is a gas-phase phenomenon, its rate depending on the rate at which vapors are released from the droplet. This process is considered to take place in two ways: 1) by the distillation of the lighter oil components; and 2) by the release of gases and the evaporation of volatile liquids produced by the thermal decomposition of the heavier components leaving a carbonaceous residue. Clearly both mechanisms are temperature-dependent, and it is understood that liquid-phase thermal cracking progressively predominates as the droplet temperature rises. Although an Arrhenius-type relationship has been suggested[6] for the rate of liquid-phase thermal cracking, the lack of experimental information at this stage prevents all but the most general estimates of activation energies. This makes it difficult to predict at what stage thermal cracking or the extent of associated changes in fuel composition becomes significant. However, it is well known that fuels of high asphaltene content have a greater particulate-forming tendency. The results in Tables 2 and 3 and Fig. 5 show that droplet mass burning rates, which may reflect the rate of thermal cracking, increase with asphaltene content. This suggests that, in the

presence of asphaltene, mass burning rates can be associated with particulate formation in sprays. In this context, not only should the high mass burning rates of the coal-derived liquids be noted, but also that they form large residues, which are slow to burn out.[7] The addition of emulsified water and other volatiles appears to reduce mass burning rates, as shown in Tables 3 and 5, resepctively. This may, in part, explain the improved performance of such dumbbell mixtures. It has been suggested[6] that emulsified water causes a delay in the rise in droplet temperature, thus reducing the extent of thermal cracking at similar times in droplet history. The fractional distillation of other dumbbell mixtures also may modify droplet temperture gradients, with similar effect.

In this study, preignition behavior also is seen to be influenced by the "added" component. The reduced rate of droplet heating clearly accounts for[6] the increased ignition delays observed for water emulsions.[6] When the added component is a volatile liquid, the increased hydrocarbon vapor pressure and its flammability cause the reduced induction times.[6] Both of these effects have been noted in spray systems.[6] In the case of coal-oil mixtures, the increase in the thermal conductivity of the mixture raises the droplet

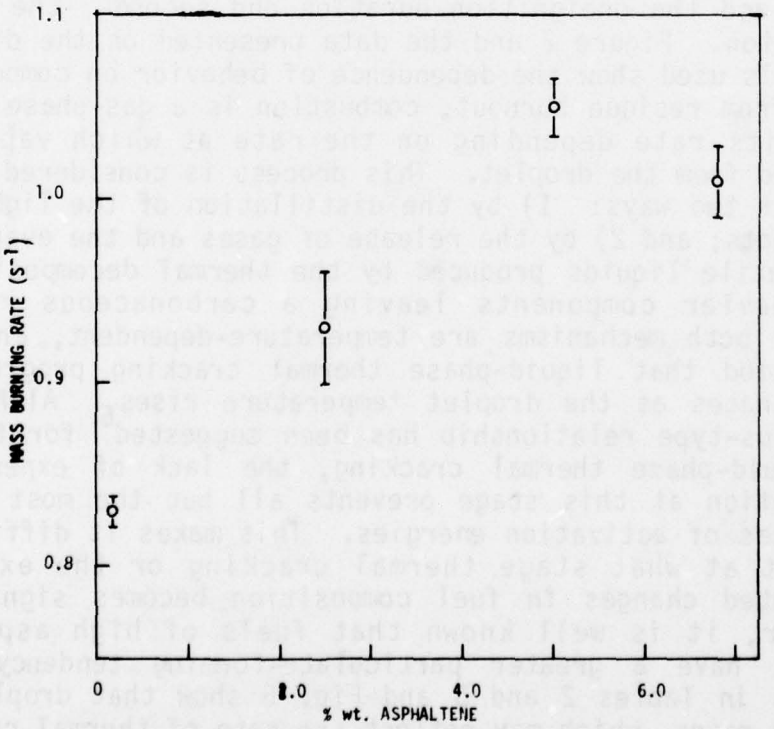


Fig. 5 Variation of mass burning rate with asphaltene content.

heating rates, although the coal moisture content and volatile content also may influence the observed reduction in ignition delays. Clearly the magnitude of preignition disruptive mass loss observed in each dumbbell mixture examined is influenced not only by the volatility of the added component but also by the extent to which it changes the physical properties, surface tension, viscosity, thermal conductivity, and specific heat of fuel mixture. However, general trends can be identified.

Conclusion

By considering the combustion of suspended fuel droplets in terms of mass rather than size, this paper indicates the potential of the gravimetric technique. The combusion of asphaltic fuels is characterized in a more useful way, which has focused attention on criticial processes relevant to the spray situation. These are the extent of disruptive behavior of dumbbell mixtures during the induction period and the rate of mass loss during the combustion period. Furthermore, the technique can be applied to problems associated with diffusion flames, in which case inert furnace atmospheres or combusion products can be used. Clearly much further work is required on the combustion of alternative fuels in single droplets and simple sprays.

Acknowledgments

We are indebted to Esso Research and the Science Research Council for financial support (JBJ), the Science Research Council for an equipment grant, and the National Coal Board for samples of coal-derived liquids. We also are indebted to D. F. Rosborough (Esso) and G. M. Kimeber (National Coal Board) for very useful discussions.

References

[1] Williams, A. "The Mechanism of Combustion of Droplets and Sprays of Liquid Fuels," Oxidation and Combustion Reviews, Vol. 1, Jan. 1968, pp. 1-45.

[2] Williams, A., "Combustion of Droplets of Liquid Fuels: A Review," Combustion and Flame, Vol. 21, Aug. 1973, pp. 1-31.

[3] Williams, A. "Fundamentals of Oil Combustion," Progress in Energy and Combustion Science, Vol. 2, March 1976, pp. 167-179.

[4] Williams, A., The Combustion of Sprays of Liquid Fuels, Elek Science, London, 1976.

[5] Jacques, M. T., Jordan, J. B., and Williams, A., "The Combustion of Emulsions of Water and Fuel Oil," Deuxieme Symposium European sur la Combustion Orleans, Sept. 1975.

[6] Jacques, M. T., Jordan, J. B., Williams, A., and Hadley-Coates, L., "The Combustion of Water-in-Oil Emulsions and the Influence of Asphaltene Content," Sixteenth (International Symposium on Combustion, The Combustion Institute, Pittsburgh, Pa., 1976.

[7] Jordan, J. B., Kimber, G. M. and Williams, A., "Ignition of Droplets of Liquid Fuels Solvent Extracted from Coal," Fuel Vol. 56, Oct. 1977, pp. 417-421.

[8] Peterson, F., "The Mass of an Oil Droplet During Combustion," Combustion Institute European Symposium, Academic Press, New York, 1973, p. 366.

DISCUSSION

DR. A. S. KESTEN (United Technologies Research Center): The mass measurements, along with diameter measurments using the suspended droplet technique, certainly provide some useful insight which is difficult to obtain with other techniques. However, the fiber support may well provide either catalytic effects or it may provide a site for nucleation of carbonaceous residues. We certainly have found that it does influence what happens during the combustion of an emulsified fuel, but is there a way at least to examine the potential catalytic effects or the potential for nucleation sites by either changing the size or the nature of the support?

MR. JORDAN (University of Leeds): It is fair to say that the present system provides a method for comparing the behavior of different fuels under similar conditions. One has to assume that the effects of a particular fiber will remain the same for each fuel examined.

DR. KESTEN: Looking at different fuels is certainly a meaningful thing to do, but I think it also might be easy to change the size of the fiber and to change the material, because there are certainly questions of the influence of the fiber that you might want to pursue. I think it is incumbent upon anyone doing suspended droplet experiments to investigate the influence of the support on which the droplet is suspended.

DR. F. L. DRYER (Princeton University): I would like to strengthen Dr. Kesten's points further by suggesting that one

should be careful about speaking of expressions on mass vs time, as mass burning. I beleive that more properly it is mass loss vs time curves. In similar tests at Princeton on suspended droplets, using emulsions, we have seen significant amount of mass ejected from the primary droplet. I am at a loss as to how one defines what that mass loss rate is. It is certainly a stochastic process. I know of no way of taking that into account in calculating the mass burned because most of the mass that is ejected is not burned at the time of ejection. It is burned much later.

Second, I might also suggest that mass ejection from the primary droplet is the reason for your variation of ignition delay time with emulsion structure. It is secondary initiation (or ignition of the primary droplet caused by the much smaller droplets which are ejected from the primary droplet) which results in the ignition you have reported.

Third, I am currently confused as to whether a suspended droplet technique, no matter what the extension of it is, will ever contribute to understanding residual oil emulsion combustion merely because of the nucleation site problem. When one adds a solid surface within the internal structure of the droplet, one provides sites at which nucleate vaporization of the internal phase can occur. When one does that, one changes the temperature at which internal vaporization occurs, and it significantly alters the time at which the micro-explosion phenomenon, if you will, occurs.

I would like to make one other comment with regard to the role of water in these systems; it is certainly not entirely in the liquid phase and liquid phase reactions. We are convinced that water vapor diffusing away from the droplet surface has a significant effect on gas phase kinetics in the vicinity of the diffusion flame.

One final question. In your emulsification studies, have you classified the internal phase size distribution which is produced by your ultrasonic emulsifier?

MR. JORDAN: Perhaps, in this instance, one should qualify the terms "mass" and "mass loss" as being those of the suspended droplet, and "mass burning rate" as the rate of mass loss of the suspended droplet in the period after ignition and prior to flame extinction. Regarding your second point, we have observed, in our studies of residual oil-water emulsions at Leeds, that the suspended or primary drop can ignite in two distinct ways. One is caused, as you described, by the smaller drops thrown off during a period in which the

primary drop swells and froths disruptively because of the evaporation of the water. We have found that this mode of ignition is difficult to reproduce experimentally and have called it "premature" ignition as opposed to the second, conventional mode. The latter occurs much later, after the "disruptive" swelling has subsided, and in the same way as a residual fuel oil droplet--that is, in the absence of smaller "secondary" droplets.

From photomicrographs of the emulsions produced by our ultrasonic emulsifier we have found that mean water droplet diameters are in the range of 3-5 μ, depending on the asphaltene content (I.P.143/57) of the oil used.

Certainly our experience with emulsions and residual fuel oils also has led us to question the effects of the suspending fiber, and we are currently developing a system for studying the combustion of freely moving oil droplets.

FLAME EMISSIVITIES: ALTERNATIVE FUELS

Adel F. Sarofim*
Massachusetts Institute of Technology, Cambridge, Mass.

Abstract

Synthetic fuels may yield heat-transfer rates that differ significantly from those of conventional fuels as a consequence of variations in their adiabatic flame temperatures and differences in parameters, such as hydrogen/carbon ratio and ash content, which may influence flame emissivity. The data available for predicting the differences in the emissivities of the products of combustion of fossil fuels and their derivatives are reviewed, and the implications of differences in emissivities on the performance of different practical systems are examined. Existing experimental and theoretical correlations for the emissivities of the dominant contributors to radiation from the common products of fossil fuel combustion, although still subject to some uncertainty, are shown to be adequate for purposes of assessment of total heat trasnfer. Calculations performed of the luminous and nonluminous contributions to radiation in furnaces, internal combustion engines, and gas turbines underline the importance, in oil-fired systems, of the contribution to radiation by soot. There is a need for a method for predicting soot formation as a function of fuel composition and combustion variables. For coal-fired systems, data also are needed on the factors that determine the particle size distribution and optical properties of the ash.

Nomenclature

A	= area, length^2
b	= line half-width, cm^{-1}
C	= mass concentration, kg/m^3
C_c, c_w	= pressure correction factor for CO_2 and for H_2O
C_p	= specific heat of combustion products, energy/(mass)(deg)
d	= particle diameter, m
f_v	= fraction of space occupied by particles, (volume particles)/(volume of space)

*Professor of Chemical Engineering.

H_{in} = enthalpy flux in fele and air at furnace inlet, energy/time
h = convection heat-transfer coefficient, energy/(length)^2(time)(deg)
k = complex part of refractive index (n-ik)
k' = dimensional constant in expression for soot emissivity
k_s = attentuation coefficient of soot suspension per unit concentration of soot, $m^{-1}/(kg/m^3)$
L = path length in flame, mean beam length, m
$\dot{m}$ = mass flow of combustion products, m/time
n = real part of refractive index
n/V = number concentrations of particles, number/volume
P = total pressure, atm
p = partial pressure, atm; subscripts denote component: c(for CO_2), w(for H_2O), or molecular symbol for other species
Q = total heat transfer to sink, energy/time
T = absolute temperature, deg
V = volume, length^3
X_a = absorption efficiency, (cross section for absorption)/(projected area)
Σ = emissivity; subscript a for a cloud of ash particles, c for CO_2, w for H_2O, c + w a CO_2-H_2O mixture, g combustion products, s sink surface or a cloud of soot particles, t total
λ = wavelength
ρ = density, kg/m^3
τ = transmissivity, subscript c + w for a mixture of CO_2 + H_2O, a and s for clouds of ash and soot particles, t for mixture of CO_2, H_2O, ash, and soot.

Introduction

An understanding of radiative heat transfer from combustion products is needed for the prediction of thermal efficiency and heat-flux distribution in furnaces and for the estimation of the thermal punishment of the confining walls in internal combustion engines and gas turbines. The major contributors to radiation in conventional combustors fired by fossil fuels are carbon dioxide, water vapor, coked oil cenospheres, burning coal char, soot, and inorganic particulates. Although carbon monoxide and unburned hydrocarbons can contribute significantly to the emission and attenuation of radiation within flames, their contributions are localized and are of secondary importance in evaluating total system performance. The contributions of sulfur dioxide and nitric

oxide to heat transfer can be neglected justifiably for normal concentrations of these minor constituents in the combustion products.

A number of problems can be anticipated with the increasing use of coal and coal-derived fuels, including low- and intermediate-Btu gas and solvent-refined coal. The concerns are with effects of variations in ash, char, and soot production on radiation in coal-fired furnaces, the effects of both flame temperature and gas emissivity on performance of furnaces fired with coal-derived gases, and the augmentation of the radiative punishment of the confining walls of gas turbines and internal combustion engines by increases in the soot contribution to radiation.

Before examining the potential changes in performance which may result from the introduction of alternative fuels, it is necessary first to assess the confidence with which emissivities can be calculated. Although the major changes anticipated are in the luminous contributions due to the increased sooting tendencies of low H/C fuels, it is necessary to determine all of the contributions to radiation in order to obtain the incremental effect of any increased soot formation.

Emissivities of Combustion Products

Data on emissivities of carbon dioxide and water vapor originally were developed for purposes for calculating radiation in furnaces,[1-7] and these have been supplemented by data gathered for evaluating the radiation from rocket exhaust plumes.[8-15] The availability of data obtained by different methods, by different investigators, at different times provides a basis for estimating the validity of the measurements. Partial results from a recent detailed comparison[16] of these data are provided below, followed by a discussion of the contributions by particulates to emissivities.

Carbon Dioxide

Data are available on total emissivities at atmospheric[1,5] and elevated pressures[17] on spectral band emittances at atmospheric and elevated pressures,[18-20] and semi-empirical models are available for the detailed spectral emissivities.[14,15] The total emissivities derived from the data in these diverse sources are found to be in remarkably good agreement.[16] As an example, the data of Hottel and Manglesdorf obtained in the 1930's are compared with total emissivities obtained by investigation of the spectral information provided by Ludwig and Malkmus in Fig. 1. A maximum

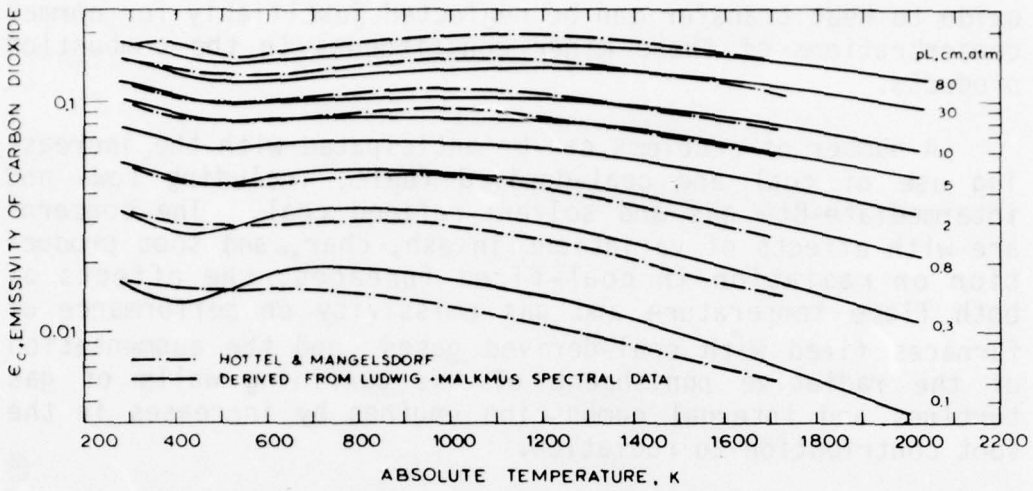


Fig. 1 Total emissivity of carbon dioxide, derived from a) total radiation measurements at 1 atm by Hottel and Mangles-dorf and Eckert and at higher pressures by Akhunov et al.; b) band correlations of Edwards and Balakrishnan based on spectral measurements; and c) semiempirical detailed spectral model by Ludwig and Malkmus.

discrepancy of about 20% is observed at low pL's. In the range of practical interest in large-scale combustors, the difference between the two sources is less than 5%. Total emissivities are primarily a function of the number of emitting molecules, conventionally represented by the product of the partial pressure p_c of the gas in question and the beam length L and temperature T. In addition, because the half-width b of the spectral lines is determined by collision broadening, the emissivity is also a weak function of total pressure P and composition. The data in Fig. 1 are reported as is conventional for a vanishingly small partial pressure of $CO_2 (p_c \rightarrow 0)$ in nitrogen at 1 atm. To convert the data to other pressures or gas compositions, a correction factor is defined by:

$$C_c \equiv \frac{\epsilon_c(p_c L,\ T,\ p_c,\ P,\ \text{composition})}{\epsilon_c(p_c L,\ T,\ p_c=0,\ p_{N_2} = 1\ \text{atm})} = f(b, T, p_c L) \qquad (1)$$

It readily may be shown that the correction factor is dependent only on the spectral line half-width $p_c L$, and temperature. The following empirical correlation is available[15] for b:

$$b = \sqrt{273/T}\left(0.07p_{H_2O} + 0.07p_{N_2} + 0.09p_c + 0.069p_{O_2} + 0.08p_{H_2} + 0.06p_{CO}\right)\ \text{cm}^{-1} \qquad (2)$$

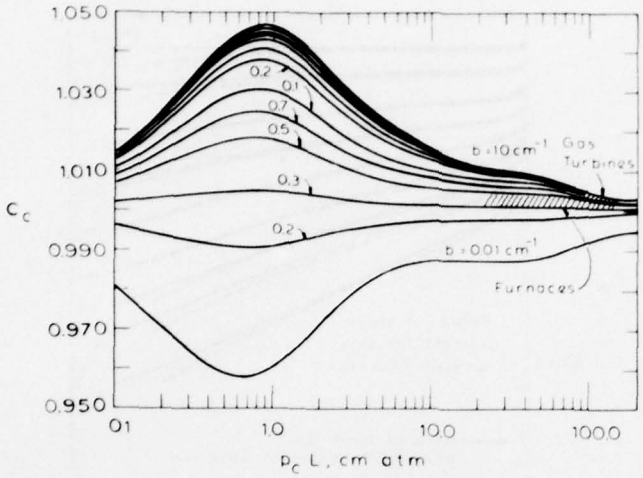


Fig. 2 Pressure correction factor for CO_2 emissivities at 2000 K. Lines correspond to different values the half-width b of 0.01, 0.02, 0.03, 0.05, 0.07, 0.1, 0.2, 0.3, 0.5, 0.7, 1, 2, and 10 cm^{-1} ($b = 0.007\ p_c + 0.026\ P$).

Noting that the coefficient on the partial pressure of the major gas constituents are all about 0.07, except for CO_2, Eq. (2) can be simplified to yield

$$b = \sqrt{273/T}\ (0.02p_c + 0.07P)cm^{-1} \qquad (3)$$

where P is the total pressure. Values of the correction coefficient have been evaluated for temperatures of practical interest;[16] a representative plot is shown in Fig. 2 for a temperature of 2000 K. It can be seen that, for CO_2 at high temperatures, the value of C_c is close to unity even at the high pressure encountered in gas turbine combustors.

Water Vapor

Similarly for water vapor, data are available for total emissivity at 1 atm[1,3] on the contribution to the emission of the spectral bands[19,20] and on the more detailed spectral distribution.[8-15] Comparison[16] of the total emissivities derived from the different sources after correction to a zero partial pressure of water vapor in nitrogen shows general agreement and some irreconcilable differences. The largest discrepancies, of the order of a factor of 2, are at the lowest pL's (0.05 cm atm). In the range of pL's and temperatures expected in large-scale equipment, the differences are fortunately small. Figure 3 provides a partial comparison of the data compiled from spectral band correlations[19,20] with the values derived from spectral data (mainly data from Ref. 15, modified at low temperatures to include the compilations by McClatchey et al.)[21,22] As for CO_2, a correction factor

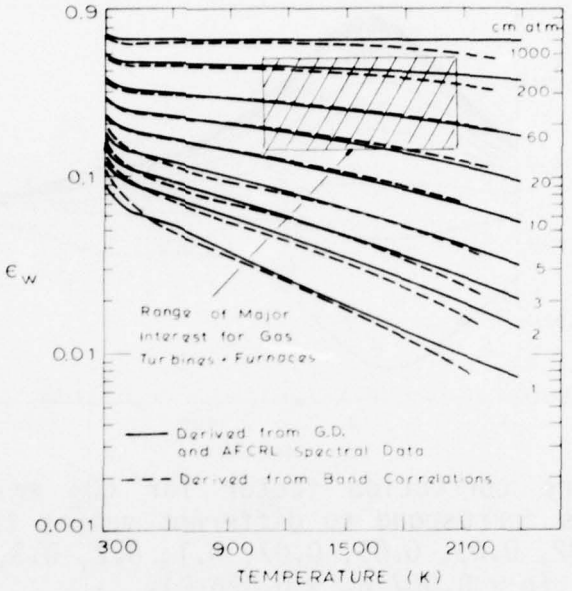


Fig. 3 Total emissivity of water vapor based on a) spectra data compiled by Ludwig et al. and McClathley et al., and b) band correlations by Edwards and Balakrishnan.

is needed to allow for changes of pressure and composition from the reference values ($p_w = 0$, $p_{N_2} = 1$ *atm*). *The empirical* correlation[15,23,24] for the spectral line half-width is given by

$$b + 0.44\ (273/T)\ p_w + \sqrt{273/T}\left(0.09\ p_w + 0.09 p_{N_2} + 0.13 p_c + 0.04\ p_{O_2} + 0.05\ p_{H_2} + 0.01\ p_{CO}\right)\ \text{cm}^{-1} \qquad (4)$$

For combustion products in which molecular nitrogen is the dominant component, the summation in the parentheses can be approximated by 0.09 P, so that

$$b = 0.044\ (273/T)\ p_w + \sqrt{273/T}\ (0.09\ P)\ \text{cm}^{-1} \qquad (5)$$

An example of the pressure correction for water vapor for a temperature of 1500 K is shown in Fig. 4. The correction factor is seen to be appreciable for combustors operated at high pressure, being of the order of 1.45 for the range of conditions of interest in gas turbines. A set of correction charts has been calculated[16] and will be published soon.

Overlap Correction Factor

The emissivity ϵ_{c+w} of a mixture of water vapor and carbon dioxide is smaller than the sum of the individual

contributions, since the emission bands of CO_2 and H_2O overlap at 2.7 μ and in the far infrared, resulting in the attenuation of the emission of one constituent by the other. A correction factor is defined to allow for this overlap, as follows:

$$\Delta\epsilon = \epsilon_c + \epsilon_w - \epsilon_{c+w} \tag{6}$$

The overlap correction factor $\Delta\epsilon$ is a function of the variables that define ϵ_c and ϵ_w, or

$$\Delta\epsilon = f[T, (p_c + p_w)L, p_w/(p_w + p_c), p_c, P) \tag{7}$$

where p_c and p_w refer to the partial pressures of CO_2 and H_2O. It again is convenient to define a "standard" correction factor for P = 1 atm and $p_w = p_c = 0$. The overlap correction chart presented in Fig. 5 gives $\Delta\epsilon$ as a function of temperature for selected partial pressure path length product $[Lp_c + p_w)L]$ and two values of $p_w/(p_w + p_c)$. The values of the overlap correction factor were calculated[16] using the spectral data from Ref. 15; they are found to be in good agreement with the limited measurements by Hines and Edwards.

Pressure broadening may be allowed for, to a good approximation, by multiplying the correction factor $\Delta\epsilon$ by the product of the pressure correction factors for $CO_2(C_c)$ and $H_2O(C_w)$, each evaluated without allowance for presence of the other. Therefore,

$$\Delta\epsilon\left[T,(p_c + p_w)\,L, \frac{p_w}{p_w + p_c}, p_c, P\right] = \Delta\epsilon\left[T, (p_c + p_w)L, \frac{p_w}{p_w + p_c}, p_c = 0, P_t = 1\right] \cdot C_c[T, p_cL, p_c, P] \cdot C_w[T, p_wL, p_w, P] \tag{8}$$

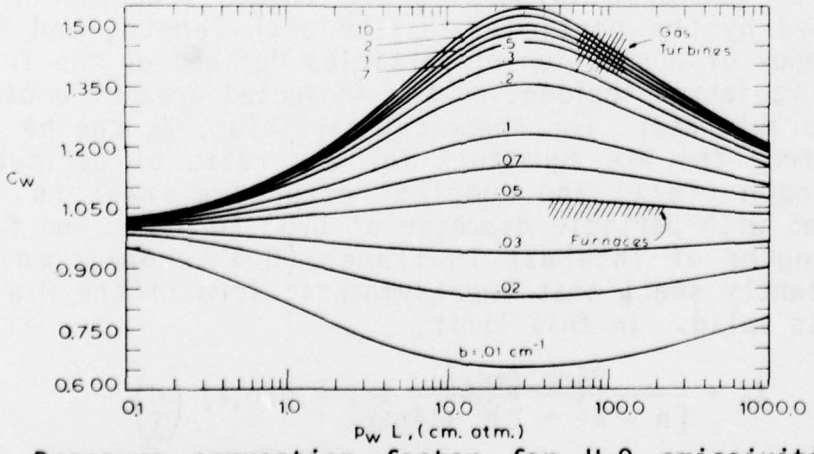


Fig. 4 Pressure correction factor for H_2O emissivities at 1500 K for different values of the line half-width b (b = 0.08 p_w + 0.0384 P).

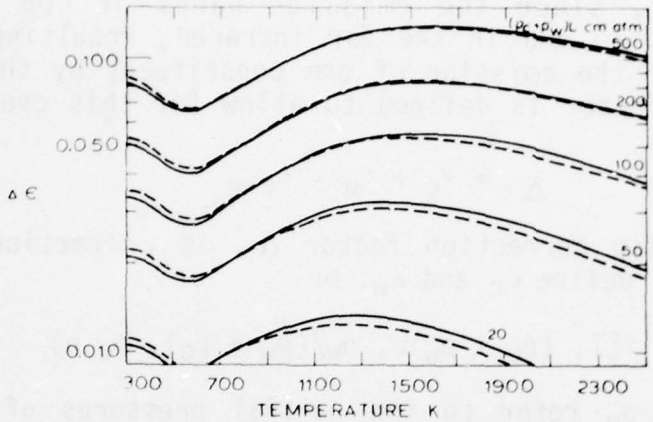


Fig. 5 Overlap correction factor for CO_2, H_2O mixtures, P = 1 atm, $p_w \longrightarrow 0$, $p_c \longrightarrow 0$, for $p_w/p_c = 1$ (solid lines), $p_w/p_c = 2$ (dashed lines).

In order to obtain the emissivity of a mixture of CO_2 and water vapor, it therefore is necessary to evaluate the five terms in Eq. (9):

$$\epsilon_{c+w} = \epsilon_c \cdot C_c + \epsilon_w \cdot C_w - \Delta\epsilon \cdot C_c \cdot C_w \qquad (9)$$

Soot

The emissivity of clouds of particles in suspension can be shown readily to be given by

$$\epsilon_s = 1 - \exp\left(-\frac{n}{v}\frac{\pi d^2}{4} X_a L\right) = 1 - \exp\left(-1.5 f_v \frac{X_a}{d} L\right) \qquad (10)$$

where d is effective particle diameter, n/v the number of particles per unit volume, f_v the volume fraction of space occupied by the particles, L the path length, and X_a the efficiency of absorption of particles defined as the fraction of the radiation incident on the projected area of a particle that is absorbed. For spherical particles, X_a can be calculated from the Mie equations for any ratio of perimeter to wavelength ($\pi d/\lambda$) and complex refractive index (n - ik). For soot with particle diameter of 0.03 to 0.1μ and for the wavelengths of interest in flames (0.5 to 6μ), $\pi d/\lambda$ is sufficiently small that the asymptotic form of the Mie equations is valid. In this limit,

$$X_a = \frac{24nk\ (\pi d/\lambda)}{[n - k^2 + 2]^2 + 4n^2k^2} \equiv g(n,k)\left(\frac{d}{\lambda}\right) \qquad (11)$$

where g(n,k) is the function of n and k defined by the foregoing identity. Substitution of X_a from Eq. (11) into Eq.

(10) yields

$$\epsilon_s = 1 - \exp\left[-1.5\, f_v g(n,k) L/\lambda\right] \qquad (12)$$

This gives the well-known result that the emissivity of a soot cloud is determined by the volume of soot present and is independent of particle size.

Knowledge of the optical constants of soot therefore is needed in order to calculate the radiation from clouds of soot particles. The optical constants are expected to be a function of the hydrogen/carbon ratio of the soot and its thermal history. Values of n and k/n are shown in Fig. 6 for soots produced in propane and acetylene diffusion flames,[26] for a pyrographite,[27] and for graphite.[28] The data were obtained from the reflectance or change in state of polarization on reflectance or change in state of polarization on reflectance for samples of graphite or polished samples of compressed soot. The data show an increase in n and k near constancy of k/n with increases in wavelength. The differences in spectral emissivity resulting from the differences in optical constant are shown in Fig. 7 for a graphite,[28] a pyrographite,[27] and a propane soot.[26] The data are considered to be sufficiently representative of soots in flames to provide a basis for estimates of the luminous soot contribution to flame radiation. That there is a need for additional data on optical properties of soot should be apparent from the qualifications on the data noted in the following sections.

Limited additional data are available on the optical constants of soots[29] and coals.[30] These show that the optical constants, in particular k, decrease as the H/C ratio increases. For soots in the postflame zone where the H/C ratio is 0.2 or smaller, the variations in optical constants resulting from variations in H/C ratio are probably small enough to be neglected. For high H/C ratios such as that encountered in the early stages of soot formation in premixed flames, a significantly lower attenuation coefficient than that reported in Fig. 7 is expected. Indeed, the absorption coefficient in the early portion of a low-pressure acetylene flame[31] has been found to be an order of magnitude lower than the values expected for a more mature soot with a lower H/C ratio.

Another complicating factor is introduced by the question of the temperature dependence of the optical constants. The radiative properties of a number of carbons have been found to be essentially independent of temperature,[32-34] suggesting that the optical constants are temperature-indepen-

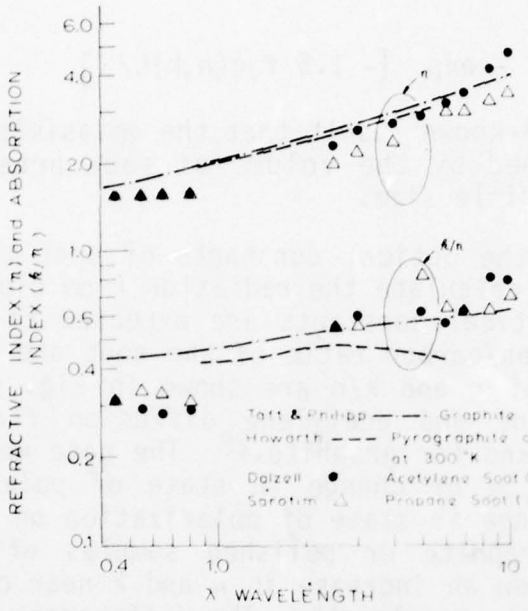


Fig. 6 Data on the complex refractive index, n-ik, of two soots, a graphite, and a pyrographite.

dent. However, theoretical estimates[27,35] of the effect of temperature on dispersion coefficients fitted to the optical constants of soot suggest a strong temperature dependence. Data on radiation from soot in flames are conflicting. Several studies[36,37] show similarity of the dispersion coefficient ($\equiv$ d ln k_λ/d ln λ) of soot measured in flames with that at ambient temperatures, and this result has been attributed to the temperature independence of the optical constants. The data on soot radiation in a rocket exhaust plume reported in Ref. 15, however, show a marked increase of the absorption coefficient with temperature for temperatures exceeding 1700 K. There obviously is need for resolution of the conflicting information.

A source of an additional minor uncertainty in the optical constants of soots has been noted by Graham.[38] The measurements of Dalzell and Sarofim[26] and Foster and Howarth[29] were obtained on polished samples of compressed soot. Any voids present in the skin depth contribution to the reflectance should be taken into account in the interpretation of reflectance data. Such effects, if present, would result in an underestimation of the absorption coefficient derived from the optical constants by an amount corresponding to the void fraction, by an amount of probably less than 30%. Despite the preceding qualifications, uncertainties in the absorption coefficients of soot do not constrain the determination of the

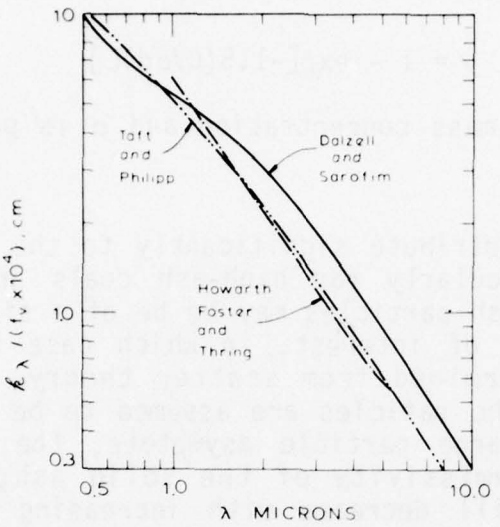


Fig. 7 Spectral absorption coefficient for a cloud of small particles calculated using the refractive index for a propane soot,[23] a graphite,[25] and a pyrographite.[24]

contribution of soot to radiative transfer, since errors introduced by uncertainties in the soot loading usually greatly exceed those due to uncertainties in the optical constants.

The premise that the optical constants on soot are adequate for purposes of providing rough estimates of radiation in furnaces is supported by data on a large-scale turbulent diffusion flames. Measurements of soot radiation, simultaneously with temperature and soot concentrations, yielded absorption coefficients within a factor of 2 of those calculated from Mie theory, using laboratory data for optical constants.[39] The differences between theory and experiment were ascribed to the difference in properties of soot between different flames.

Carbonaceous Particles

The radiation from combustion particles may be augmented by the emission from carbonaceous particles found in both coal flames and in the combustion of residual oils, particularly those containing significant amounts of asphaltenes, which crack to yield carbonaceous cenospheres. These particles tend to be large relative to the wavelength of light and have surfaces with a high absorptivity. X_a is therefore close to unity, and the flame emissivity then is given simply by

$$\epsilon = 1 - \exp[-n/V, \ (\pi d^2/4) \ L] \qquad (13a)$$

or

$$\epsilon = 1 - \exp[-1.5(C/\rho d)L] \qquad (13b)$$

where C is the mass concentration and ρ is particle density.

Ash

Ash may contribute significantly to the emision of coal flames,[43] particularly for high-ash coals and when the ash is fine. The ash particles may be be of a size comparable to the wavelengths of interest, in which case the value of X_a should be determined from scatter theory. If as a first approximation the paticles are assumed to be large enough to approach the large particle asymptote, the X_a is approximated by the emissivity of the solid ash; for a typical silicate, X_a will decrease with increasing temperature and range from 0.3 to 0.7.

Emissivities of Mixtures of Solids and Gases

Since the solid radiation is continuous and changes only moderately with wavelength, the total emissivity ϵ_t of combustion products containing CO_2, H_2O, soot, and ash may be obtained by equating the total transmissivity of the mixture to the product of transmissivities of the constituents:

$$\tau_t = \tau_{c+w}\, \tau_s\, \tau_a \qquad (14a)$$

or

$$(1-\epsilon_t) = (1 - \epsilon_{c+w})\,(1 - \epsilon_s)\,(1 - \epsilon_a) \qquad (14b)$$

or

$$\epsilon_t = \epsilon_{c+w} + \epsilon_s + \epsilon_a + \epsilon_{c+w}\epsilon_s\epsilon_a - \epsilon_a\epsilon_s - \epsilon_a\epsilon_{c+w} - \epsilon_s\epsilon_{c+w} \qquad (14c)$$

Implications of Shifts to Alternative Fuels on the Performance of Practical Devices

The preceding sections provide a basis for evaluating the emissivity of the combustion products of fossil fuels or their derivatives. The calculations in the following sections will illustrate the relative contribution to emissivity of the different constituents in combustion products of alternative fuels, and the implications of shifting to fuels with a low H/C ratio which have a high sooting potential.

Furnaces Fired with Low- or Intermediate-Btu Gas

Interest has been shown in substituting fuels derived from oxygen- or air-blown coal gasifiers for natural gas.

Table 1 Composition and radiative properties of medium- and low-Btu Gases:[a] comparison of methane

Fuel	CO	H_2	CO_2	CH_4	N_2	H_2O	T_{AF}, °F	$-\Delta H_c$,[b] Btu/SCF
Methane (M)	...	...	...	100	...	...	3565	913
Lurgi oxygen (L-O)	18.5	40.2	29.4	9.4	0.6	1.9	3156	254
Winkler oxygen (W-O)	32.9	41.2	20.0	3.0	1.0	1.9	3327	244
Koppers-Totzek oxygen (KT-O)	52.1	34.5	9.2	0.5	1.8	1.9	3578	264
Wellman-Galusha air (WG-A)	26.3	14.3	7.4	2.6	47.5	1.9	2948	146
Winkler air (W-A)	21.1	13.0	6.9	0.6	56.5	1.9	2579	108

Fuel	10% Excess Air			Moles product / moles fuel	SCF product / 10^6 Btu
	$\%CO_2$	$\%H_2O$	$\%O_2$		
Methane (M)	9.3	18.7	1.9	10.7	11,720
Lurgi oxygen (L-O)	18.8	20.0	1.6	3.04	11,970
Winkler oxygen (W-O)	21.9	19.3	1.5	2.55	10,450
Koppers-Totzek oxygen (KT-O)	22.7	13.7	1.6	2.72	10,300
Wellman-Galusha air (WG-A)	17.8	10.5	1.3	2.03	13,900
Winkler air (W-A)	16.7	9.4	1.1	1.72	15,930

[a]Abstracted from Ref. 42.

[b]Lower heating value.

Examples of the composition and selected properties of medium- and low-Btu gases that may be produced by the current generation of gasifiers are shown in Table 1. The influence of such a substitution on the thermal efficiency of a radiant section of a petroleum heater (see Fig. 8) will be examined here. The radiant chamber is assumed to be 6.1 m (20 ft) deep, 3.05 m (10 ft) wide, and 4.57 m (15 ft) high, to have its sidewall and roof covered with a single tube row with an effective plane emissivity of 0.8, and to be fired at a rate of 13.2 MW (4.5×10^7 Btu/hr). The end walls and the floor of the enclosure are assumed to be radiatively adiabatic refractory surfaces. The tube temperature is assumed to be 604 K (700°F) and the convective transfer to the tube walls 11.3W/(m^2)(K) [2 Btu/(hr)(ft^2)(°F)]. A good approximation for the thermal efficiency of the radiant section can be obtained by using the well-stirred furnace approximation.[41] For simplicity, the speckled furnace formulation by the sink (the tubes) is approximated by the fraction of the total furnace envelope A_T covered by refractory. For this case, the governing equations for the rate of heater $\dot{Q}$ between gas and sink are

$$\dot{Q} = \frac{A_T}{(A_T/A_S\epsilon_S) + (1/\epsilon_g) - 1} \sigma (T_g^4 - T_s^4) + hA_S(T_g - T_S) \quad (15)$$

$$\dot{Q} = H_{in} - \dot{m}C_p (T_g - T_o) \quad (16)$$

where A_S, ϵ_S, and T_S are the sink area, emissivity, and temperature, T_g the well-mixed gas temperature, h the convective heat-transfer coefficient to the tubes, H_{in} the enthalpy flux of the fuel and air measured above a reference temperature of T_o, $\dot{m}$ the mass flow rate of combustion products, and C_p the mean specific heat of the combustion prod-

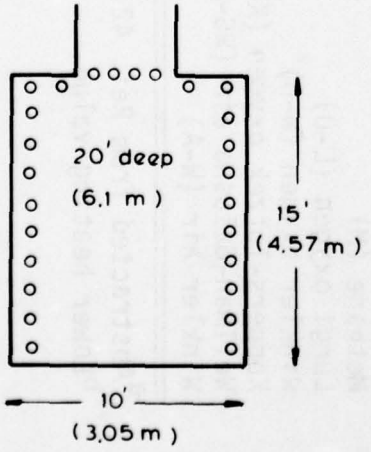


Fig. 8 Schematic of the radiant chamber of a petroleum heater.

Table 2 Emissivities and thermal efficiencies for radiant chamber fired by methane or medium- or low-Btu gas

	ϵ_g	$\dot{Q}/H_{in}$
Methane	0.32	0.587
Lurgi-oxygen	0.34	0.587
Winkler-oxygen	0.36	0.638
Koppers-Totzek-oxygen	0.32	0.633
Wellman-Galusha-air	0.288	0.515
Winkler-air	0.280	0.457

ucts between T_g and T_o. Equations (15) and (16) can be solved for $\dot{Q}$ and T_g. The calculated values of the gas emissivity ϵ_g and the radiant chamber thermal efficiency $\dot{Q}/H_{in}$ are summarized in Table 2.

High thermal efficiency is favored by a high gas emissivity, a high adiabatic flame temperature, and a small volume of product per unit heat release. As a consequence of the combined effect of these factors, the medium-Btu gases produced by the Koppers-Totzek oxygen and Winkler oxygen gasifiers yielded the highest thermal efficiencies, even higher than that expected for natural gas (methane). The lowest efficiencies were for the low-Btu gases produced by air-blown gasifiers, which, as a consequence of the nitrogen diluent in the fuel gas, have low emissivities, low adiabatic flame temperatures, and a relatively large volume of product gases per unit heat release. Experiments on a pilot-scale furnace[42] on the effect of retrofitting furnaces with low- and medium-Btu gases have yielded values for gas emissivity and heat transfer which are in good agreement with the values derived by procedures such as those just described. It is, therefore, possible to estimate with some confidence the changes in the thermal performance of furnaces that are fired with coal-derived gases, since the nonluminous radiant contribution is dominant.

Effect of H/C Ratio on Nonluminous Contribution to Emissivity

Examination of the composition of the combustion products in Table 1 shows a variation in the CO_2/H_2O ratio from about 1/2 to 2. With discussions of potential fuel gases that range from pure CO to pure hydrogen, it is of interest to examine the effect of changes in the H/C ratio on the nonluminous contribution to radiation of combustion products.

The ratio of the emissivity of CO_2 to that of pure H_2O is shown as a function of pL in Fig. 9 for a temperature of 1390 K (2500°R). At low pL's such as those encountered in low-pressure flat flames, the emissivity of carbon dioxide is more than twice that of water vapor. At longer pL's of interest in gas turbines and larger boilers, water vapor is the more effective emitter. The inset plot shows the emissivity of the products of the nonluminous products of combustion of a hydrocarbon fuel burned under stoichiometric conditions as a function of the atomic ratio H/(C + H). Emissivities increase with hydrogen content up to a value of H/(C + H) of about 0.85. For a change from a petroleum-derived distillate fuel [(CH_2) or H/(C+H) = 0.67] to a highly aromatic fuel [$(CH)_n$ or H/(C+H) = 0.5], the emissivity would decrease about 10% from 0.345 to 0.31. It can be concluded that, although extreme changes in H/C ratio from pure hydrogen fuel to a pure carbonaceous can yield a twofold variation in emissivity for a given pL product, the expected shift from petroleum-derived oils to coal-derived liquids would have only a modest effect on the nonluminous contribution to radiation in a large-scale combustor.

Emissivity of Coal Combustion Products

Although significant operational experience is available with pulverized coal combustion, furnace manufacturers still encounter problems in obtaining the desired gas temperatures

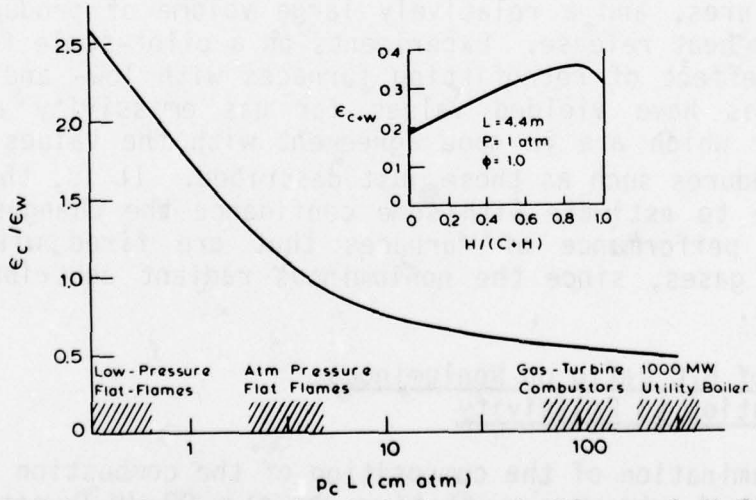


Fig. 9 Ratio of the emissivities of CO_2 and H_2O, $p_cL = p_wL$, for $p_c = p_w \longrightarrow 0$, P = 1 atm, T = 1500 K. Inset plot, ϵ_{c+w} at T = 1500 for the products of combustion of a stoichiometric fuel/air ratio, P = 1 atm, L = 4.4. m, as a function of the atom fraction of H in the fuel.

at the superheaters. Part of this uncertainty can be attributed to problems of surface fouling which affect the absorptivity and heat transfer to the bounding surface walls. Part of the problem probably is due to variations in flame radiation. The luminous contributions of coal char, soot, and ash must be added to the nonluminous contributions of CO_2 and H_2O. The problem of estimating radiation from coal flames had received relatively little attention until recently.[40,43] In the early portions of the flame when coal is heated rapidly by the recirculated combustion products, rapid devolatilization occurs, and significant amounts of soot may be fored in locally fuel-rich pockets. As air is mixed with the combustion products, the soot burns out rapidly, but char combustion may require several hundred milliseconds for completion. As the char combustion is completed, an ash residue is formed in amounts that are determined by the original mineral content of the ash. The ash particles are produced primarily by the agglomeration of the mineral matter distributed in the coal, and their size distribution is governed by the fragmentation of the coal particles during combustion; from 1 to 20 ash particles may be produced per original coal particle.[44,45] In addition, some fine ash particles, in the aerosol range, are produced by vaporization and recondensation of low-boiling-point compounds. From this discussion, it is apparent that the concentrations of the contributors to the radiation from coal flames vary widely within a furnace, and that the concentration and size of the particular matter may be incompletely defined. The following calculations are intended to provide a rough measure of the contributions to flame emissivity by the different constituents.

Consider a bituminous coal with 11% ash, 2.5% moisture, and an ultimate analysis, on a dry-ash-free basis, of 83% carbon, 5.2% hydrogen, with the balance nitrogen, sulfur, and 9.5% oxygen. The contributions to the emissivity of the flame produced on combustion of the coal with 20% excess air are to be evaluated at a gas temperature of 1500 K (2700°R) and a path length through the flame of 2.11 m. For complete combustion, the partial pressures of CO_2 and H_2O are 0.146 and 0.0578 atm, respectively. The nonluminous contribution to emissivity is given by

$$\epsilon_{C+W} = \epsilon_C + \epsilon_W \times C_W - \Delta\epsilon = 0.13 + 1.02 \times 0.095 - 0.022 = 0.205$$

The initial contribution to emissivity by the unburned char may be estimated assuming that the mean coal particle size is 50 μ, that the char particles are the same size (i.e., swelling is negligible), and that the particles are black.

For coal particles with an original specific gravity of 1.3, this would yield a value of 1.32×10^{-5} for f_v of $0.4 m^{-1}$ and a maximum contribution by the char to the emissivity of 0.566. The actual contribution by char to the emissivity will depend on the fractional burnout of the char and whether the char burns as a shrinking sphere or at constant diameter. Experience shows a burnout mechanism intermediate to these extremes.[46] In practice, char radiation is found to dominate the flame radiation early during combustion[47,48] and contributions by large solids to the absorption coefficient of 0.4 to 0.7 m^{-1} have been estimated.[40] When allowance is made for burnout in a large boiler, the char contributions to the radiation is estimated to be localized and to contribute a relatively small fraction of the total heat transfer.[43] The contribution by soot also is strongly dependent on local concentrations. Soot loadings corresponding to 0.5 to 3% of the carbon in the coal have been reported.[40] For a soot concentration corresponding to 0.5% of the carbon, $f_v = 4.0 \times 10^{-8}$ at 1500 K. This soot concentration would yield an emissivity of 0.16 for the assumed flame width of 2.11 m (assuming optical constants equal to those for a propane soot[23]).

The volume fraction f of space occupied by ash is 6.3×10^{-7}, for an assumed ash specific gravity of 2.7. (Cenospheres will have a smaller specific gravity but account for a small fraction of the ash.) The contribution to the cloud emissivity is dependent on the surface emissivity of the ash and particle size. The emissivity of the particles is dependent on composition and is expected to show trends similar to refractory solids, with values ranging from about 0.2 in the visible to close to 1.0 for wavelengths greater than 4 μ. Measurements[49] of fly-ash-laden stack gases show an increase in spectral emissivity with wavelength as expected. A value of 0.5 for the emissivity, which falls within the range of measured values,[50] is assumed here. The particle size of ash depends upon the combustion conditions and is found to correspond to the formation of from 3 to 25 ash particles per coal particle.[44] For a mean particle diameter of 7.5 (corresponding to about 16 particles of ash per coal particle based on Austrailian experience[44]), the contribution by ash to emissivity is 0.125. If a single ash particle per coal particle had been formed, the contribution of the ash to the emissivity would have been only 0.05; if a coal with a higher ash content had been used, the ash contribution would have been the dominant one. To summarize, for the postulated coal, combustion conditions, and flame width, the potential contributions to emissivity are 0.205 and CO_2 and H_2O after completion of combustion, a maximum of 0.566 for char early in

the flame before any appreciable consumption of the char, 0.16 for soot for an assumed concentration corresponding to 0.5% of the carbon in the coal, and 0.125 for ash for an 11% ash coal and a mean ash particle size of 7.5 μ. The composite emissivity, assuming complete char burnout, is approximately 11 - (1-0.205)(1-0.16)(1 - 0.125), or 0.42. The luminous contribution therefore results in an approximate doubling of the nonluminous contribution, with soot and ash contributing about equally to the increase. A realistic model of the contributions of char and soot should include allowance for their burnout,[43] since their concentrations vary widely in the combustion chamber.

The preceding sample calculations emphasize the need to consider the contributions due to ash. This subject is receiving major attention by Stewart and co-workers, who have prepared a definitive review on the subject.[44] In order to define better the radiation from ash, more data are needed on the factors that define ash particle size and on the optical constants for ash. Mie theory needs to be used to calculate the asborption and scatter cross sections for particles and wavelength combinations for which the absorption efficiency X_a no longer can be approximated by the emissivity of the bulk ash. Allowance should be made for the change with temperature of optical constants, particularly for inorganic oxides that show a pronounced increase in absorption index with temperature as a consequence of the increased importance of electronic transitions.[51,52] In addition, for large boilers multiple scatter may modify the effective emissivity of the clouds of ash particles.

Diesel Engines

Interest in calculating heat transfer in internal combustion engines is motivated principally by the need to estimate thermal stresses on critical components, and to a minor extent by consideration of coolant requirement and engine efficiency. (Annad[49] provides an excellent review of heat transfer in internal combustion engines.) In contrast to the situation in large furnaces in which radiation may contribute as much as 95% of the total heat transfer, the radiation contribution to heat transfer in internal combustion engines is secondary to that of convection. Nevertheless, the contribution is not negligible, and it is likely to increase in soot formation which will result when low H/C ratio fuels derived from coal will be substituted for petroleum products. This section will review the literature on radiative transfer in engines and evaluate the potential consequences of increased soot formation on the heat-transfer rate.

The radiation in engines, being dependent on temperature raised to a power of about four (departures from blackbody radiation ususally result in an exponent slightly lower than four), will peak when the crank angle is close to top-dead-center (TDC) and decrease rapidly with the decrease in temperature during expansion. Measurements of radiation in compression-ignition engines[54-59] indicate that radiation may account from 10 to 40% of the total heat transfer averaged over a cycle. The measurements by Flynn et al.[59] on a supercharged (pressure 2 atm) 114-mm bore engine with a compression ratio of 16.7:1 are indicative of the variations of emissivity and radiative flux during an engine cycle. Measurements were made of the emission from a zone about 80 mm long cut through the central cone of the toroidal combustion chamber. The spectral energy distribution measured at seven wavelengths was well fitted by the equation.

$$\varepsilon = 1 - \exp\left(-k'L/\lambda^{0.95}\right)$$

This is consistent with the data on soot shown in Fig. 7. It is of interest that the exponent of 0.95 on is identical to the value recommended for soot in the infrared by Hottel and Broughton in 1932.[71] The total emissivity derived from the spectral data reached a peak of 0.8 to 0.9 shortly after the piston passed through TDC. (Injection advances was 20 deg B TDC.) A corresponding maximum of about 1.2 MW/m^2 was absorbed in the radiant flux. The emissivity and flux showed a secondary maximum at about 60 deg crank after TDC which has been attributed to the late burning of fuel located in the viewing passage.[53] (A secondary maximum in radiant flux also can be observed in the data of Dent and Williams.[58]) The apparent peak temperature in the runs of Flynn et al. was about 2300 K. It can be inferred from the peak emissivity of 0.8 at a temperature of 2300 K in a path length of 8 cm that $f_v = 10^{-5}$ (corresponding to about 0.02 kg/m^3 of soot at the peak pressure of around 120 atm). The emissivity decreased during the expansion stroke in a manner consistent with the expected decrease in f_v because of the pressure reduction. The emissivities near TDC were near black and provide poor discriminants of effects of operating variables. The emissivities during the expansion stroke decrease with decreases in fuel/air ratio over the range 0.015 to 0.049.

Measurements by Sitkei[60] of radiation in an 84-m-bore two-stroke Diesel engine with a compression ratio of 15 showed that emissivity decreased with decreasing fuel/air ratio, showing a peak value of about 0.4. He also observed an 18% decrease in total radiation integrated over a cycle on the addition of 1 wt % of an additive (presumably a barium salt)

to the Diesel oil. The total carbon in the exhaust was estimated from smoke meter readings to be in the range of 10^{-4} to 5 x 10^{-4} to 5 x 10^{-4} kg/m^3, which corresponds to soot loadings, at 2300 K and 120 atm, of about 1.5 x 10^{-3} to 7.8 x 10^{-3} kg/m^3 inferred by Annad[53] from the data of Flynn et al. That the concentrations in Sitkei's experiments were lower than Flynn et al.'s peak values may be attributed partially to differences in operating conditions and partly to partial burnout of the soot before it is exhausted from the engine. Calculations by Khan and Greeves,[61] admittedly using a questionable rate constant and an approximate model, suggest that 60% of the soot formed may be burned before leaving the engine. The observed values of 0.002 to 0.02 kg/m^3 for soot concentrations at peak temperature and pressure and a fuel/air mass ratio of 0.034 correspond to fractional conversions to soot of 0.5 to 5% of the carbon in the fuel. These conversion efficiencies of fuel carbon to soot provide a useful basis for obtaining rough estimates of soot radiation in Diesel engines. The upper value of 5% was inferred from radiation measurements by Annad using the correlation between a mean soot absorption coefficient k in m^{-1} and soot concentration C in kg/m^3 given by Field et al.,[72] namely, k = 1200 C m^{-1}. This correlation is not too different from that inferred using the optical constants in this study. A conversion efficiency of carbon to soot of 5% appears high and may be a consequence of neglecting increases in soot absorption coefficient with temperature.

The availability of correction factors for emissivity for the high pressures existing in engines permits the prediction of nonluminous radiation for different postulated combustion models at any point in the expansion stroke. For purposes of orientation, assume that, for a crank angle a little after TDC, the pressure is 100 atm the temperature 2200 K, the mean beam length (approximately 3.5 volume/surface area) 0.02 m the fuel equivalence ratio 0.5 (F/A $\cong$ 0.034), and the combustion products well mixed. Under these conditions, $p_W = p_C$ = 7 atm, $p_W L = p_C L$ - 14 cm-atm, ϵ_C = 0.07, $\epsilon_W \times c_W$ = 0.08 x 1.2, and $\Delta\epsilon$ = 0.02, yielding ϵ_{C+W} = 0.014. The nonluminous contribution is therefore negligible. The luminous contribution will be evaluated for a 2% conversion of carbon in the fuel to soot. This yields a soot loading of 0.009 kg/m^3 or, for a soot with a specific gravity of about 2, f_V= 4.5 x 10^{-6}; this yields $f_V L$ = 9 x 10^{-8}m, an emissivity of about 0.3 using the optical constants for a propane soot from Fig. 7, and a flux density of 0.4 MW/m^2. These values could be matched with measured emissivities[59,60] of 0.2 to 0.8 and measured peak radiant fluxes of 0.1 to 1.3 MW/m^2 by adjustment of the soot loadings (and, possibly, the optical

constants). If the increase in soot concentration resulting from the use of alternative fuels with lower H/C ratios can be predicted, the foregoing simplified procedures would provide a useful measure of the anticipated increases in heat transfer to the walls. For Diesel engines, the effect on total heat transfer would at most be 30% since the convective heat transfer is dominant.

Gas Turbines

The greatest potential impact of increases in radiation anticipated with increases in the C/H ratio of fuels is in the design of gas turbine combustors, where increases in heat transfer to the walls may be associated with a large penalty in terms of increased combustor liner temperatures or increased film cooling requirements. As an example of the effect of C/H ratio on flame radiation under conditions pertinent to gas turbines, Schirmer[62] has shown a systematic increase in radiative fluxes with increases in C/H ratio and with combustor pressure. The transverse radiation measured across a 5-cm-diam combustor operated at 5 atm increased from 50 kW/m^2 with a fuel of n-heptane (atomic C/H ratio = 0.44) to 240 kW/m^2 with toluene (C/H ratio = 0.88); the corresponding fluxes at 15 atm were 252 kW/m^2 with n-heptane and 460 kW/m^2 with toluene. Blazowski[63] studied the effect of C/H ratio on the liner temperature of a T56 test rig by blending xylene (C/H = 0.8) with JP-4 (C/H = 0.49). The peak liner temperature increased from the 1100 K to a little under 1200 K as the C/H ratio of the blend was increased from the base case of 0.49 to 0.57. Blazowski also was able to correlate the data on the liner combustor of several other engines with the fuel C/H ratio (or its equivalent, fuel hydrogen content). These studies illustrate the importance of fuel composition on the radiative transfer in gas turbines, but care must be taken not to draw generalizations, since the soot radiation is dependent on a number of other factors, including pressure, inlet temperature, air/fuel ratio, air/ fuel mixing patterns, and combustor dimensions.[64-66] As a consequence of the interplay of these other parameters, two scenarios can be constructed under which increased use of high C/H ratio fuels will have no impact on flame radiation. The first is that fuel/air mixing can be improved to the point that soot formation is suppressed effectively, an optimistic view based on test results.[67] At the other extreme, it has been postulated[68] that as gas-turbine pressures continue to increase the soot concentration will increase to the point that blackbody radiation is approached and that, in this limit, incremental amounts of soot will have a small effect. This latter point of view is

supported by measurements[68] of radiative fluxes, brightness temperatures, and metal temperatures in combustors 9.5 and 14.3 cm diam operated over a range of pressures from 4 to 30 atm. An emissivity of about 0.8 was observed at 20 atm, and consequently further increases in pressure resulted in only modest increases in emissivity and radiant intensity. Predictions of wall temperature in fact suggest that the temperature may pass through a maximum at about 25 atm, since at higher pressures the increases in the convective heat-transfer coefficient between the cooling air and metal more then compensate for the modest increases in radiative flux.[69] Knowledge of the soot loadings for different combustor designs and operating conditions is needed in order to evaluate when either of the preceding limits is approached.

In order to determine when changes in C/H of a fuel and the consequent change in soot formation will have a significant influence on the radiative transfer to the combustor walls, consider a primary combustion zone 26.7 cm in diameter (or a mean beam length of 24 cm) fired with a (CH_2) fuel. For stoichiometric combustion with air at 30 atm and 2000 K, the nonluminous contribution to emissivity may be derived from the correlations described earlier as follows:

$$\epsilon_{c+w} = \epsilon_c x C_c + \epsilon_w x C_w - \Delta\epsilon$$

$$= 0.13 \times 1.005 + 0.28 \times 1.24 - 0.065 \times 1.24 \times 1.005$$

$$= 0.40$$

If 1 % of the carbon in the fuel is converted to soot, $f_v = 1.43 \times 10^{-6}$, $f_v L = 3.45 \times 10^{-5}$ cm, and $\epsilon_s = 0.6$. The total emissivity thus is estimated to be 0.76 and the direct radiation from the gas to the walls 650 kW/m^2. (This flux is consistent with the range of values cited in the literature[68,70] when allowance is made in differences in path length or pressure.) From the foregoing, one can conclude that the effect of fuel composition can be neglected when either 1) the mixing of fuel and air is sufficiently good to reduce the efficiency of carbon conversion to soot to less than 0.05%, at which point the nonluminous contribution to radiation would become dominant, or 2) the conversion to soot exceeds 2 to 3%, at which point the flame emissivity would be close enough to unity that further changes in soot concentration would have a minor effect. The efficiency for conversion to soot in combustors of current design usually falls between these limits, and, therefore, for the conditions of the preceding calculation, one would expect changes in soot loading to influence liner temperatures significantly. Obviously, this conclusion must depend on experimental conditions.

The foregoing calculations illustrate that, despite small residual uncertainty in the value of CO_2 and H_2O emissivities and in the optical constants of soot, the influence of changes in composition of combustion products on radiative transfer usually can be made with fair confidence. The major source of uncertainty in the calculation of the radiative transfer from flames continues to be the uncertainty in the concentration of soot.

Acknowledgment

Figures 1-5 are drawn from the Sc.D. thesis by I. H. Farag and are to be incorporated in a publication on a more complete description of the emissivities of CO_2 and H_2O.

References

[1]Hottel, H. C. and Mangelsdorf, H. G., AIChE Transactions, Vol. 31, 1967, p. 517.

[2]Hottel, H. C. and Egbert, R. B., Transactions of ASME, Vol. 63, 1941, p. 297.

[3]Hottel, H. C. and Egbert, R. B., AIChE Transactions, Vol. 38, 1942, p. 531.

[4]Schmidt, E., Forschung auf dem Gebiete des Ingenieur Wesens, Vol. 3, 1932, p. 57.

[5]Eckert, E., Forschungheft, Vol. 387, 1937, pp. 1-20.

[6]Eckert, E. and Schmidt, E., Forschung auf dem Gebiete des Ingenieur Wesens, Vol. 8, 1937, p. 87.

[7]Hottel, H. C. and Smith, V. C., Transactions of the ASME, Vol. 57, 1935, p. 463.

[8]Ludwig, C. B. and Ferriso, C. C., Journal of Quantitative Spectroscopy & Radiative Transfer, Vol. 7, 1967, pp. 7-26.

[9]Ludwig, C. B., Ferriso, C. C., and Abeyta, C. N., Journal of Quantitative Spectroscopy & Radiative Transfer, 1965, pp. 281-290.

[10]Ludwig, C. B., Ferriso, C. C., and Acton, L., Journal of the Optical Society of America, Vol. 56, 1966, p. 1685.

[11]Ludwig, C. B., Ferriso, C. C., Malkmus, M., and Boynton, F. P., Journal of Quantitative Spectroscopy & Radiative Transfer, Vol. 5, 1965, pp. 697-714.

[12]Ludwig, C. B., et al., "Study on Exhaust Plume Radiation Prediction," General Dynamics/Convair, Repts. DBE 66-017, 001A, 1966.

[13]Ludwig, C. B., et al., "Study on Exhaust Plume Radiation Prediction," NASA CR-61233, 1968.

[14]Ludwig, C. B. and Malkmus, W., "Band Model Representations for High Temperature Water Vapor and Carbon Dioxide," Proceedings of a Specialists Conference on Molecular Radiation, NASA TM X-53711, 1968, p. 19.

[15]Ludwig, C. B., Malkmus, W. Reardon, J. E., and Thomson, J. A. L., Handbook of Infrared Radiation from Combustion Gases, edited by R. Goulard and G. A. L. Thomson NASA SP-3080, Washington, D. C., 1973.

[16]Farag, I. H., Sc.D Thesis, Massachusetts Institute of Technology, Aug. 1976.

[17]Akhunov, N. Kh., Panfilovich, K. B., and Usmanov, A. G., High Temperature, Vol. 9, 1972, p. 643 (English transl.).

[18]Edwards, D. K., Journal of the Optical Society of America, Vol. 50, 1960, p. 617.

[19]Edwards, D. K., "Studies of Infrared Radiation in Gases," Univ. of California, Los Angeles, Calif., Final Rept., NSFG 11968, Rept. 62-65, Jan. 1963.

[20]Edwards, D. K. and Balakrishnan, A., International Journal of Heat and Mass Transfer, Vol. 16, 1973, pp. 25-40.

[21]McClatchey, R. A., et al., "AFCRL Atmospheric Absorption Line Parameters Compilation," Air Force Cambridge Research Lab., AFCRL-TR-73-0096, 1973.

[22]McClatchey, R. A., et al., "Optical Properties of the Atmosphere," 3rd ed., Air Force Cambridge Research Lab., AFCRL-72-0497, 1972.

[23]Benedict, W. S., "Theoretical Studies of Infrared Spectra of Atmospheric Gases," Johns Hopkins Applied Physics Lab., Baltimore, Md., Final Rept., AF19(604)-1001, 1956.

[24]Benedict, W. S. and Kaplan, L. D., Journal of Quantitative Spectroscopy & Radiative Transfer, Vol. 4, 1964, p. 453.

[25]Hines, W. S. and Edwards, D. K., Chemical Engineering Progress Symposium Series, Vol. 82 (64), 1968, pp. 173-180.

[26]Dalzell, W. H. and Sarofim, A. F., Journal of Heat Transfer, Vol. 91, 1969, p. 100.

[27]Howarth, C. R., Foster, P. J., and Thring, M. W., Proceedings of the Third International Heat Conference, Vol. 5.

[28]Taft, E. A. and Philipp, H. R., as cited by A. D'Alessio and M. Abrosio, La Termotecnica, Vol. 9, 1976, p. 460.

[29]Foster, P. J. and Howarth, C. R., Carbon, Vol. 6, 1968, p. 719.

[30]McCartney, J. T. and Ergun, S., Fuel, Vol. 37, 1958, p. 272.

[31]Wersborg, B. L., Fox, L. K., and Howard, J. B., Combustion and Flame, Vol. 24, 1975, p. 1.

[32]Autio, G. W. and Scala, E., Carbon, Vol. 4, 1966, pp. 13-28.

[33]Plunkett, J. D. and Kingery, W. D., Proceedings of the Fourth Carbon Conference, Pergamon Press, Oxford, 1960, p. 457.

[34]Willis, C., Journal of Physics D: Applied Physics, Vol. 3, 1970, p. 1944.

[35]Stull, V. R. and Plass, G. N., Journal of the Optical Society of America, Vol. 50, 1960, p. 121.

[36]D'Alessio, et al., Fourteenth Symposium (International) on Combustion, The Combustion Inst., Pittsburgh, Pa., 1973, p. 941.

[37]Millikan, R. C., Journal of the Optical Society of America, Vol. 51, 1961, p. 698.

[38]Graham, S. C., Proceedings of the Royal Society of London, A344, 1975, p. 259.

[39]Beer, J. M. and Howarth, C. R., Twelfth Symposium (International) on Combustion, The Combustion Inst., Pittsburgh, Pa., 1973, p. 1489.

[40]Wall, T. F. and Stewart, I. M., Fourteenth Symposium (International) on Combustion, The Combustion Inst., Pittsburgh, Pa., 1973, p. 1489.

[41]Hottel, H. C. and Sarofim, A. F., Radiative Transfer, McGraw-Hill, New York, 1967.

[42]Shoffstall, D. R. and Waibel, R. T., "Boiler Burner Design Criteria for Retrofit with low Btu Gas," Inst. of Gas Technology, Chicago, Ill., Rept. EPA-600/7-77-073C, 1977.

[43]Lowe, A., Wall, T. F., and Stewart, I. M., AIChE Journal, Vol. 23, 1977, p. 440.

[44]Wall, T. F., Lowe, A., Wibberley, L. J., and Stewart, I. M., "Mineral Matter in Coal and Its Effect on the Thermal Performance of Pulverized-Coal-Fired Furnaces," Progress in Energy and Combustion Science (to be published).

[45]Sarofim, A. F., Howard, J. B., and Padia, A. S., Combustion Science and Technology, Vol. 16, 1977, p. 187.

[46]Essenhigh, R. H., Sixteenth Symposium (International) on Combustion, The Combustion Inst., Pittsburgh, Pa., 1976, p. 353.

[47]Beer, J. M., Journal of the Institute of Fuel, Vol. 37, 1964, p. 286.

[48]Sherman, R. A., Transactions of the ASME, Vol. 56, 1934, p. 177.

[49]Lowe, A., "Ash and Gas Radiative Data for Mathematical Model of P.F. Flames," Symposium on Furnace and High Temperature Heat Transfer, Univ. of Newcastle, Australia, Feb. 1977.

[50]Street, P. J. and Twamley, C. S., Journal of the Institute of Fuel, Vol. 44, 1971, pp. 477-478.

[51]Mularz, E. J. and Yuen, M. C., Journal of Quantitative Spectroscopy & Radiative Transfer, Vol. 12, 1972, p. 1553.

[52]Carlson, D. J., Tenth Symposium (International) on Combustion, The Combustion Inst., Pittsburgh, Pa., 1965, p. 1413.

[53]Annad, W. J. D., Heat Transfer in Flames, edited by N. H. Afgan and J. M. Beer, Halsted Press (Wiley), New York, 1974, Chap. 24.

[54]Belinkii, L. M., "Thermal Radiation in the Combustion Chamber of a High-Speed Compression-Ignition Engine," Trudi, N.I.L.D., No. 1, Moscow, 1955.

[55]Ebersole, G. D., Myers, P. S., and Uyehara, O. A., "The Radiant and Convective Components of Diesel Engine Heat Transfer," Society of Automotive Engineers, Summer Meeting, Paper 701C, 1963.

[56]Ogari, T. and Hsi-Tang, H., "Radiant Heat Transfer in the Cylinder of a Diesel Engine," Japan Automation Research Inst., Tech. Memo. 2, 1971, p. 263.

[57]Sitkei, G. and Ramaniah, G. V., "A Rotational Approach for the Calculation of Heat Transfer in Diesel Engines," Transactions of the Society of Automotive Engineers, Vol. 81, 1972.

[58]Dent, J. C. and Williams, H. S., "The Magnitudes of Radiative and Convective Heat Transfer in a Diesel Engine," International Seminar on Heat Transfer in Flames, Trogir, Yugoslavia, Aug. 1973.

[59]Flynn, P., Mizusawa, M., Uyehara, O. A., and Myers, P. S., "An Experimental Determination of the Instantaneous Potential Radiant Heat Transfer within an Operating Diesel Engine," Transactions of the Society of Automotive Engineers, Vol. 81, 1972.

[60]Sitkei, G., "Flame Radiation in High Speed Diesel Engines," Heat Transfer in Flames, edited by N. H. Afgan and J. M. Beer, Halsted Press (Wiley), New York, 1974, Chap. 26.

[61]Khan, I. M. and Greeves, G., Heat Transfer in Flames, edited by N. H. Afgan and J. M. Beer, Halsted Press (Wiley), New York, 1974, Chap. 25.

[62]Schirmer, R. M. and Quigg, H. T., "High Pressure Combustor Studies of Flame Radiation as Related to Hydrocarbon Structure," Phillips Petroleum Co., Bartlesville, Okla., Progress Rept. to U.S. Bureau of Naval Weapons, AD-842818, May 1965.

[63]Blazowski, W. S., "Combustion Considerations for Future Jet Fuels," Sixteenth Symposium (International) on Combustion, The Combustion Inst., Pittsburgh, Pa., 1970, p. 1631.

[64]Schirmer, R. M., "Effect of Fuel Composition on Particulate Emissions from Gas Turbine Engines," Emissions from Continuous Combustion Systems, edited by W. Cornelius and W. G. Agnew, Plenum Press, New York, 1972.

[65]Macfarlane, J. J., Twelfth Symposium (International) on Combustion, The Combustion Inst., Pittsburgh, Pa., 1969, p. 1255.

[66]Lefebvre, A. H., Twelfth Symposium (International) on Combustion, The Combustion Inst., Pittsburgh, Pa., 1969, p. 1247.

[67]Bahr, D. W., "Control and Reduction of Aircraft Turbine Engine Exhaust Emissions," Emissions from Continuous Combustion Systems, edited by W. Cornelius and W. G. Agnew, Plenum Press, New York, 1972.

[68]Marsland, J., Odgers, G., and Winter, J., Twelfth Symposium (International) on Combustion, The Combustion Inst., Pittsburgh, Pa., 1969.

[69]Kretschmer, D. and Odgers, J., "A Simple Method for the Prediction of Wall Temperatures in Gas Turbines," prepublication draft of manuscript, 1977.

[70]Davis, L. B., Farell, R. A., and Hill, W. E., "Total Flame Radiation and Two Color Flame Temperature in Industrial Gas Turbine Combustion Systems," American Society of Mechanical Engineers, Paper 76-HT-57, 1976.

[71]Hottel, H. C. and Broughton, F. P., Industrial and Engineering Chemistry, Analytical Edition, Vol. 4, 1932, p. 1.

[72]Field, M. A., Gill, D. W., Morgan, B. B., and Hawskley, P. G. W., "Combustion of Pulverized Coal," British Coal Utilization Research Assoc., Leatherhead, England, 1967.

DISCUSSION

DR. C. MOSES (Southwest Research Institute): We did some work in the last year with a combustor of small size, in which we were looking for sensitivites of flame radiation to fuel properties. In this case, we were able to correlate flame radiation quite well with the hydrogen/carbon ratio. Another thing that we were trying to determine was whether this correlation depended on the combustor operating conditions, particularly pressures and burner inlet temperatures.

We found with this particular burner that, once there was a luminous flame and once there was a certain level of radiation, the flame radiation was not dependent upon the combustor operating conditions. Do you have any experience or knowledge of any other work of this type that would agree or disagree with the observations of the sensitivity of flame radiation to the fuel properties and the dependency of flame radiation upon the combustor operating conditions?

DR. SAROFIM: Do you have a measure of how black your flame was?

DR. MOSES: Quite black.

DR. SAROFIM: Basically, that is a question that Hodges addresses in his 12th Combustion Symposium paper. At pressures of 30 atm in a gas turbine combustor, they were getting into a sufficiently high emissivity range where they began to find insensitivity of emissivities to pressure. So, really, once you are black, then you are in a regime where you are relatively insensitive to soot loadings. A difference between 0.95 and 0.99 for flame emissivity is something that would be lost in the scatter of the experimental data.

In combustors, such as furnaces, where the sooting regime fills a small part of the combustion chamber, although the local flame radiation is highly dependent on soot concentration, the soot burns out rapidly enough so that again total furnace performance can be insensitive to flame radiation.

The point that I want to make is that really, once you know where you are in terms of soot loadings and where the soot is, then you can do a fair job of estimating flame radiation without going into the lab and making measurements. However, I think our ability to calculate radiation has outstripped our ability to calculate soot concentrations.

DR. W. S. BLAZOWSKI (Exxon Research): I would like to go back to a comment that Professor Lefebvre made earlier, which was that he did not think that carbon particle formation was important in overall combustor heat transfer, since this point affects Prof. Sarofim's discussion of radiative heat transfer in gas turbines. Based on the data that the U.S. Air Force and NASA have developed and other data that have been generated over the years, the combustor liner sensitivity to hydrogen content and the fact that reduction in hydrogen content causes the exhaust smoke to increase clearly show the existence of a flame luminosity problem that can be influenced by fuel composition. The fact that carbon particle formation is a problem is further demonstrated by the difficulties that engine manufacturers have had in meeting the smoke limitations that the EPA has promulgated.

The only gas turbine combustor that I am aware of that is not sensitive to fuel hydrogen content is the one that I discussed in my paper, the double annular GE CF6-50 design developed in the NASA EECP Program. However, it needs to be pointed out and emphasized that this combustor is a develop-

mental design which is significantly different from the designs that are in use today. Although that combustor has been rig-tested, much additional work needs to be done before it can become operational. For this reason, realization of a combustion system which is not sensitive to fuel characteristics would seem to be a big step from the current state-of-the-art.

DR. A. H. LEFEBVRE (Purdue University): I very much enjoyed your presentation, Professor Sarofim. As one who spent many weeks poring over Hottel's charts, with their pressure corrections, etc., I was pleased indeed to hear of the progress you have made. I very much hope that these new charts will be made generally available, because I think they will prove invaluable to people working in combustion.

Returning to Dr. Blazowski's comment that, as the fuel becomes dirtier the exhaust smoke increases and therefore the emissivity rises, this is not necessarily true because, once the emissivity reaches unity, then the smoke will increase but the liner walls will not get any hotter. On this point, I would like to say that many years ago I thought flame radiation was important. More recently I felt it was much less so for the reason that has been fully discussed, namely, that above a certain pressure a completely black flame is obtained no matter what liquid fuel is used. Now, it would appear that flame radiation is becoming important again because, as Professor Sarofim has pointed out, in many engines the pressure is high enough for flame emissivity to be significant, but not sufficiently high as to make it independent of fuel type. This provides new incentive for studying flame radiation.

There is another aspect that I would like to touch on briefly. Years ago one of the biggest problems in measuring and predicting flame radiation was that nearly all the fuel injectors used were of the swirl pressure type, where every time you changed the fuel flow, the gas pressure, or the fuel type, then everything else changed, including the drop size, the cone angle, and the penetration of the fuel spray. In consequence it was a hopeless task to try to assess or predict anything in the field of flame radiation.

With the advent of airblast atomizers and with the general trend toward premixing fuel with air prior to combustion, we are now entering an era of fewer variables. For example, the fuel drops are now airborne, and the air flow pattern is built into the combustor and remains constant. By eliminating many of the variables that previously affected flame radiation, we now have more incentive than ever before to study flame radiation, and a better hope than ever before of quantifying it.

Chapter III - Pyrolysis and Oxidation Kinetics of Alternative Fuels

PRECEDING PAGE NOT FILMED
BLANK

PYROLYSIS AND OXIDATION OF AROMATIC COMPOUNDS

David M. Golden*
SRI International, Menlo Park, Calif.

Abstract

Understanding of the chemistry involved in alternate fuel combustion requires the general understanding of mechanisms of pyrolysis and oxidation. The object is to write a mechanism and to evaluate individual rate constants within the confines of a theoretical model (usually transition state theory) from date on prototype reactions. The immediate problem with respect to aromatic compounds is the identification of mechanism and prototype reactions for experimental determination. Aromatic compounds can be divided into two classes for discussion purposes, those with and those without side chains. Those with side chains have particularly labile bonds, which are susceptible to rupture at modest temperatures and thus to initiation of radical chain reactions in both pyrolysis and oxidation systems. Those without side chains are predominantly attacked by radicals in an addition step (which may be pressure dependent) and have strong C-H and C-C bonds and are thus poor initiators of chain reactions. Mechanisms of aromatic pyrolysis and oxidation are discussed with reference to those for aliphatic compounds. Individual rate constants are evaluated and/or estimated in the framework of transition state theory. Specific experiments, designed to test major assumptions, are suggested.

Introduction

In the parochial view of a chemist, the questions associated with the use of alternate fuels (especially coal-derived liquids) demand knowledge of the chemical mechanism of pyrolysis and oxidation of aromatic compounds. Both pyrolysis and oxidation are important, because fuel-rich conditions may mean that pyrolysis is competitive with oxidation. Soot formation is certainly a pyrolysis problem for instance. (Soot formation is also indicative of kinetic rather than thermodynamic control.)

---

*Thermochemistry and Chemical Kinetics Group.

PRECEDING PAGE NOT FILMED
BLANK

A goal for the chemist might be to know the elementary chemical steps, their thermochemistry, their rate constants, and the dependence of these rate constants on experimental conditions (temperature, pressure, etc.) so well that, with the aid of an appropriate computer program, all relevant engineering parameters in the real system would be known. Such an ambitious goal eludes us still, but typically we begin by attempting to model the chemistry alone, unaffected by inhomogeneities imposed by such factors as turbulence and specific fuel and air injection sites. Needless to say, even under these simplified conditions of pure chemistry, we are not ready to handle very complex systems in total detail. Luckily, we may generalize the chemistry by classes of molecules, thus simplifying the problem somewhat. In this paper we shall discuss the criteria for generalization of the chemistry and the criteria for critical evaluation of rate constants and their temperature and pressure dependences and suggest some areas where more information is required.

Background

Historically, detailed mechanistic investigation of pyrolysis and oxidation has concentrated on aliphatic hydrocarbons. As a result, we shall discuss aromatic hydrocarbons by comparison to the relatively well-developed understanding of aliphatics.

Pyrolysis of Hydrocarbons

The gas-phase pyrolysis of hydrocarbons is one of the older subjects of gas kinetics. Particular attention has been paid to alkane (paraffin) pyrolysis, and several recent reviews exist.[1] Alkene (olefin) pyrolysis tends to differ from alkanes in that the initiation processes are different (often bimolecular), and at certain temperatures polymerization is prevalent.[2]

A generalized mechanism may be written as follows:

Initiation

$$R - R' \rightarrow R + R' \qquad (P)$$

Propagation

$$H + RH \rightarrow H_2 + R$$

$$R' + RH \rightarrow R + R'H$$

$$R \rightarrow \text{olefin} + R' \qquad (P)$$

H Addition

$$H + \text{olefin} \rightarrow R' \qquad (P)$$

Termination

$$R + R' \rightarrow \text{combination products} \qquad (P)$$
$$\rightarrow \text{disproportionation products}$$

where (P) signifies a pressure-dependent rate constant. As we deal with larger complex molecules, the number of species represented by the symbols R + R' gets quite large.

Oxidation of Hydrocarbons

The gas-phase oxidation of hydrocarbons has been studied extensively, and a generalized mechanism may be written as well:[3]

Initiation

$$RH + O_2 \rightarrow R\cdot + HO_2$$

$$R\cdot' + RH \rightarrow R'H + R\cdot$$

$$R\cdot \rightarrow R\cdot' + \text{olefin} \qquad (P)$$

Oxidation Reactions of Alkanes

$$R\cdot + O_2 \rightarrow \text{olefin} + HO_2$$

$$R + O_2 \rightleftarrows RO_2 \qquad (P)$$

Propagation

$$RO_2 + R'H \rightarrow RO_2H + R'$$

Isomerization

$$RO_2 \rightarrow \cdot QOOH$$

Termination

various

Codification and Extrapolation

It is important to realize that, even in the case of aliphatic compounds, the vast majority of studies have been performed at temperatures that are low compared to combustion interests. This leads to a need for a framework within which

to view the data for purposes of extrapolation to different conditions.

There have been many studies of individual rate constants from these generalized sets. Some classes of reactions have well-measured rate constants, and others only recently have begun to be measured correctly. Even those processes for which good data have existed for a relatively long time, for instance reactions like $CH_3 + RH \rightarrow CH_4 + R$, generally have been studied in relatively narrow temperature ranges, usually below the temperature of interest in combustion problems.[4] Recent work[1,4] suggests very strongly that the simple two-parameter Arrhenius representation of such data is insufficient to describe the temperature dependence over long temperature ranges. This type of finding opens up the question of how well we understand the physical basis for thermal rate constants. Is it necessary to measure all processes of interest over the entire temperature (and pressure) range of possible interest,or can we extrapolate with some reasonable degree of confidence?

Thermochemistry

It is impossible to begin a discussion of the theoretical basis for critical evaluation and extrapolation of thermal rate data without first disucssing methods for estimating thermochemical quantities such as $\Delta H^0_{f,T}$, ΔS^0_T, and $C^0_{p,T}$ for molecules.

Group additivity

When a sufficient data base exists, we have found[5] the method of group additivity to best fit the need for accuracy and ease of operation. The basic concept and assumptions involved in the group additivity method are as follows. For the disproportionation reaction

$$RNN'R + SNN'S \rightleftharpoons RNN'S + SNN'R$$

and additivity approximation assumes that $\Delta\Phi = \Delta\Phi_\sigma$, where Φ is any molecular property, and $\Delta\Phi_\sigma$ is the contribution to that property due to symmetry changes and optical isomerism. For the molecular properties of interest here, $\Delta H_T \rightarrow 0$, $\Delta C_{p,T} \rightarrow 0$, and $\Delta S_T \rightarrow S_\sigma = R \ln K_\sigma$, where $K_\sigma = \sigma(RRNN'R)_\sigma(SNN'S)/\sigma(RNN'S)\sigma(SNN'R)$, $\sigma(X)$ being the symmetry number including both internal and external symmetry. An additional term for entropy of mixing because of the existence of optical isomers, also must be included.

If the molecular framework NN' is two atoms or greater, these relationships imply the additivity of group properties, which include all nearest-neighbor interactions, since a group is defined as an atom together with its ligands [e.g., in the group $C-(H)_3(C)$, the central C atom is bonded to three H atoms and one C atom]. Thus, the equation

$$CH_3OH + CH_3CH_2OCH_3 \rightleftarrows CH_3CH_2OH + CH_3OCH_3$$

implies the additivity of the properties of the groups $C-(H)_3(C)$, $C-(H)_3(O)$, $O-(C)(H)$, $C-(H)_2(C)(O)$, and $O-(C)_2$, if the appropriate $\Delta\Phi = \Delta\Phi_\sigma$.

The basic approximation of group additivity makes no allowance for next-nearest-neighbor interactions, but there are some molecules in which such interactions have considerable influence on the molecular properties. Such refinements are taken into account under the label of conformational corrections. We have developed group additivity methods that permit the estimation, for many organic chemicals in the gas phase, of heats of formation to $\pm$ 1 kcal/moel, and of entropies and heat capacities to $\pm$ 1 cal/(mole-K), from which free energies of formation can be derived to better than $\pm$ 2 kcal/mole.

Group additivity can be readily extended to the liquid phase. For example, group additivity allows the estimation of heat capacities of liquids to better than $\pm$ 1.5 cal/(mole-K), compared with $\pm$ 4 cal/(mole-K) by previous methods.

It should be noted that entropy and heat capacity are molecular properties that can be estimated accurately under much less stringent conditions than energy (or enthalpy). Thus, the method of bond additivity seems to work quite well [$\pm$ 1 cal/(mole-K)] for estimating the former properties, but not at all well ($\pm$ 4 cal/mole) for the latter.

Although most of the simple thermodynamic relationships that are used are derived by assuming no temperature dependence for ΔH and ΔS, large temperature extrapolation of these quantities is performed by making the corrections

$$\Delta S^o_{T_2} - \Delta S^o_{T_1} = \langle \Delta C_p \rangle \ln(T_2/T_1)$$

$$\Delta H^o_{T_2} - \Delta H^o_{T_1} = \langle \Delta C_p \rangle (T_2 - T_1)$$

where

$$\langle \Delta C_p \rangle = [\Delta C^o_{p,T_2} - \Delta C^o_{p,T_1}]/2$$

(If $T_2 - T_1 \geq 500°$, the correction can be applied in several temperature increments.

Examples of the use of group additivity may be found in Benson's monograph.[6] Recent extension[7] of these methods has allowed the prediction of thermochemical properties of polycyclic aromatic species.

Structural considerations and model compounds

If sufficient thermochemical data are lacking for the estimation of group properties, entropy and heat capacity often can be estimated adequately from structural parameters of the molecule. (Enthalpy estimates are more difficult, requiring a better knowledge of potential functions than is usually available.) The methods of statistical thermodynamics may be used to calculate C_p^o and S^o directly for those molecules where a complete vibrational assignment can be made or estimated.

Also, "reasonable" structural and vibrational frequency "corrections" to the corresponding established thermodynamic properties of "reference" compounds may be made. A suitable choice of reference compound, i.e., one similar in mass size and structure to the unknown, assures that the external rotational and translational entropies and heat capacities of the reference and unknown compounds will be the same and that many of the vibrational frequencies will be similar. The basic assumption is that S^o and C_p^o differences can be estimated closely by considering only low-frequency motions thought to be significantly changed in the unknown. Fortunately, entropies and heat capacities are not excessively sensitive to the exact choice of these vibrational frequencies, and estimates of moderate accuracy may be made with relative ease.

Table 1 shows examples of the similarity in entropy and heat capacity of structurally similar molecules. It should be understood that free radical species can be treated in the same way as normal molecules.

Kinetics

The extension of thermochemical estimation technqiues to the evaluation of kinetic data rests largely on the validity of transition state theory. The transition theory expression for a thermal rate constant is

$$k = (kT/H) \exp[- \Delta G_T^{o\neq} /RT]$$

(These units are sec^{-1} for first order and $atm^{-1} - sec^{-1}$ for second order.) Also,

$$\Delta G_T^{o\neq} = \Delta H_{300}^{\neq} - T\Delta S_{300}^{o\neq} + \langle \Delta C_p^{\neq} \rangle [(T-300) - T\ln(T/300)]$$

(In the ideal gas approximation, we can drop the standard state notation on $\Delta H^{\neq}$ and $\Delta C_p^{\neq}$.) If the empirical temperature dependence is represented by

$$k = AT^B \exp(-C/T)$$

then

$$A = \left[k/h(300)^{\langle \Delta C_p^{\neq}/R \rangle}\right] \exp\left[(\Delta S_{300}^{\neq} - \langle \Delta C_p^{\neq} \rangle)/R\right]$$

$$B = (\langle \Delta C_p^{\neq} \rangle + R)/R$$

$$C = L\Delta H_{300}^{\neq} - \langle \Delta C_p^{\neq} \rangle (300)\rfloor/R$$

where

K = Boltzmann's constant

h = Planck's constant

$\Delta S_{300}^{o\neq}$ = entropy of activation at 300K, standard state of 1 atm

$\Delta H_{300}^{\neq}$ = enthalpy of activation at 300K

$\langle \Delta C_p^{\neq} \rangle$ = average value of the heat capacity at constant pressure of activation over the temperature range 300 T K.

If we wish to express second-order rate constants in concentration units instead of pressure units, we must multiply by RT in the appropriate units. This has the effect of writing

$$k = A'T^{B'} \exp(-C/T)$$

where $A' = AR$ and $B' = B + 1 = (\langle \Delta C_p^{\neq} \rangle + 2R)/R$.

Thus, simple "Arrhenius behavior" is characterized for first-order reactions by $\Delta C^{\neq} = -R$ ($\Delta C_p^{\neq} = \Delta C_v^{\neq} = \Delta C^{\neq}$), and for second-order reactions using concentration units by $\Delta C_p^{\neq} = -2R$ (or $\Delta C_v^{\neq} = -R$). In the case of simple Arrhenius behavior,

$$k = A \exp(-B/T)$$

$$\log A = \log(ek\langle T \rangle/h) + \Delta S^{\neq}/R \; ; \; B = (\Delta H^{\neq} + R\langle T \rangle)/R$$

Table 1 Thermodynamic quantities

Species (gas)	σ , n	C_p^o, 300 K[a]	S^o, 300 K (intrinsic)[a]
$CH_3CH_2CH_3$	18, 1	17.7	70.2
CH_3OCH_3	18, 1	15.8	69.4
CH_3NHCH_3	9, 1	16.6	69.8
CH_3CH_2OH	3, 1	15.7	69.8
$CH_3CH_2NH_2$	3, 1	17.6	69.9

[a] C_p^o and S^o are in units of cal/mole-K. The absolute entropy differs from the intrinsic entropy by the quantity $R \ln(n/\sigma)$, where n is the number of optical isomers and σ the symmetry number.

Thus, the quantities $\Delta H^{\neq}$, $\Delta S^{\neq}$, and $\Delta C_p^{\neq}$ are of interest. We apply similar methods to those already discussed with respect to thermochemistry to view rate data in a rational framework. These techniques are discussed in some detail by Benson,[6] but certain points are worthy of re-emphasis here, particularly with regard to the high temperatures of combustion processes.

We begin by classifying reactions as unimolecular or bimolecular. (The only termolecular processes of interest to us will be energy-transfer-controlled bimolecular processes.)

1) Unimolecular processes

Simple fission: $AB \rightarrow A + B$

Complex fission: molecule → molecule + molecule (or radical)

Isomerization: intramolecular atom rearrangement

2) Bimolecular processes

Direct metathesis: $A + BX \rightarrow AX + B$

Addition: A + molecule → stable adduct (reverse of complex fission)

Association: A + B → A - B (reverse of simple fission)

The first thing to notice is that, of all of these reactions, only the direct metathesis ones are not subject to becoming energy-transfer-limited at high temperatures and low pressures (i.e., in the "fall-off" region!). This means that, not only does the so-called high-pressure rate constant need to be estimated or known, but the extent of fall-off as well. Methods are available for making fall-off correction,[8] but these need to be modified for use at high temperatures and the expected lower collision efficiencies for energy transfer implied.[9]

In hydrocarbon pyrolysis and oxidation, including those of aromatic compounds, we may expect that most direct metathesis reactions will involve the exchange of a hydrogen atom between larger groups. A simple, semiempirical prescription exists[6] for estimating the value of $\Delta S^{\neq}$ for these types of reactions. First, one realizes that these values are limited between "loosest" possible model (A-factor equals gas kinetic collision frequency) and the "tightest" possible model in which R...H...R' is represented to the molecule R-R'. Experience using data in the range $300 < T/K < 700$ has taught us that generally the $\Delta S^{\neq}$ value corresponds to a transition state only slightly looser than the tightest possible value. If we estimate transition state frequencies to agree with these lower-temperature experimental values, we may use these same frequencies to predict $\Delta C_p^{\neq}$ and thus the curvature of simple Arrhenius plots. Values of $\Delta H^{\neq}$ are more difficult; often we may use the values of $\Delta S^{\neq}$ and $\Delta C_p^{\neq}$ to obtain $\Delta H^{\neq}$ from the rate constant at a given temperature. It is also reasonable to expect that certain classes of reactions, such as H-atom metathesis, will have similar values of $\Delta H^{\neq}$. This is substantiated by experiment.

In the particular case of the well-studied reaction

$$CH_3 + H(CO)CH_3 \rightarrow [CH_3 \cdot H \cdot (CO)CH_3]^{\neq} \rightarrow CH_4 + \cdot(CO)CH_3$$

a least-squares Arrhenius fit to all of the data between 300 and 525 K leads to the expression[4]

$$\log (k/M^{-1}\ s^{-1}) = 7.93 - 6.0/\theta$$

This A-factor, in turn, leads to a value of the entropy of activation which indicates a transition state only a bit looser than acetone (see Table 2). The same transition state is used to predict an A-factor at 1200 K of $\sim 10^{9.5}$ m^{-1}-sec^{-1}, which is two orders of magnitude lower than the reported value.[10] Several other pyrolysis studies [1] also suggest

"high" Arrhenius parameters for CH_3 abstraction reactions. This is a serious question in need of more definitive experiments.

Since the other two classes of bimolecular processes are the reverse of unimolecular reactions, we may consider them in that direction. (The equilibrium constant is either known or estimable.) Once again, using experimental results as our guide, we note that model transition states that correspond to the values of $\Delta S^{\neq}$ are generally "tight." That is, we may visualize them as minor modifications of the reactant molecule, usually involving some increase in rotational entropy due to slight enlargement of certain bonds. The dominant entropic feature is usually the stiffening of internal rotations as a result of multiple bond formation or ring formation.[6]

Bond scission reactions present a particular problem, since it is particularly difficult to locate a transition

Table 2 Entropy of activity $CH_3 + H(CO)CH_3$

	$\Delta S^{\circ\neq}_{300}$	$\Delta S^{\circ\neq}_{1200}$
Model reaction [TS = $CH_3(CO)CH_3$]	-39.0	-43.2
Spin	1.4	1.4
Symmetry	1.4	1.4
Rotation	(1.2)[a]	1.2
2(C·H·C) 700[c]	0.6	4.8
(C-C) 1000 → (C·H·C) 700	0.2	0.6
[C-(CO)-C]400 → [C·H)-(CO)-C] 280	0.6	0.8
2(CH_3 rock) 900 → 600	0.6	1.6
(CH_3CO rock) 700 → 500	0.4	0.6
	(-32.6)[b]	-30.8

[a]Adjusted to give experimental $\Delta S^{\neq}$.

[b]From log $(A/M^{-1}\ s^{-1})_{300}$ = 7.9.

[c]Frequency in cm^{-1}.

state. Recent work,[6,11] both experimental and theoretical, indicates that these reactions can be modeled with a transition state that becomes tighter as the temperature rises. This tightening is a result of the change in position of the centrifugal barrier.

Aromatic Compounds

Aromatic compounds really should be thought of as divided into two classes for our purposes: first, unsubstituted ring compounds, such as benzene, naphthalene, etc., and second, those with nonaromatic side chains, such as toluene, ethylbenzene, etc. This simple division is prompted by the strength of the C-H bonds on the rings and the weaknesss of the benzylic C-H bonds and their higher analogs.

Pyrolysis

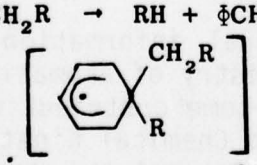
The pyrolyses of unsubstituted aromatic compounds have been studied by several workers and reviewed by Fitzer et al.[12] Unfortunately, the mechanistic interpretations are most likely incorrect, since they rely on the assumption that the reactions are homogeneous, proceeding with initiation by Aryl-H bond breaking. The high activation energy [BDE(Ø-H) = 110 kcal/mole^{-1}] and relatively low A-factor (log A/s^{-1} ~14) for this process make this unlikely at the reported temperatures (700°-1000°C). The products, largely dimers and higher polymers, suggest a radical mechanism, perhaps heterogeneously initiated.

There is also a good deal of work on substituted aromatics, tending to confirm the idea that reaction is associated with the stability of the benzyl radical and its higher homologs.[12] Here, a homogeneous chain mechanism might be imagined as

$$\Phi CH_2 - R \rightarrow \Phi \dot{C}H_2 + \dot{R}$$

$$\dot{R} + \Phi CH_2R \rightarrow RH + \Phi \dot{C}HR$$

$$\dot{R} + \Phi CH_2R \rightleftarrows$$



$$\rightarrow \Phi{-}R + \dot{C}H_2R$$

$$\Phi \dot{C}HR \rightarrow \Phi CH{=}C\langle + R' \text{ (depends on R)}$$

However, it is difficult to write a mechanism that would involve any ring rupture.

Oxidation

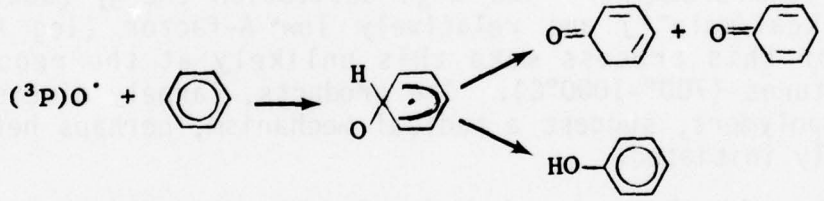
Very little mechanistic information on unsubstituted aromatic oxidation exists. Some data are reviewed by Santoro

and Glassman.[13] One might expect that, just as in the case of hydrocarbons,[3] O_2 might sensitize the pyrolysis of unsubstituted aromatics; thus,

$$\Phi H + O_2 \rightarrow \dot{H}O_2 + \dot{\Phi}$$

would serve as an initiation step that yields Φ radicals for further reaction, although the reaction is ~63 kcal/mole endothermic. Of course, this is most certainly the case for substituted aromatics, where O_2 will abstract the "benzylic" hydrogen atom as an initiation step.

Some data exist[14] at low temperatures which suggest that cresols formed from OH addition to toluene can be further degraded in the presence of NO and O_2. However, these addition reactions might be exepcted to compete poorly with abstraction at flame temperature. Several studies[15] of the reaction of O atoms with aromatics reveal a modestly rapid process at low (< 500 K) temperatures. The mechanism is not discerned. If addition is followed by rapid isomerization, such pathways would be possible under combustion conditions as well:



Since the O atom is a triplet, however, we would need to be able to know something about the fate of the initial triplet adduct. Does slow spin interconversion render these pathways inconsequential? This same question of the fate of triplet species must be considered in thinking about possible addition reactions of ground state O_2 with unsaturated species.

Considerable additional information is needed to understand the combustion chemistry of aromatics. I should like to think that we are making some contributions in this direction in the Thermochemistry and Chemical Kinetics Laboratory at SRI International. Thus, in the past two years, we have developed group additivity methods to include the polycyclic aromatic compounds[7] and have estimated the thermochemical properties of hydrogenated polycyclic aromatics by structural and additivity considerations.[16]

We also have estimated the heats of formation of the higher homologs of benzyl radical[17] and currently are engaged

in an extensive program of experimental investigation of these radical stabilities. We have, in fact, measured the heats of formation of benzyl and the napthyl analog[18] and find the latter to be ~3 kcal/mole more stable than the former, as predicted. This has a profound effect: 3 kcal/ mole yields a factor of ~3 in rate constants when translated as an Arrhenius activation energy at 1500 K.

Recommendations and Conclusions

To understand the general mechanisms of aromatic pyrolysis and oxidation, a study of some prototype systems is required. A detailed understanding of the prototype experiments will necessitate the study of individual rate constants in separate experiments. These, in turn, should be evaluated critically, based on some of the techniques that we have discussed. Thermochemical as well as rate data will be necessary. It would be just an exercise to write all of the possible elementary rate processes that might be studied. Some specific elementary rate processes for which data is necessary are

$$\Phi CH_2CH_2\Phi \rightleftarrows 2\Phi CH_2$$

(using the symbol Φ as a general representation of aromatic systems). This process is an important radical initiation-termination step. We have no good measurement of its rate or its temperature and pressure dependence for any species:

$$\Phi CH_2R + O_2 \rightarrow \Phi\dot{C}HR + HO_2$$

$$+ O \rightarrow \text{products}$$

These may be important reactions in initiation of oxidation:

$$\Phi CH_2R + R' \rightarrow R'H + \Phi\dot{C}HR$$

This is surely an important process whose rate parameters need careful study with a specific eye toward "Arrhenius curvature" and the effects of stabilization energy on activation energy.

Reactions of the ubiquitous OH radical with aromatics, both substituted and unsubstituted, need study. What determines relative abstraction and addition rates, and even relative addition at distinguishable ring sites? What are the products and their subsequent reactions? The same questions can be asked concerning other radicals, particularly $\Phi\cdot$ -type systems.

We have not discussed at all in this paper questions relating to NO_x formation or SO_x formation. There are certainly research needs in these areas, including such natural extensions of topics that we have covered as pyrolysis and oxidation of fuel-bound nitrogen and sulfur, as well as reactions of high-temperature fragments, many of which are important for aliphatic combustion also.

Continued efforts are necessary in the direction of understanding unimolecular rate theory as applicable to modest-size molecules at combustion temperatures and pressures. A simplified method is sought which will take into account low collision efficiencies and which will be of sufficient accuracy nearer to the low-pressure limit than current methods.

Thus, we conclude in summary with the recommendation that considerable research effort be put forth to obtain a general understanding of pyrolysis and oxidation of aromatic systems by the study of prototypes, such as a controlled flame of a specific fuel coordinated with studies of specific elementary rate constants and associated phenomena, such that it may become possible to generalize the chemistry.

Acknowledgments

The author's time has been supported generously by the Air Force Office of Scientific Research, the Energy Research and Development Agency, the Environmental Protection Agency, NASA, and SRI International. The specific help of D. F. McMillen and D. G. Hendry in the preparation of this paper is appreciated. The author's debt to his long-time colleague, S. W. Benson, is always a pleasure to acknowledge.

References

[1]a) Bradley, J. N., "General Mechanism for High Temperature Pyrolysis of Alkanes. Pyrolysis of Isobutane," Proceedings of the Royal Society (London), Vol. A337, No. 1609, March 1974, p. 199; b) Leathord, D. A. and Purnell, J. H., Annual Review of Physical Chemistry, Vol. 21, 1970, p. 197.

[2] Bradley, J. N., and West, K. O., "Single-Pulse Shock Tube Studies of Hydrocarbon Pyrolysis," Journal of the Chemical Society, Faraday I, Vol. 72, Pt. 3, March 1976, p. 558.

[3]a) Walker, R. W., "Reaction Kinetics," Specialist Periodical Report, edited by P. G. Ashmore, Chemical Society, London, 1975, Vol. 1, p. 161; b) Walker, R. W., "Gas Kinetics and Energy Transfer," Specialist Periodical Report, edited

by P. G. Ashmore and R. J. Donovan, Chemical Society, London, 1977, Vol. 2, p. 296.

[4] Kerr, J. A. and Parsonage, M. J., Evaluated Kinetic Data on Gas Phase Hydrogen Transfer Reactions of Methyl Radicals, Butterworths, London, 1976.

[5] Benson, S. W., Cruickshank, F. R., Golden, D. M., Haugen, G. R., O'Neal, H. E., Rodgers, A. S., Shaw, R., and Walsh, R., "Additivity Rules for the Estimation of Thermochemical Properties," Chemical Reviews, Vol. 69, No. 3, June 1969, p. 279.

[6] Benson, S. W., Thermochemical Kinetics, 2nd ed., Wiley, New York, 1976.

[7] Stein, S. E., Golden, D. M., and Benson, S. W., "Predictive Scheme for Thermochemical Properties of Polycyclic Aromatic Hydrocarbons," Journal of Physical Chemistry, Vol. 81, No. 10, Oct. 1977, p. 314.

[8] Golden, D. M., Solly, R. K., and Benson, S. W., "A Comparison of RRK and RRKM Theories for Thermal Unimolecular Processes," Journal of Physical Chemistry, Vol. 75, No. 10, May 1971, p. 1333.

[9] Troe, J., "Theory of Thermal Unimolecular Reactions of Low Pressures. 1. Solutions of the Master Equation," Journal of Chemical Physics, Vol. 66, No. 11, June 1977, p. 4745.

[10] Colket, M. B., III, Naegeli, D. W., and Glassman, I., "High Pressure Pyrolysis of Acetaldehyde," International Journal of Chemical Kinetics, Vol. 7, No. 2, March 1975, p. 223.

[11] Smith, G. P. and Golden, D. M., "Application of RRKM Theory to the Reactions of OH + NO_2 + N_2→ $HONO_2$ + N_2 (1) and ClO + NO_2 → $ClONO_2$+ N_2 (2); A Modified Gorin Model Transition State, International Journal of Chemical Kinetics (to be published).

[12] Fitzer, E., Mueller, K., and Schaefer, W., The Chemistry and Physics of Carbon Formation, Marcel Decker, New York, 1969, p. 237.

[13] Santoro, R. J. and Glassman, I., "A Review of Oxidation of Aromatic Compounds," Combustion Science and Technology (to be published).

[14] Hendry, D. G., private comunication, 1977.

[15] Kerr, J. A. and Ratajczak, E., Third Supplementary Tables of Biomolecular Gas Reactions, University of Birmingham, England, 1977.

[16] Shaw, R., Golden, D. M., and Benson, S. W., "Thermochemistry of Some Six-Membered Cyclic and Polycyclic Compounds Related to Coal," Journal of Physical Chemistry, Vol. 81, July 1977, p. 1716.

[17] Stein, S. E. and Golden, D. M., "Resonance Stabilization Energies in Polycyclic Aromatic Hydrocarbon Radicals," Journal of Organic Chemistry, Vol. 42, No. 5, March 1977, p. 839.

[18] McMillen, D. F., Trevor, P. K., and Golden, D. M., "Very Low-Pressure Pyrolysis of 1-Ethylnaphthalene and Ethylbenzene. Determination of Resonance Stabilization Energy and Combination Rate for the 1-Naphthylmethyl," Journal of Physical Chemistry (to be published).

DISCUSSION

DR. A. E. AXWORTHY (Rocketdyne): As you know, there is a rather large gap between basic chemical kinetic theory and its application to combustion theory. I wanted to bring up three of the areas you mentioned for additional comment. One is the temperature dependence of unimolecular reactions. When you look at computer codes that people are using to model high-temperature combustion, a pressure dependence is usually assigned only to the recombination reactions that form diatomic molecules. For example, the rate constant for the recombination of H atom and methyl radical at high temperature generally is taken to be pressure independent. I would be inclined to put that at the low pressure limit. I think it is something that should be looked at.

DR. GOLDEN (SRI International); Yes, methane sounds small enough to be in the low-pressure limit at high temperatures, so it probably is. I was trying to make the point strongly that unimolecular reactions can be pressure dependent by labeling possibly pressure-dependent reactions with the letter P.

DR. AXWORTHY: I just wanted to emphasize that. One other point you mentioned, of course, was temperature extrapolation. This is one of the major problems. If you are modeling a stirred reactor where everything is at one temperature, the computer codes work very well. However, when you try to model ignition or a premixed flame, where you pass through a low-temperature region, some of the reaction rates essentially blow up and dominate because of the activation energies involved and the uncertainty of this large temperature extrapolation. There is essentially a need for kinetic data over a wider temperature range but, of course, this is difficult to obtain.

The last point I want to bring up is one you mentioned near the end. In heavy fuels, and I am not sure about jet fuels, most of the aromatics have highly substituted side chains. At least with the heavier fuels, I am inclined to consider a simple model where you just assume most of the reaction occurs in the side chains until you get to very high temperatures. I think this is probably true under pyrolysis conditions.

DR. GOLDEN: That is what I wrote. The problem with that is that, at least when you start writing, you do not write any reactions that lead easily, for instance, to soot formation, yet you know that soot is formed.

Let me also comment, because I think it is important, that if we were in our own small fraternity of kineticists, I would let you get away with the comment concerning the large gap between basic kinetics and applied combustion. We know that at the level I was talking about, there is a long distance to go to a practical combustion system. Given this audience, however, I cannot let you get away with that statement. I think what needs to be said is that any time there is a real practical problem and you talk about basic research and some results in a short time frame, you are always going to come up with the same conclusion. You cannot get any real help in this short time frame, but if we keep going through that exercise all the time, we will stay in the same place. There has to be enough room in the general support structure of science in this country to have enough effort in the basics so that eventually we can get to the point where we can see how these problems can be answered a little bit easier.

DR. AXWORTHY: I did not mean to imply that basic research in this area is not important.

DR. I. GLASSMAN (Princeton University): As you know, we did a survey of the aromatic literature which you critiqued for us. I think one of the interesting things is that the ratio of CO_2 to CO formed in the oxidation of the aromatics is generally higher, particularly on the fuel-rich side. The CO_2 is higher. We suggested the high CO_2 to CO ratio occurs because when you break up the aromatics, no matter how you break them up, carboxyl radicals form. Do you or do you not agree with that?

DR. GOLDEN: The fact is that it seems to me that that is not unreasonable. I do not know enough to agree or disagree. That is, if you make an organic acid, it seems to me that one of the bonds that could break is the bond that gives you the species



which could eventually, by a disproportionation, abstraction, or something else, easily give you CO_2. So, yes, that seems like an explanation. I am not sure why you should not get as many organic acids in the alkane case, but that does not mean you should not. It is rather complicated.

DR. J. P. LONGWELL (M.I.T.): I think it is a good thing to get started on the aromatic problem. When you start thinking about the problem in any detail, it becomes a pretty horrendous thing. For example, the fuels you are talking about might have several hundred different aromatics as a mixture. One way to get at it might be to decide which chemistry problem is really most important technologically. I do not really think it is the final stages or even the intermediate stages of combustion, because these things really burn fine if the oxygen is there.

What seems to be a real problem is the polymerization of radicals which might be related to just the first couple of steps in the sequence, and therefore might be amenable to some kind of basic and systematic approach. The problem I

am referring to is soot formation. If you start with a large aromatic, there is some evidence that the route to soot is the polymerization of those aromatics, rather than breaking down to acetylene and back up again.

Then there is a series of related problems that are really quite important. These are the deposits that you get on the walls of combustion chambers, I.C. engines, or anything else. They are strongly related to polymerization reactions, probably the first radical or two that are made. So maybe that would be a good place to start.

In some work that I have seen on coal lilquefaction and pyrolysis of heavy hydrocarbons, the tendency of these polynuclear aromatics to dealkylate is striking. This is actually a big problem. Almost anything you do to coal liquids or these heavy fuels ends up making a lot of methane and aromatics. Apparently, if you have an alkyl group on an aromatic, the aromatic-alkyl group bound becomes progressively weaker as you go to bigger and bigger molecules, perhaps because there is more resonance stabilization and more stable aromatic free radicals.

DR. GOLDEN: The mechanism for that is probably that a hydrogen atom adds to the ring at the same place where the alkyl group is. Then the alkyl group is what comes off.

DR. LONGWELL: The alkyl group leaves, yes. However, on these larger ones, apparently the free radicals that can be formed are also stable enough to have a long lifetime but will polymerize with each other. So that was a class of reactions that you really did not touch on.

DR. GOLDEN. You have to be careful. As the rings get bigger, they get more stable, but not as the chain gets bigger.

DR. LONGWELL: I am talking about polynuclear aromatics.

DR. GOLDEN: Yes, with a radical on the side chain.

DR. LONGWELL: Right, and the bigger they are the more likely the radical is to just pop off.

DR. GOLDEN: Yes, that is what I was talking about in terms of the things we had both predicted and were trying to verify, but actually there is very little hard information on that. This naphthyl one that we have just done, or the naphthyl analog of benzyl, is the only one besides benzyl that I am aware of for which there is a number.

DR. LONGWELL: What I am really suggesting is that this class of reactions, which is simple enough to study in detail, plus the next few reactions having to do with increase in molecular weight, might give us a lever on some of the practical problems such as deposits, soot, and the like.

DR. GOLDEN: I would just add to that that I think it is important that one marries these approaches, that is, looks in a fundamental way at the practical problems. I would go beyond that, though, to say that we are really not at the stage in chemical kinetics, chemistry, and whatever to make a lot of absolute statements that we would like to make. It is part of the real practical problem, at least over the long term. We have to pick key model reactions and systems that answer some of these generalized questions I have raised.

DR. GLASSMAN: I think this is the real key in answer to the papers in earlier sessions. Longwell gave a beautiful example of where chemistry really plays a role and where it is really important to get some fundamental data just the way it has been described here. I cannot emphasize this too much, and I would really like to support it. I think it is the answer to Bracco and others whose papers did not make clear that there are certain elements, such as in soot formation and emissions, in which the chemistry is important if we are ever going to find out how to modify the problem in a technological way, as Longwell described.

DR. CALCOTE (Aero Chem Research): In your use of transition state theory to extrapolate low-temperature data to high-temperature data, one would expect, espeically in the aromatics, that electronic contributions would play a part at the high temperatures. Do you include them?

DR. GOLDEN: No. I had not thought of it, but it seems to me that the lowest lying electronic states are 60 or 70 kcal above the ground state. So you have to go to much higher temperatures.

DR. F. P. TULLY (Georgia Institute of Technology): One point that I would like to make is that some studies have been performed on the reactions of hydroxyl radicals with benzene, toluene, and higher aromatic hydrocarbons. In these experiments, the OH-aromatic hydrocarbon reaction rate constants were found not to vary smoothly with increasing temperature. The typical reaction rate constants for these processes increases with temperatuare at low temperatuares, then sharply decreases throughout a slightly higher temperature interval, and finally increases again up to the limiting measurement temperature of 500 K. At low temperatures OH addition to the aromatic nucleus is the dominant reaction pathway; at somewhat higher temperatures, however, the addition complex is thought to be unstable with respect to decomposition back to reactants. The temperature interval in which the rate constant decreases with increasing temperature, then, corresponds to the region in which the addition reaction channel is effectively becoming closed. At higher temperatures, hydrogen abstraction by OH is thought to be the dominant reaction channel. The observation of increasing rate constant with increasing temperature above 400 K is consistent with this interprtation. Similar reaction selectivities with temperature can be inferred for oxygen and hydrogen atom reactions with aromatic hydrocarbons from existing data. The point to be made in this discussion, then, is that both the magnitude of the total reaction rate constant and the applicability of a particular reaction mechanism may be highly temperature specific. Thus studies of the variations in radical-aromatic hydrocarbon reaction rate constants and mechanisms with temperature are badly needed.

DR. GOLDEN: I could not agree more. In most of these studies that exist on O atoms and OH radicals adding to aromatic compounds, just because of experimental limitations what is known usually is a pseudo first-order disappearance of the species that is easy to measure, like OH or O atoms, and no product studies.

DR. C. T. BOWMAN (Stanford University): Notwithstanding earlier comments that alternative fuels burn well,

combustion engineers will still want to try to calculate oxidation rates and energy release rates for aromatic fuels. Hence, we need some data to form the basis for these calculations. I am not talking about measuring elementary rate coefficients. We need data that can be interpreted in terms of global models.

COMBUSTION CHEMISTRY OF CHAIN HYDROCARBONS

Frederick L. Dryer* and Irvin Glassman+
Princeton University, Princeton , N.J.

Abstract

Recent results have permitted the general characterization of high-temperature alkane oxidation. Methane is found to exhibit a very long induction period and is not typical of the higher paraffins due to the relative difficulty of oxidizing methyl radicals. The induction period for the higher hydrocarbons is short relative to the fuel lifetime and can be neglected under most combustion modeling situations. The oxidation of these higher hydrocarbons proceeds through three sequential but overlapping steps: alkane to alkene conversion, alkene oxidation to carbon monoxide and water, and lastly conversion of carbon monoxide to carbon dioxide. The olefins which form are primarily ethene, propene, and butene and their qualitative importance can be predicted. It has been found possible to prescribe global rate processes for the oxidation of methane, ethane, and carbon monoxide. Ethane oxidation, however, requires additional overall rate expressions for the conversion to ethene, and the choice of the proper expression depends on the competitive rates of ethyl radical pyrolysis and ethyl radical attack of oxygen. Those overall rate expressions that ignore the olefin formation step are shown to be invalid.

Introduction

Numerical modeling may play an ever-important role in our understanding of complex combustion systems. In this regard, then, accurate representation of combustion kinetics becomes a very necessary and important element in advancing the analytical tools required to guide development of hardware compatible with alternative fuels. Recent work has led to improved, conceptual understanding of high-temperature hydrocarbon pyrolysis and oxidation chemistry. However, detailed modeling of hydrocarbon reaction systems other than methane

*Research Engineer and Lecturer, Dept. of Aerospace and Mechanical Sciences.
+Professor, Dept. of Aerospace and Mechanical Sciences.

has not been successful because of more complex kinetics (e.g., see Ref 1). Both the lack of understanding of the elementary reactions required to model these systems over extended ranges of temperature and pressure and the lack of accurate elementary rate data contribute to the problem. Furthermore, although it has been demonstrated frequently that relatively large systems of elementary reactions can be handled numerically, even in simplified fluid-mechanically coupled simulations, the numerical complexities and code size required to model real energy conversion systems with large detailed mechanisms remains prohibitive. Thus much of the modeling to date has employed some approximation to the chemical kinetics in order to predict the interactions of chemistry and fluid mechanics which result in energy release distributions and the date of production of pollutants. This paper summarizes the available information from which realistic kinetic approximations for hydrocarbon chemistry can be formulated, discusses past and current efforts for developing models, and suggests future experimental and analytical needs for improving approaches that approximate the true hydrocarbon combustion chemistry. Quantitative detailed chemistry of $H_2/CO/O_2$ mechanism also will be discussed in relation to hydrocarbon combustion. Another paper[2] in this workshop considers aromatics. Because of a lack of high-temperature data on other hydrocarbons and for expediency, this discussion will be limited primarily to the normal alkanes, although some limited analysis of branched chain structures will be presented.

General Modeling Considerations

Let us first consider the general oxidation characteristics of the normal alkanes. We shall exclude discussion of methane oxidation because it has received considerable attention in terms of detailed modeling (e.g., Refs. 3 & 4) and because its oxidation is dominated by (the difficulty of) methyl radical oxidation. This trait is not characteristic of any of the higher alkane oxidation systems and is the reason methane should not be used in experimental programs to represent a general hydrocarbon oxidation process. In these discussions, it should be kept in mind that any empirical model must be quantitatively valid over a variety of fuel/air ratios and relatively wide ranges of pressure, temperature, and residence times if it is to be useful in practical combustion modeling. Some recent experimental work at Princeton[5] adequately demonstrates many of the qualitative features of the hydrocarbon oxidation process and will be used later in the paper to assess empirical modeling formulations quantitatively.

Much of the conceptual approach given throughout this paper stems from our work with the Princeton turbulent flow reactor extensively described in several earlier publications.[5-9] By restricting experiments to highly diluted mixtures of reactants and extending the reactions over large distances, concentration gradients in this reactor are such that diffusion is negligible relative to the convective component; thus, the measured species profiles are a direct result of chemical reaction alone. This fact has been corroborated recently in the modeling of methane/oxygen and moist carbon monoxide/oxygen experiments.

It is important to re-emphasize that, in this flow reactor, uniform turbulence results not only in rapid mixing of the initial reactants but also in radially uniform, one-dimensional flow characteristics. Thus, real "time" is related to distance through the simple plug flow relations. However, the relation of a specific axial coordinate to real time is now well defined, since the initial time coordinate occurs at some unknown location within the mixing region. One would suspect that the initial mixing history therefore could alter reaction phenomena occuring downstream. However, the existence of very fast elementary kinetics, which initiate chemical reaction before mixing is complete, permits rapid

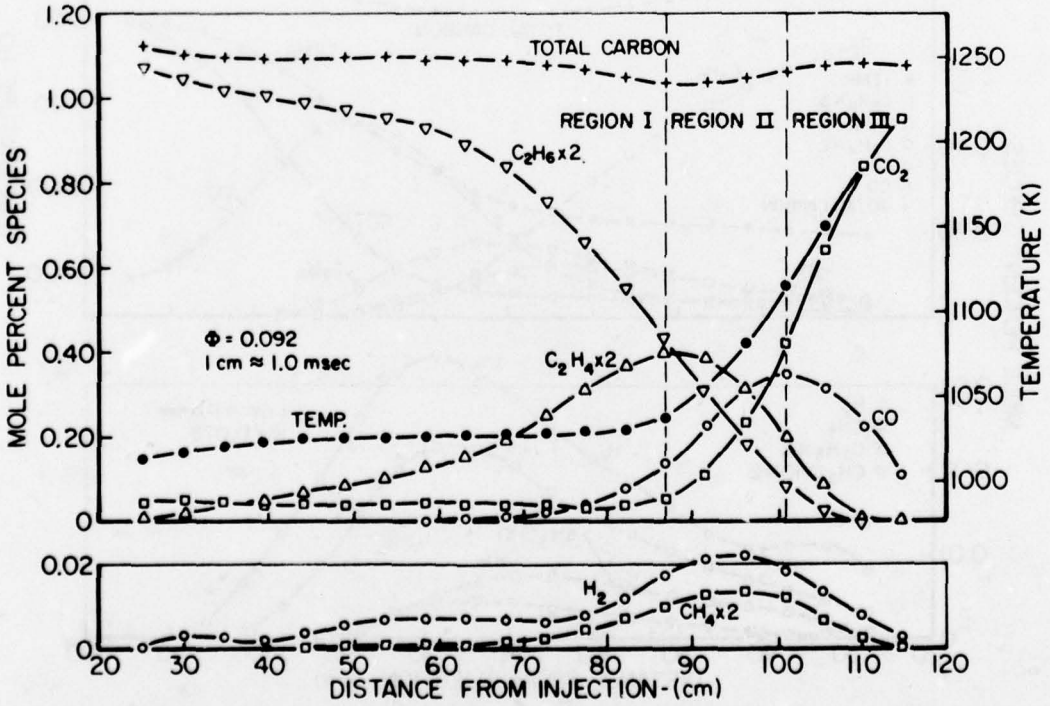


Fig. 1 Chemical composition of spread ethane-air reaction.

adjustment of the chemistry to local conditions as the flow approaches radial uniformity. Furthermore, the large dilution of the reactants and rapidity of the kinetics reduce the coupling of turbulence and chemistry to the point that local kinetics are predicted closely by local mean flow properties.[10] This conclusion also is verified experimentally by excellent agreement of the derived elementary chemical kinetic data with that obtained from shock tubes and static reactor systems at other temperatures[8,9] as well as by the initial analytical modeling efforts. These calculations also substantiate that the reactor surfaces do not affect the gas-phase kinetics of the large reactor core significantly where measurements are made. Comparison of flow reactor data from reactor tubes of significantly different surface-to-volume ratio also corroborates this conclusion. Finally, and most importantly, the turbulent flow reactor approach permits kinetics measurements over a range of temperatures, 800 - 1400 K (reaction times 10-200 msec), which generally are inaccessible to low-temperature methods (fast-flow electron spin resonance, kinetic spectroscopy techniques, static reactors, etc.) and high-temperature techniques (shock tubes, low-pressure postflame experiments, stirred reactors) but which are important to combustion processes.

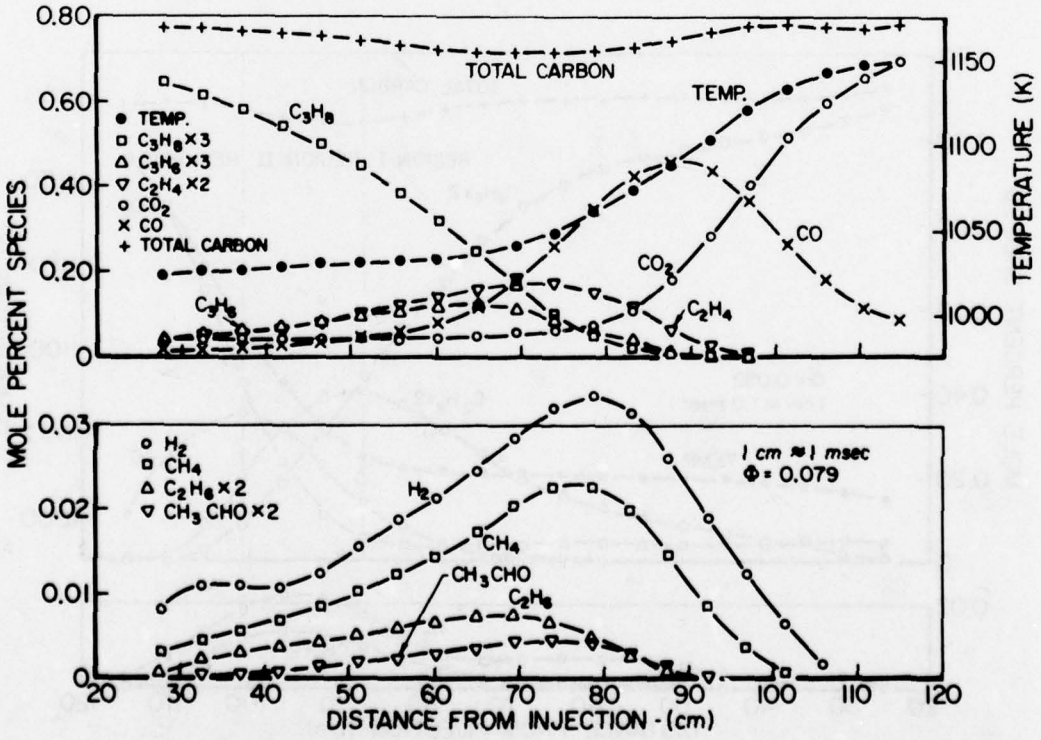


Fig. 2 Chemical composition of spread propane-air reaction.

Figures 1-4 present data from the flow reactor for very fuel-lean oxidation of several alkane hydrocarbons above methane. The observed reaction profiles correspond to the "postinduction" phase of the oxidation. The induction period, i.e., the reaction period dominated by initial thermal or chemical attack on a CH bond of the fuel and other secondary chemical kinetic initiation processes, typically occurs in the mixing region of the flow reactor and is extremely short. (There are some exceptions to this general statement which will be discussed later.) The induction phase of the chemical kinetics process can be modified significantly or even eliminated in practical systems by backmixing or diffusion of partially oxidized species and radicals produced in the postinduction zone, and thus initiation chemistry is generally not of great importance in most combustion systems.

Figures 1-4 clearly show that even in very lean oxidation there appears to be an initial isoenergetic region in which the decomposition of the alkane takes place. The conversion of the alkane appears to be primarily to alkenes and is clearly an endothermic process. However, the hydrogen formed during this pseudopyrolysis step simultaneously reacts to form water. This reaction essentially compensates the endothermicity of the initial "pyrolysis" step.

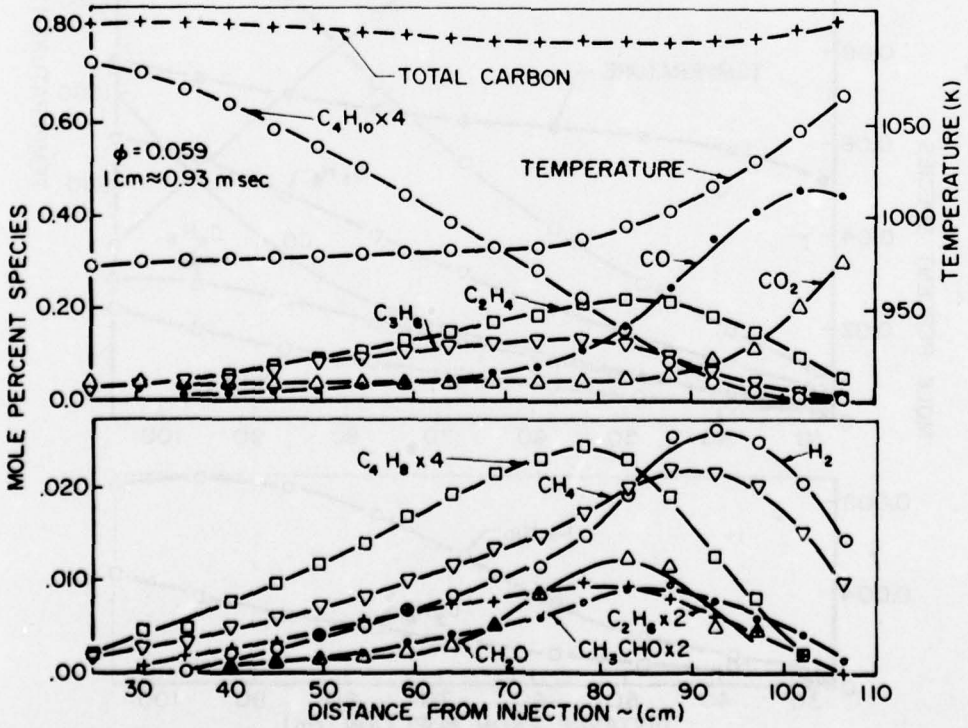


Fig. 3 Chemical composition of spread n-butane-air reaction.

Subsequently, and with some energy release, the unsaturated hydrocarbons are converted to carbon monoxide and hydrogen while the hydrogen present and being formed continues to oxidize. Finally, the large amount of carbon monoxide formed is oxidized to carbon dioxide, and most of the heat of reaction of the overall step

$$C_nH_{2n+2} + [(3n+1)/2]O_2 \rightarrow n\ CO_2 + (n+1)\ H_2O$$

is released during this final reaction segment.

Earlier experimental investigations substantiate these qualitative observations for temperatures above 1000K. As early as 1963, Orr[11] presented shock-tube results at 1 atm for n-heptane and iso-octane and suggested similar behavior

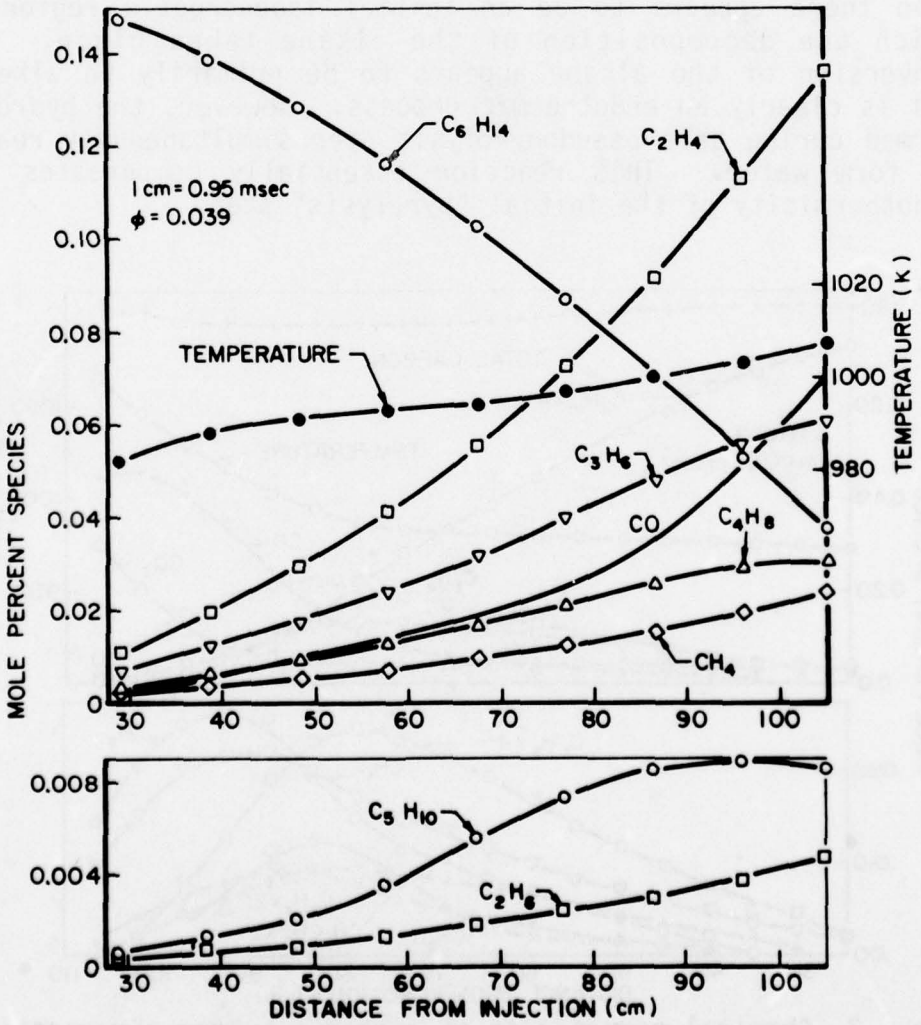


Fig. 4 Chemical composition of spread n-hexane-air reaction.

for these higher chain hydrocarbons. Levinson[12] later repeated, confirmed, and extended these earlier studies on n-heptane. Initial decompostion of alkanes through olefin formation in shock-tube studies of "ignition delay" also has been noted by several other authors.[13-15] It should be noted that the induction period as defined earlier and ignition delay measurements correspond closely only for methane. For the higher hydrocarbons, shock-tube ignition delay (especially when determined by pressure rise) corresponds more closely to the characteristic time required for carbon monoxide oxidation to begin. Major reaction of the initial fuel (and even the olefins formed) logically should occur more to the oxidation of carbon monoxide, since the reaction rate constants of the reactions are one to two orders of magnitude faster than that for carbon monoxide.[16] The shock-tube observations of Hawthorne and Nixon[17] qualitatively confirm these arguments by the fact that ignition delays for propane and its decompostion products (mixtures of propene and hydrogen) were found to be very similar.

It is well known that if a tertiary carbon exists in a hydrocarbon the hydrogen attached to it will be abstracted first, and, if no tertiary-carbon atom is available, a hydrogen atom will be abstracted from the secondary carbon in the chain. There is no doubt that the initial attack on alkanes is a hydrogen abstraction by OH, H, and O radicals, and, in fact, the elementary rate data[16] show that the position of attack is a question of relative rates. Multiple tertiary carbon atoms normally are not encountered in a given hydrocarbon compound, whereas one must realize that there are at least six CH bonds on terminal carbon atoms in every alkane structure. Thus, for example, if the difference in bond energy and the number of various bonds available is taken into account at 1000 K, radicals formed from attack on a secondary compared to a primary carbon for propane and n-butane will be approximately 1 and 2.

In their review, Fristrom and Westenberg[18] state that the hydrocarbon radicals thus formed decompose into a methyl radical and an olefin with one less carbon number:

$$C_nH_{2n+1} \rightarrow CH_3 + C_{n-1}H_{2n-2}$$

However, this general statement is not supported by flow reactor data for oxidation of the hexane isomers (as shown in Figs. 6 and 7). There should be a great preponderance of pentenes compared to other olefins early in the reaction if Fristrom and Westenberg's general statement were correct. However, experiments on deuterated compounds[19-22] show that,

when a radical decomposes, a bond once removed from the site is broken, since in this case both a proton and hydrogen atom shift are not required. In addition, when there is a choice between a CH bond and a CC bond in these radicals, the CC bond usually is broken due to the lower bond strength. Thus, one finds

$$CH_3 - \dot{C}H - CH_3 \rightarrow C_3H_6 + H$$

instead of

$$i - \dot{C}_3H_7 \rightarrow C_2G_4 + CH_3$$

but

$$\dot{C}H_2 - CH_2 - CH_3 \rightarrow C_2H_4 + CH_3$$

instead of

$$n\text{-}\ C_3H_7 \rightarrow C_3H_6 + H$$

In the case of butyl radicals, one finds

$$\dot{C}H_2CH_2CH_2CH_3 \rightarrow C_2H_4 + C_2H_5$$

$$CH_3\dot{C}HCH_2CH_3 \rightarrow C_3H_6 + CH_3$$

There has been some unresolved controversy over whether any decomposition through the unfavored routes can occur. Some investigators have claimed that no direct decomposition via these reactions can take place, but that an internal rearrangement must occur before decomposition can occur by an unfavored route. Others claim that reactions such as

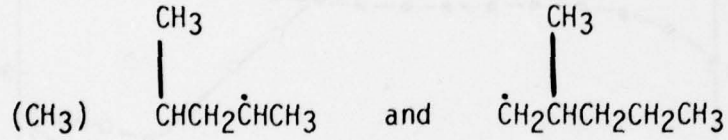
$$i - C_3H_7 + C_3H_8 \rightarrow C_3H_8 + n - C_3H_7$$

are fast and lead to the alternate routes. However, McNesby et al.'s experiments[19-22] show that although these alternate modes might occur, they are negligible below 800 K but could make some contribution above 900 K.

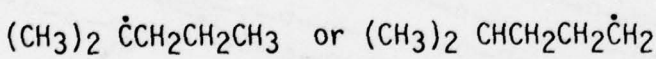
The results presented in Figs. 5 and 6 tend to confirm that one-bond-removed rule and indicate that there is little or no decomposition by unfavored paths. In the case of propane, the rate constants for hydrogen abstraction indicate that iso- and normal-propyl radicals should be formed in nearly equal amounts, and, therefore, one should find equal amounts of ethene and propene. In fact, one finds that the ethene formed is 1.5 times the propene. This result could lead one to argue for isomerization reactions, but it is more likely that the extrapolation of the rate constants of radical attack on the primary fuel leads to the discrepancy. For

butane, one predicts twice as much sec-butyl as n-butyl, but each n-butyl decomposes to an ethene and an ethyl radical, and the ethyl usually will decompose to another ethene. Thus, again one expects nearly equal amounts of ethene and propene, and again one finds 50% more ethene than propene.

The real confirmation of the rule comes from the isohexane experiments presented in Figs. 5 and 6. In the 2-methylpentane experiments, the favored radicals are

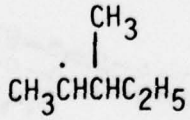


The former radical decomposes to C_3H_6 + i - C_3H_7 and therefore ultimately to two propenes, whereas the latter forms C_3H_6 + n - C_3H_7 (or 1-pentene + CH_3). Thus, C_3H_6 should greatly dominate C_2H_4, which is explicitly what is observed experimentally. Furthermore, only isobutene will form from

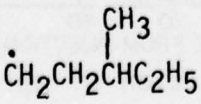


Since only one butene is observed, this result also seems to fit well with the one-bond-removed concept.

3 methylpentane, on the other hand, will react mainly to the radicals

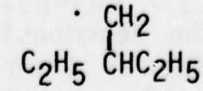


(1)



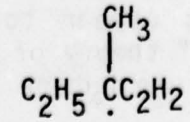
(2)

The first decomposes to 2 - C_4H_4 + C_2H_8 + C_2H_5 (ultimately 2 - C_4H_8 + C_2H_4), and the second forms C_2H_4 + sec - C_4H_9 (ultimately C_2H_4 + C_3H_6). Of the other radicals,



(3)

decompose to 1 - C_4H_8 + C_2H_5, whereas



(4)

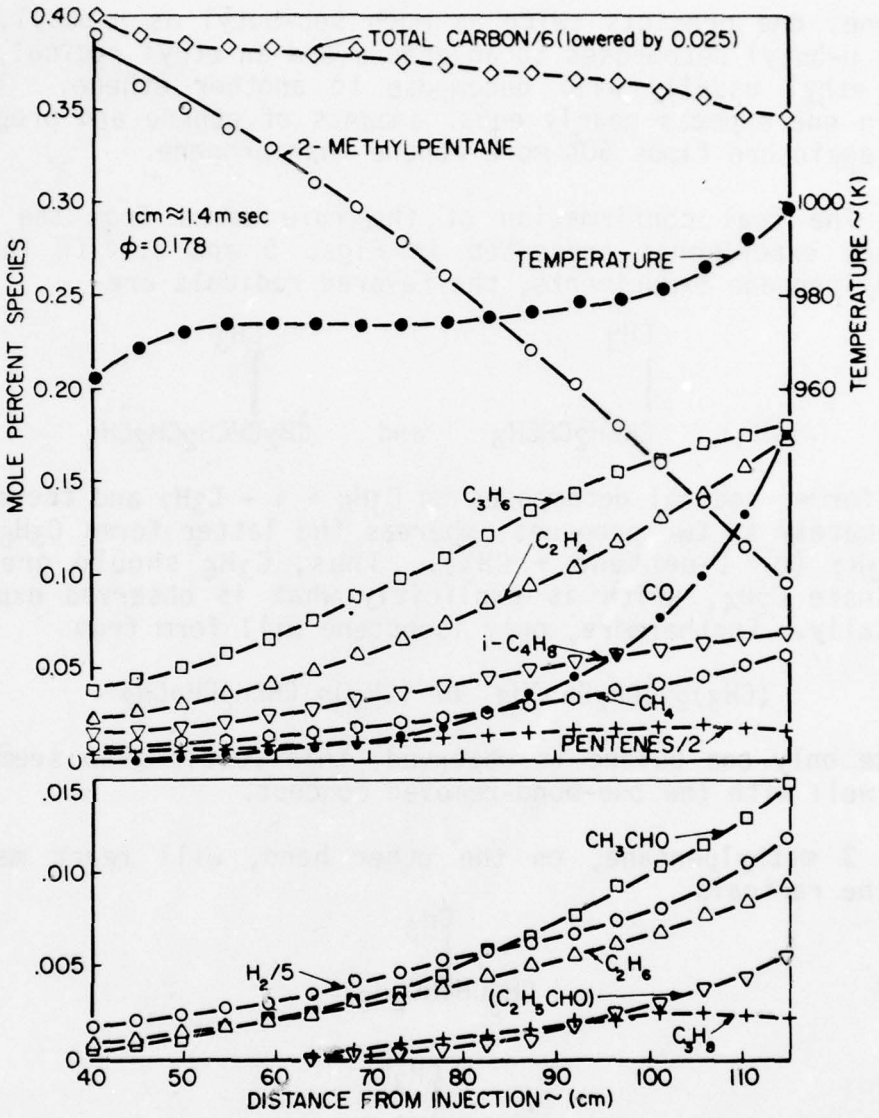


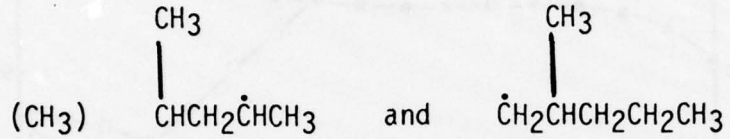
Fig. 5 Chemical composition of spread 2-methylpentane-air-reaction.

forms a pentene (2-methyl-1-butene) and a methyl radical. These predictions are also consistent with the observed results, in which $[C_2H_4] > [C_3H_6]$. The ethene is larger than butene because of the decomposition of radical (2) and because butene reacts faster than ethene. Furthermore, three butenes are observed: 1-butene, cis-2-butene, and trans-2-butene.

All of these results appear to confirm the "one-bond-away-from-the-radical-site" theory of decomposition. Furthermore, the finding of only one butene product in the 2-methyl-

butane, one predicts twice as much sec-butyl as n-butyl, but each n-butyl decomposes to an ethene and an ethyl radical, and the ethyl usually will decompose to another ethene. Thus, again one expects nearly equal amounts of ethene and propene, and again one finds 50% more ethene than propene.

The real confirmation of the rule comes from the isohexane experiments presented in Figs. 5 and 6. In the 2-methylpentane experiments, the favored radicals are

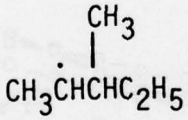


The former radical decomposes to C_3H_6 + i - C_3H_7 and therefore ultimately to two propenes, whereas the latter forms C_3H_6 + n - C_3H_7 (or 1-pentene + CH_3). Thus, C_3H_6 should greatly dominate C_2H_4, which is explicitly what is observed experimentally. Furthermore, only isobutene will form from

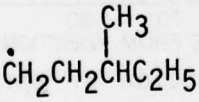
$$(CH_3)_2\,\dot{C}CH_2CH_2CH_3 \quad \text{or} \quad (CH_3)_2\,CHCH_2CH_2\dot{C}H_2$$

Since only one butene is observed, this result also seems to fit well with the one-bond-removed concept.

3 methylpentane, on the other hand, will react mainly to the radicals

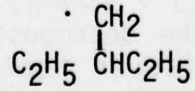


(1)



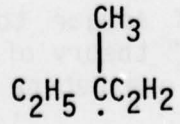
(2)

The first decomposes to 2 - C_4H_4 + C_2H_8 + C_2H_5 (ultimately 2 - C_4H_8 + C_2H_4), and the second forms C_2H_4 + sec - C_4H_9 (ultimately C_2H_4 + C_3H_6). Of the other radicals,



(3)

decompose to 1 - C_4H_8 + C_2H_5, whereas



(4)

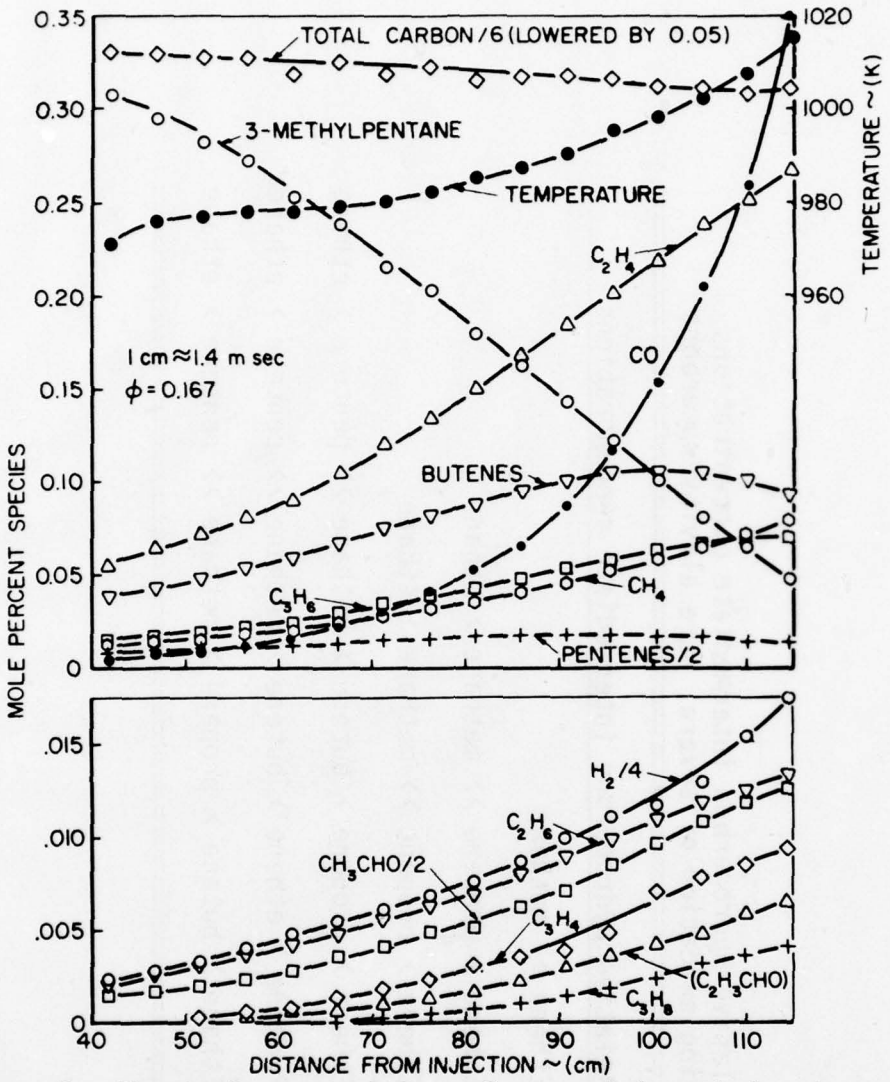


Fig. 6 Chemical composition of spread 3-methylpentane-air-reaction.

pentane oxidation indicates that the isobutyl radical does not isomerize or break down in a nonstandard fashion at 100o K, unless it is in very small amounts. Ihus, by estimating the probability of hydrogen abstraction based on the number of hydrogens available on each carbon atom, ease of removal in each case, and considering the cleavage rule discussed previously, the concentration trends of olefin and lower alkanes derived from Figs. 1-6 are quite predictable. Ihese data are presented in Table 1.

In addition to the decomposition reactions already discussed, the more complex radicals can also react directly with

Table 1 Relative hydrocarbon intermediate concentrations produced during oxidation of several pure alkylhydrocarbons

Fuel	Relative hydrocarbon intermediate concentrations
Ethane	Ethene >> methane
Propane	Ethene > propene >> methane > ethane
Butane	Ethene > propene >> methane > ethane
Hexane	Ethene > propene > butene > methane >> pentene > ethane
2-methyl pentane	Propene > ethene > butene > methane >> pentene > ethane
3-methyl pentane	Ethane > butane > propene > methane >> pentene > ethane

oxygen:

$$R + O_2 \rightarrow \text{olefin} + HO_2$$

$$R + O_2 \rightarrow \text{oxygenate} + OH$$

It is important to note here that the competitive rates of the first of the preceding reactions and the ethyl radical decomposition reaction may be particularly critical in describing oxidation of ethane and perhaps that of the higher-order alkanes. As pointed out by Walker,[16] the latter of the preceding two reactions probably occurs in two or more steps. At temperatures below 800 K, the nature of the oxygenate depends on which radical is attacked. Many other routes also are available for formation of oxygenated species.

Figures 7 and 8 present results for the oxidation of ethane at equivalence ratios near one and one and one-half. Although on these more fuel-rich studies the same overall qualitative features of the oxidation reaction hold, the relative concentrations of intermediate species vary. The comparative characteristic times of alkane and alkene conversions are different (both from concentration and temperature

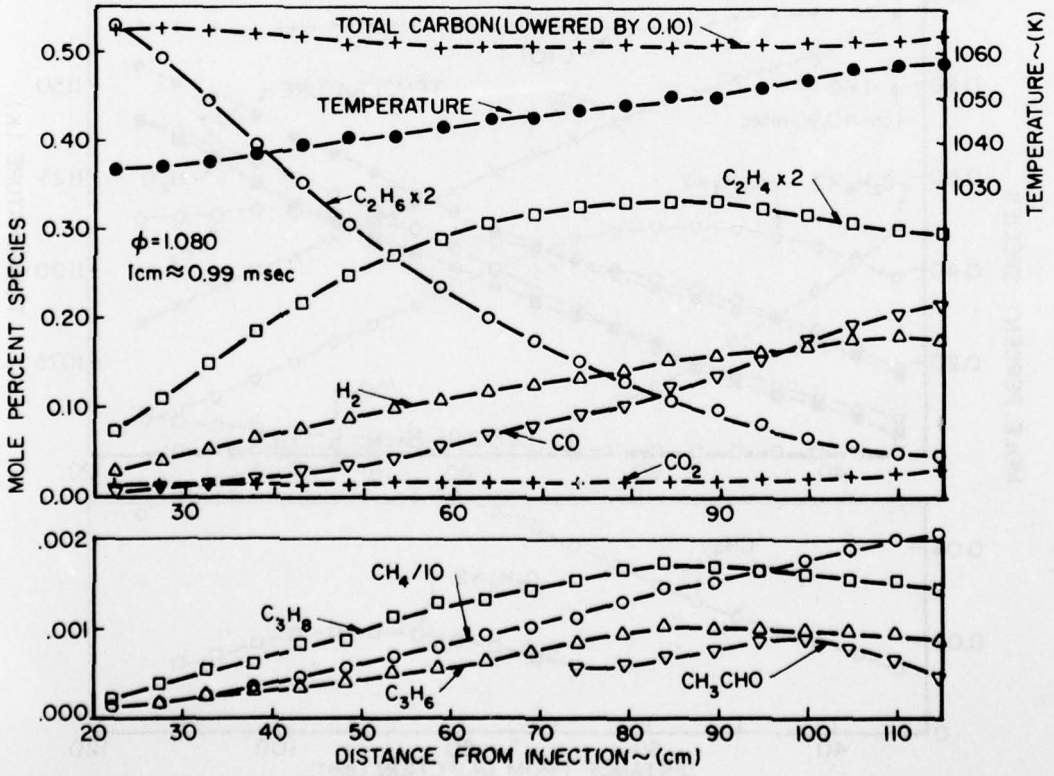


Fig. 7 Chemical composition of spread ethane-oxygen reaction.

effects), and the CO oxidation becomes almost non-existent, as the oxygen concentration is lowered. In these richer systems, hydrogen no longer is oxidized at a rapid rate to water and itself becomes an important intermediate species. Finally, it is worth noting the appearance of acetylene as an intermediate oxidation species under rich conditions. The point (time) of appearance indicates that it is an intermediate in the oxidation of the olefin, possibly produced by vinyl radical decomposition.[23] Since the production of soot precursor species most likely is related to the polymerization of acetylenic intermediates, the relation of acetylene production and oxidation to the olefin oxidation will be of value to understanding soot formation.

The general characteristics of high-temperature alkane oxidation can be summarized as follows:

1) As a result of the relatively difficult oxidation of methyl radicals, methane exhibits a very long induction period, and its oxidation is not characteristic of the higher paraffins.

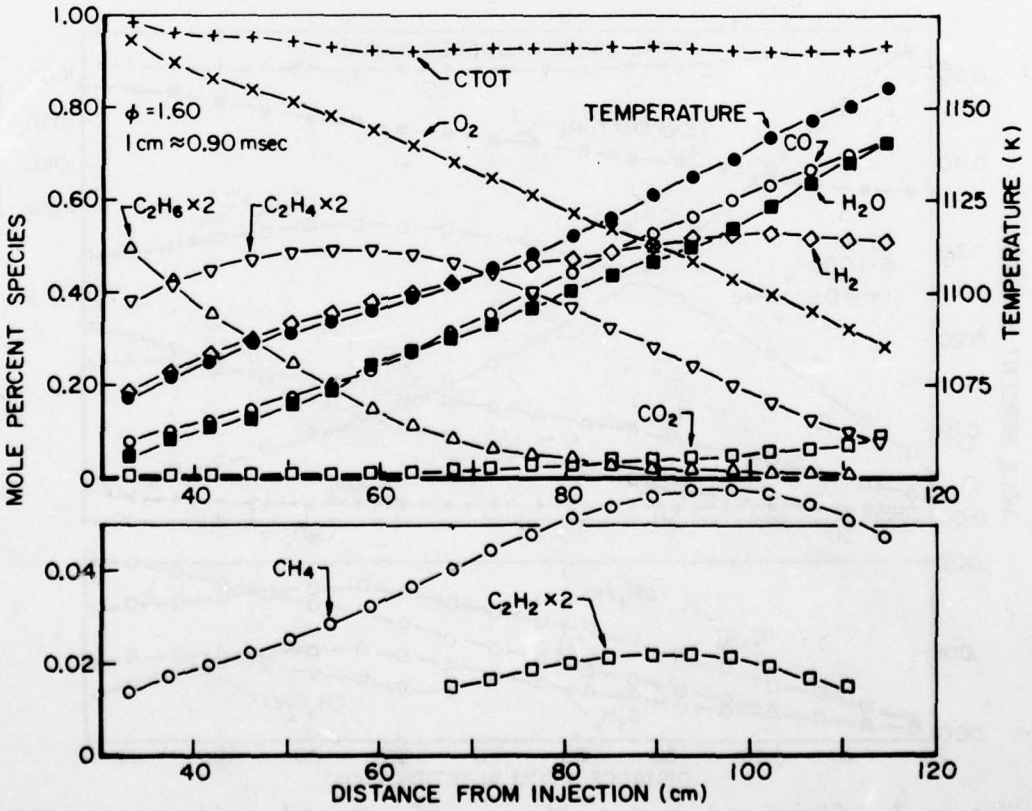


Fig. 8 Chemical composition of spread ethane-O_2 reaction.

2) The induction period for higher hydrocarbons is very short relative to the total fuel lifetime and can be neglected under most practical combustion modeling situations.

3) The oxidation of the higher paraffins qualitatively proceeds through three distinct but overlapping phases: a) conversion of the alkanes to alkenes with the available hydrogen simultaneously converted to water, b) conversion of the alkenes formed to carbon monoxide with the available hydrogen simultaneously converted to water, and c) conversion of carbon monoxide to carbon dioxide. The simultaneous

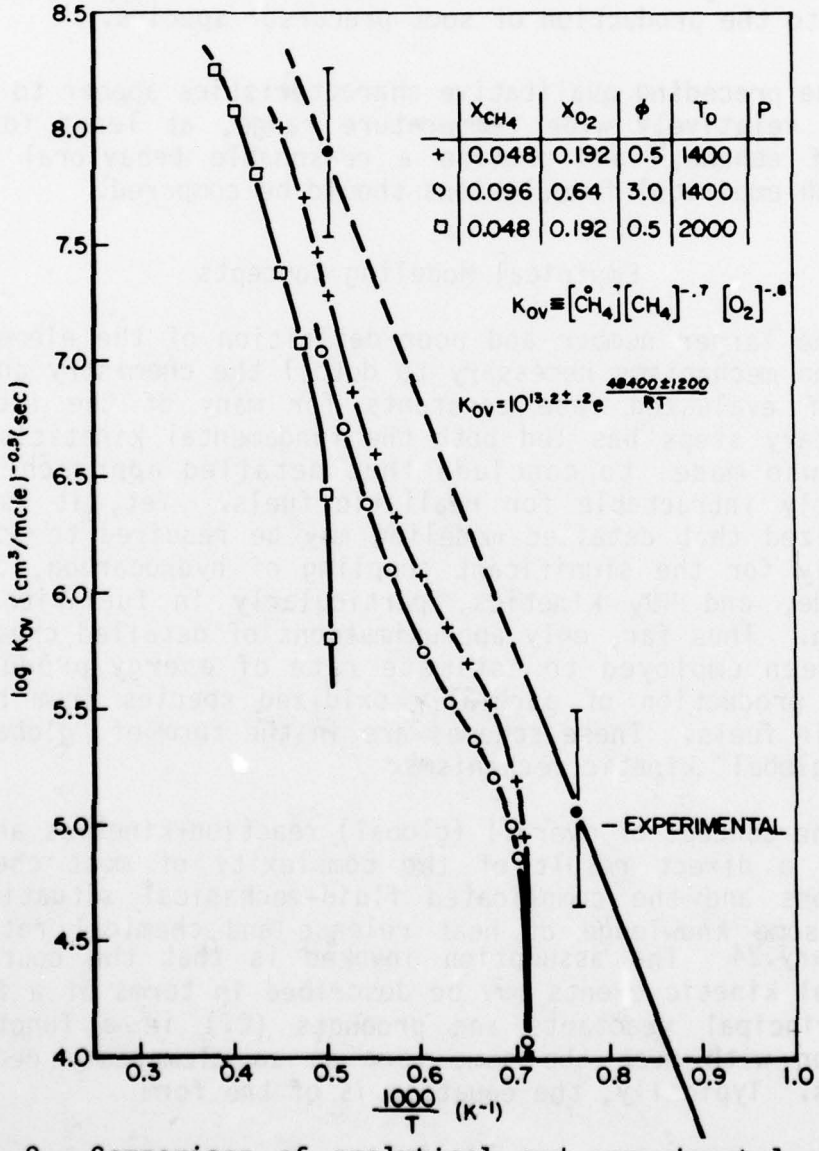


Fig. 9 Comparison of analytical and experimental overall disappearance rate of methane.

conversion of hydrogen is dependent on the amount of oxygen available and is potentially modified by the presence of hydrocarbons. Almost all of the energy release occurs from the conversion of carbon monoxide to carbon dioxide.

4) The relative quantities of olefins produced can be estimated qualitatively by considering site reactivity, the number of hydrogen abstraction sites, and "one-bond-away-from-the-radical-site" rule for decomposition.

5) In fuel-rich alkyl oxidation systems, acetylene will form, probably as a result of olefin oxidation, and may be linked to the production of soot precursor species.

The preceding qualitative characteristics appear to apply over a relatively wide temperature range, at least for the case of ethane,[5] and provide a reasonable behavioral model to which empirical formulations should be compared.

Empirical Modeling Concepts

The larger number and poor definition of the elementary reaction mechanisms necessary to detail the chemistry and the lack of evaluated rate constants for many of the included elementary steps has led both the fundamental kineticist and those who model to conclude that detailed approaches are presently intractable for realistic fuels. Yet, it is well recognized that detailed modeling may be required to account properly for the significant coupling of hydrocarbon, carbon monoxide, and NO_x kinetics, particularly in fuel-rich combustion. Thus far, only approximations of detailed chemistry have been employed to estimate rate of energy production and/or production of partially oxidized species from higher paraffin fuels. These schemes are in the form of "global" or "quasiglobal" kinetic mechanisms.

The concept of overall (global) reaction kinetics and its use is a direct result of the complexity of most chemical reactions and the complicated fluid-mechanical situation in which some knowledge of heat release and chemical rates is necessary.[24] The assumption invoked is that the course of chemical kinetic events may be described in terms of a few of the principal reactants and products (C_i) in a functional relation with much the same form as an elementary reaction process. Typically, the equation is of the form

$$C_1 + C_2 \rightarrow C_3 + C_4 + \ldots \qquad (5)$$

The rate for this process is defined by

$$\frac{-d[C_1]}{dt} = k_{ov} \prod_{i=1}^{m} [C_i]^{n_i} \qquad (6)$$

k_{ov}, the overall specific rate constant, is expressed in the Arrhenius form, where

$$k_{ov} = f(T)A\, e^{-E/RT}$$

Then n_i's are defined as the order of reaction with respect to C_i but are not necessarily equal to the stoichiometric coefficients of the overall reaction. Σn_i is termed the overall reaction order. The product of f(T) and A is termed the overall frequency factor, and E is referred to as the overall activation energy.

These relations imply nothing about the actual kinetic mechanism (in terms of elementary reactions), although the parameters in the strictly empirical rate relation sometimes are governed by a single elementary step (or a number of steps), which basically controls the rate of the chemical process. Under what circumstances such an overall correlation is usable is largely dependent on both the detailed kinetic behavior of the reaction and the physical environment in which the expression is derived. For example, Levy and Weinberg[25] concluded that such an approach is not generally applicable to chemical measurements taken in flames; however, this fact may not arise from the chemistry itself but from the physical structure diffusive character of the flame studies.

Where a particular rate-determining step or sequence in the true chemical reaction mechanism occurs and the physical circumstances of the application are similar to those from which the expression was derived, the overall approximation is a valid and vastly simplifying idea. However, extension of such a correlation to experimental conditions outside the range of parameters for which it is derived should never be performed without experimental and/or analytical verification and only then with some reservation. Unfortunately, there is currently little hope of avoiding this problem in the case of modeling hydrocarbon combustion.

Single-step global reaction schemes commonly have been used in many combustion modeling exercises (e.g., Refs. 26 and 27). Yet the only actual oxidation reactions for which parameters have been derived experimentally are those of methane and moist carbon monoxide.

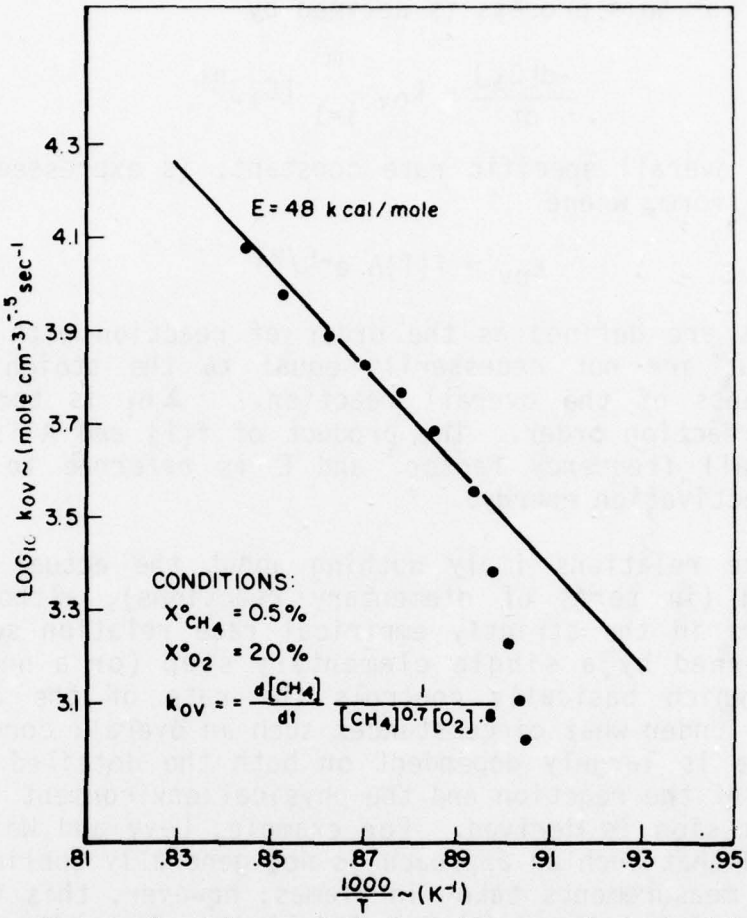


Fig. 10 Determination of E for the post induction phase oxidation of methane.

Considerable global modeling studies have been perfomed on carbon monoxide, and these have been reviewed by Dryer[6] and Howard et al.[28] Methane ignition and oxidation kinetics also have been expressed in this manner, often in conjunction with developing detailed mechanisms, and many of these studies also have been reviewed.[6]

The postinduction reaction of methane-oxygen mixtures was studied by Dryer and Glassman,[6,7] and their results lent encouragement to the belief that the rate of hydrocarbon consumption could be expressed by a simple global expression of the form of Eq. (6).

The rate of reaction in the postinduction phase of the lean methane oxidation experimentally was found to be described well by the overall expression.

$$-d[CH_4]/dt = 10^{13.2\pm0.2} e^{-(48,400\pm1200)/RT} [CH_4]^{0.7} [O_2]^{0.8}$$

It should be noted that the parameters of this equation are significantly different from those found by investigators who have studied the induction (ignition delay) phase of this reaction in shock tubes and flow reactors. A review of available data through 1973[29] predicts the rate of reaction to be inhibited by the concentration of methane. Seery and Bowman[30] empirically correlated the ignition delay time as

$$(1/\text{reaction rate}) \sim \tau = 7.65 \times 10^{-18} e^{+51,400/RT} [CH_4]^{0.4} [O_2]^{-1.6}$$

and developed a detailed elementary mechanism that reasonably predicted the relation. Figure 9 shows a comparison of the overall rate constant derived by Dryer[6] and the results calculated from parameters predicted by detailed analytical studies of Bowman.[31] The analytical overall rate constant was calculated from

$$k_{ov} = - (d[CH_4]/dt)/([CH_4]^{0.7} [O_2]^{0.8})$$

Clearly there are two phases of this reaction which are not modeled by the same global parameters. Indeed, the experimental flow reactor data of Dryer show similar behavior (Fig. 10). As described earlier, it is the postinduction reaction that is most important to practical combustion, and it is evident from Fig. 9 that the relation which gives the overall general disappearance readily predicts the same qualitative behavior as the detailed methane oxidation mechanism over a wider temperature range and equivalence ratio than the experiments from which it was derived. Dryer[6] completed the modeling of methane oxidation using a two-step global representation:

$$CH_4 + (3/2)\ O_2 \rightarrow CO + H_2O$$

$$CO + (1/2\ O_2 \rightarrow CO_2$$

with the reaction rates described by

$$-d[CH_4]/dt = 10^{13.2 \pm 0.2}\ e^{-(48,400 \pm 1200)/RT} [CH_4]^{0.7} [O_2]^{0.8}$$

$$+ d[CO_2]/dt = 10^{14.6 \pm 0.25} e^{-(40,000 \pm 1200/RT} [CO]\ [H_2O]^{0.5}\ [O_2]^{0.25}$$

It should be noted that both the overall rate constants and the reaction orders were derived experimentally; i.e., no parameters were assumed. Westbrook and Chang[32] recently have compared calculated flame propagation through premixed

and stratified mixtures using both the detailed methane oxidation mechanism derived by Westbrook et al.[3] and a global model for methane disappearance only (i.e., the overall heat of reaction was released proportionally with respect to methane disappearance). Results showed that reasonable predictions could be achieved globally over a wide range of pressures and temperatures for propagation through premixed gases, but flame propagation through stratified mixtures was not well simulated by the single-step global model. Only Appleby et al.[33] have attempted global modeling of higher paraffin oxidation (butane); however, those studies correlated only the maximum reaction rate of the initial fuel; they are outside the temperature range of present interest ($T \simeq 800$ K) and involved modeling only of the disappearance of the initial fuel. Global reaction modeling might have some potential for describing spatial energy release and reactant/final product distribution for higher hydrocarbons only if more than one global step is used.

Edelman and Fortune[34] have extended the multistep concept by developing a "quasiglobal model" that combines the use of both global expressions and elementary reactions. Edelman and Fortune chose to approximate the higher paraffin oxidation to carbon monoxide and hydrogen as a unidirectional global reaction

$$C_n H_{2n+2} + (n/2)\, O_2 \rightarrow n\, CO + (n+1)\, H_2 \qquad (5a)$$

with the rate given by

$$-\, d[C_nH_{2n+2}]/dt = [C_nH_{2n+2}]^a\, [O_2]^b\, k_{ov} \qquad (6a)$$

and combined these equations with a number of elementary reactions from the hydrogen/oxygen and carbon monoxide/oxygen reaction mechanisms (Table 2). Values of $a = 1/2$ and $b = 1$ were assigned, and

$$k_{ov} = 1.8 \times 10^9\, \bar{w}^{-0.5}\, [T/1111 - 0.5]\, T^{0.5_p - 0.2_e - 13{,}740/RT}$$

was determined initially from results of an analytical study of propane ignition kinetics.[34] $\bar{w}$ is the average gram molecular weight of the reacting system, and dimensions in this equation are cal, K moles-cm^{-3}, atm, and sec. Edelman and Fortune suggested 800 - 3000 K as the applicable temperature range. An attempt to validate the assumption that a quasiglobal model based on propane characteristics also applied to higher paraffins was made by comparing the magnitudes of the ignition delay determined in the shock-tube experiments of Nixon et al.[35] These experiments identified

Table 2 C-H-O chemical kinetic reaction mechanism for the Edelman quasiglobal model[35] [$k_f = AT^b \exp(-E/RT)$][a]

Reaction	Forward A	Forward b	Forward E/R
$CO+OH = H+CO_2$	5.6×10^{11}	0	543
$OH+H_2 = H_2O+H$	2.19×10^{13}	0	2590
$OH+OH = O + H_2O$	5.75×10^{12}	0	393
$O+H_2 = H+OH$	1.74×10^{13}	0	4750
$H+O_2 = O+OH$	2.24×10^{14}	0	8450
$M+O+H = OH+M$	1×10^{16}	0	0
$M+O+O = O_2+M$	9.38×10^{14}	0	0
$M+H+H = H_2+M$	5×10^{15}	0	0
$M+H+OH = H_2O+M$	1×10^{17}	0	0

[a]Dimensions are cal, K, moles-cm^{-3}, atm, sec; reverse rate constants k_r are obtained from k_f and the equilibrium constant k_c.

some similarity in the functional behavior and the order of magnitude of the ignition delay times for propane/ and n-octane/oxygen mixtures. The quasiglobal model using various global reaction rates (Table 3) and in some cases an extended set of CHO reactions (Table 4) has been employed extensively by its developers in combustion ignition[36] and combustion-emission modeling,[37,38] and notable successes have been reviewed on several occasions.[39,40] The variation in the overall rate constant expression used for paraffin oxidation was a result of accumulating new experimental data from which the rate constant was derived.[41] Although the variation at 1 atm has been over a factor of 30 at times (Fig. 11), the first and the most recently quoted values are very similar (within a factor of 4 over 1000 to 2000 K). However, the pressure dependences of the relations are different, and, as pressure increases, the more recent expression will predict a slower reaction rate. It should be noted that only in Ref. 34 (expression 1, Table 4) are the dimensions of the reported expression explicitly defined. In all other publications,[36-40] the dimensions of the expressions are defined

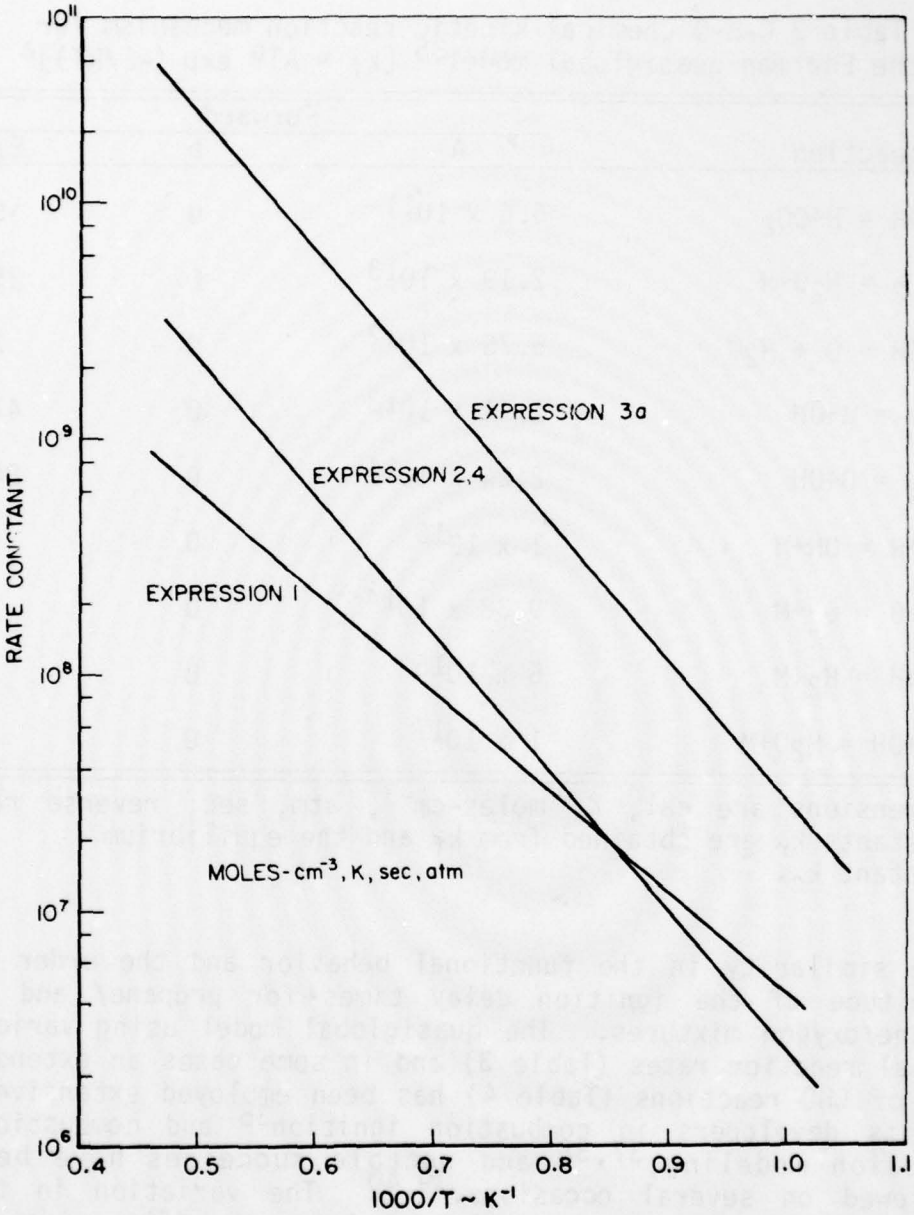


Fig. 11 Overall rate constants for paraffin oxidation of Table 4 at 1 atm pressure.

implicity by listing the rate constant expression in tables of elementary reaction rate constants reported in cm, gm-mole, sec, K, atm units. Mellor[42] also has noted dimensions of the later correlations as a footnote in Table 8 of his publication. However, the correlation itself has pressure and temperature dependence slightly different from those reported here. Nevertheless, Fig. 11 appears to indicate that the expressions so interpreted are consistent with the initially reported correlation.[34] It will become apparent later that

AD-A061 050 PURDUE UNIV LAFAYETTE IND PROJECT SQUID HEADQUARTERS F/G 21/4
ALTERNATIVE HYDROCARBON FUELS: COMBUSTION AND CHEMICAL KINETICS--ETC(U)
OCT 78 C T BOWMAN, J BIRKELAND N00014-75-C-1143
UNCLASSIFIED SQUID-PU-R2-78 NL

4 OF 5
AD
A061050



Table 3 Global rate used by Edelman and others for the Edelman quasiglobal model{$C_n H_m + (m/2)\ O_2 \longrightarrow (m/2)\ H_2 + n\ CO$ $- d[C_mH_m]/dt = k_{ov}\ [C_mH_m]^{0.5}\ [O_2]1.0$}[a]

Rate constant k_{ov}	References
(1) $b[1.8 \times 10^9/(\bar{w})^{0.5}]\ [T(K)/1111 - 0.5]\ T^{0.5} p^{0.-2} e^{-13,700/RT}$	34
(2) $5.52 \times 10^8\ T^{1.0}\ p^{-0.825}\ e^{-24,400/RT}$	37
(3) $6.9 \times 10^9\ T^{1.0}\ p^{-0.825}\ A\ e^{-EQR/RT}$	36
a) A = 1.0, EQR = 24,400, paraffin oxidation	
b) A = 347, EQR = 39,300, cyclic oxidation	
(4) $5.52 \times 10^8\ T^{1.0}\ p^{-0.825}\ e^{-24,800/RT}$	38-40

[a]Dimensions are cal, K, moles-cm^{-3}, atm, sec.

[b]$\bar{w}$ = average molecular weight.

there is some unsolved difficulty with the correlations as published in all of the references mentioned.

Modified mechanisms based on the quasiglobal concept[34] also have appeared in the literature. In attempting to predict gas turbine combusion NO_x emissions, Mellor[42,43] has replaced (5a) with

$$C_nH_n + [n/2) + (m/4)]\ o_2 \overset{\infty}{\rightarrow} n\ CO + (m/2)\ H_2O \qquad (5b)$$

and defined the rate constant of Eq. (6a) as infinite. This modification was based upon the results of Marteney.[44] However, Bowman, in comments to Edelman et al.,[37] showed that "infinite" quasiglobal kinetics do not offer any significant advantages over the partial equilibrium approach for prediction of NO_x emissions. It should be noted that these calculations also show that quasiglobal finite and quasi global infinite kinetics are equally capable of estimating NO_x emissions for residence times that are long in comparison to the time necessary to complete hydrocarbon combustion to its equilibrium product distribution. Thus, it should be remembered that, in many cases and particularly for lean oxidation, prediction of NO_x emissions may not be a sensitive enough test to judge the qualities of a proposed hydrocarbon oxidation model. Roberts et al.[45] also have derived a combustion mechanism based upon the results of Edelman.[34] Equation (5a) initially was replaced with a set of two reactions

$$C_8H_{16} + O_2 \rightarrow 2\ C_4\ H_8O \qquad (5c)$$

$$2\ C_4\ H_8O\ 3\ O_2 \rightarrow 8\ CO + 8\ H_2 \qquad (5d)$$

and finally modified to include a third reaction[46-48]

$$C_8H_{16} + OH \rightarrow H_2CO + CH_3 + 2C_2H_2 \qquad (5e)$$

to describe the initial fuel disappearance. The model also significantly modified and extended the set of elementary reactions included by Edelman and Fortune[34] and added a number of intermediate (nonelementary) reactions of species such as HCO, H_2CO, CH_3, C_2H_4, C_2H_2, etc. (The complete mechanism appears in Ref. 46.) It is unclear in these publications how the rate expressions for reactions (5c-5e) were derived. However, it appears that the reaction orders in the associated rate correlations are equal to the stoichiometric coefficients of reactions (5c-5e) and the rate constants themselves were obtained by matching the first correlation appearing in Table 3.[42,45-47] the mechanism derived in this

Table 4 Extended C-H-O chemical kinetic reaction mechanism used in the Edelman quasiglobal model[39] [$k_f = AT^b \exp(-E/RT)$][a]

Reaction	Forward A	Forward b	Forward E/R
$CO + OH = H + CO_2$	5.6×10^{11}	0	543
$CO + O_2 = CO_2 + O$	3×10^{12}	0	25,000
$CO + O + M = CO_2 + M$	1.8×10^{19}	-1	2,000
$H_2 + O_2 = OH + OH$	1.7×10^{13}	0	24,700
$OH + H_2 = H_2O + H$	2.19×10^{13}	0	2,590
$OH + OH = O + H_2O$	5.75×10^{12}	0	393
$O + H_2 = H + OH$	1.74×10^{13}	0	4,750
$H + O_2\ O + OH$	2.24×10^{14}	0	8,450
$M + O + H = OH + M$	1.0×10^{16}	0	0
$M + O + O = O_2 + M$	9.38×10^{14}	0	0
$M + H + H = H_2 + M$	5.0×10^{15}	0	0
$M + H + OH = H_2O + M$	1.0×10^{17}	0	0
$O + N_2 = N + NO$	1.36×10^{14}	0	37,750
$N_2 + O_2 = N + NO_2$	2.7×10^{14}	-1.0	60,600
$N_2 + O_2 = NO + NO$	9.1×10^{24}	-2.5	64,600
$NO + NO = N + NO_2$	1.0×10^{10}	0	44,300
$NO + O = O_2 + N$	1.55×10^{9}	1.0	19,450
$M + NO = O + N + M$	2.27×10^{17}	-0.5	74,900
$M + NO_2 = O + NO + M$	1.1×10^{16}	0	33,000
$M + NO_2 = O_2 + N + M$	6.0×10^{14}	-1.5	52,600
$NO + O_2 = NO_2 + O$	1.0×10^{12}	0	22,900
$N + OH = NO + H$	4.0×10^{13}	0	0
$H + NO_2 = NO + OH$	3.0×10^{13}	0	0
$CO_2 + N = CO + NO$	2.0×10^{11}	-1/2	4,000
$CO + NO_2 = CO_2 + NO$	2.0×10^{11}	-1/2	2,500

[a]Dimensions are cal, K, moles-cm^{-3}, atm, sec; reverse rate constants k_r are obtained from k_f and the equilibrium constant k_c.

manner has been used in numerical calculations for gas turbine combustors to predict the formation of nitric oxide,[45,46,48] the effects of water addition on NO_x emissions,[49] carbon monoxide production in the primary zone[50] (including droplet effects[51]), and emissions produced by methanol and jet fuels.[52]

These efforts cannot be reviewed comprehensively here, but it is of importance to note that the initial publication on quasiglobal modeling[34] forms the conceptual and quantitative basis for the desired model. In light of this and the precise quantitative kinetic data on higher hydrocarbon oxidation just reported, it is interesting to investigate the predictive nature of the Edelman model for fuel disappearance and CO oxidation at temperatures near 1000 - 1200 K. This comparison should not overextend this model, since Edelman et al. earlier predicted, with considerable success,[36] continuous-flow ignition delay experiments at flow reactor conditions. Figure 12 schematically represents the Esso continuous-flow ignition delay experiment that was modeled. Prevaporized fuel is injected in a concentric configuration into a steady, preheated, high Reynolds number flow of air, and a stationary flame front is produced some distance d_i divided by the airflow velocity. This technique was used to investigate the effects of various additives on the ignition delay of both alkyl and cyclic structured hydrocarbons. Edelman et al. modeled the experiment by assuming instantaneous premixing at the injector location and a one-dimensional, adiabatic, constant-pressure, reacting flow. The quasiglobal kinetics model and rate constants reported in Tables 2 and 3 were used to describe the flow chemistry. Longitudinal diffusion was permitted, and wall effects were neglected. Figure 13 presents a comparison of the calculated and measured ignition delays of various pure hydrocarbon fuels.

One would assume from the remarkable agreement that the combustion chemistry is well described. With the exception of the constant-pressure assumption, an identical approach was used in the recent modeling of the Princeton flow reactor.[3] However, a technique was derived to circumvent the requirement of comparing absolute overall reaction times, since initial mixing was found experimentally to perturb the induction phases of the methane oxidation significantly. One should be aware of similar quantitative difficulties with the Esso experimental data and that a mixing analysis is required to justify that such simple assumptions of the reaction flow do not produce fortuitous agreement. Unfortuantely, no such analysis appears in the original publication. Furthermore, it

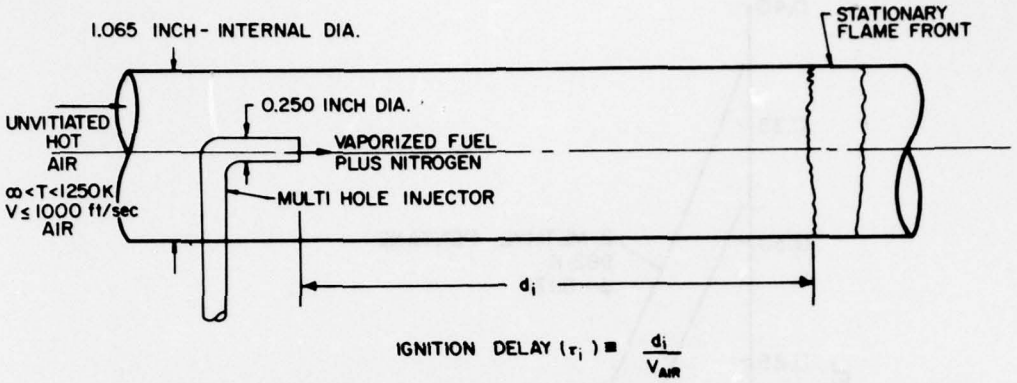


Fig. 12 Schematic of Esso research continuous flow auto-ignition test system.[36]

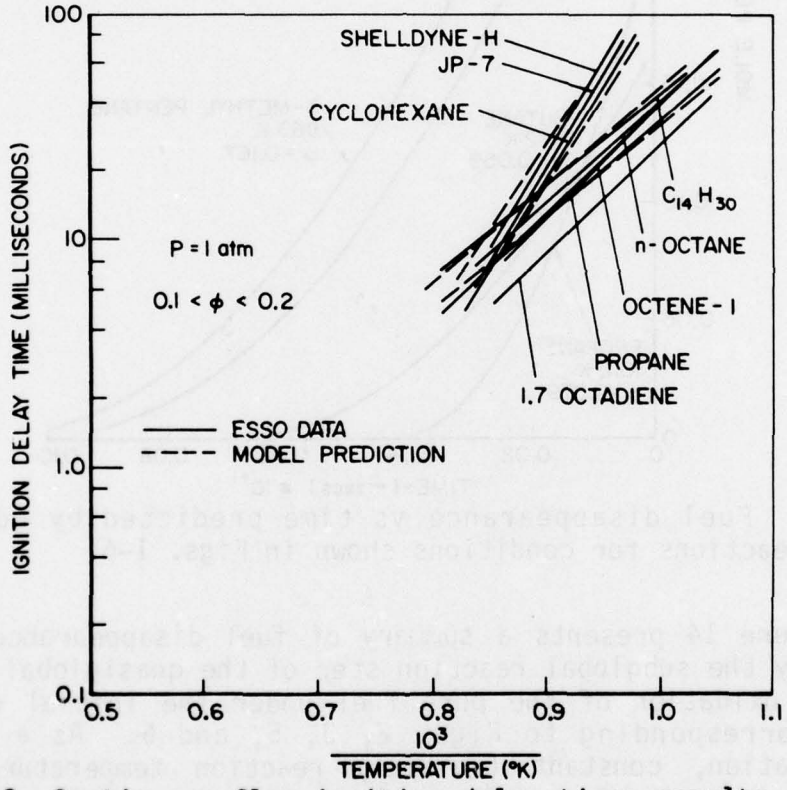


Fig. 13 Continuous flow ignition delay times results for pure fuel/air mixtures; comparison of Esso data with quasiglobal prediction of Edelman et al.[36]

is not evident in Refs. 37 and 39 that significantly different overall rate parameters were required to reproduce ignition delay measurements for paraffin and cycloparaffin hydrocarbon fuels (see Table 3).

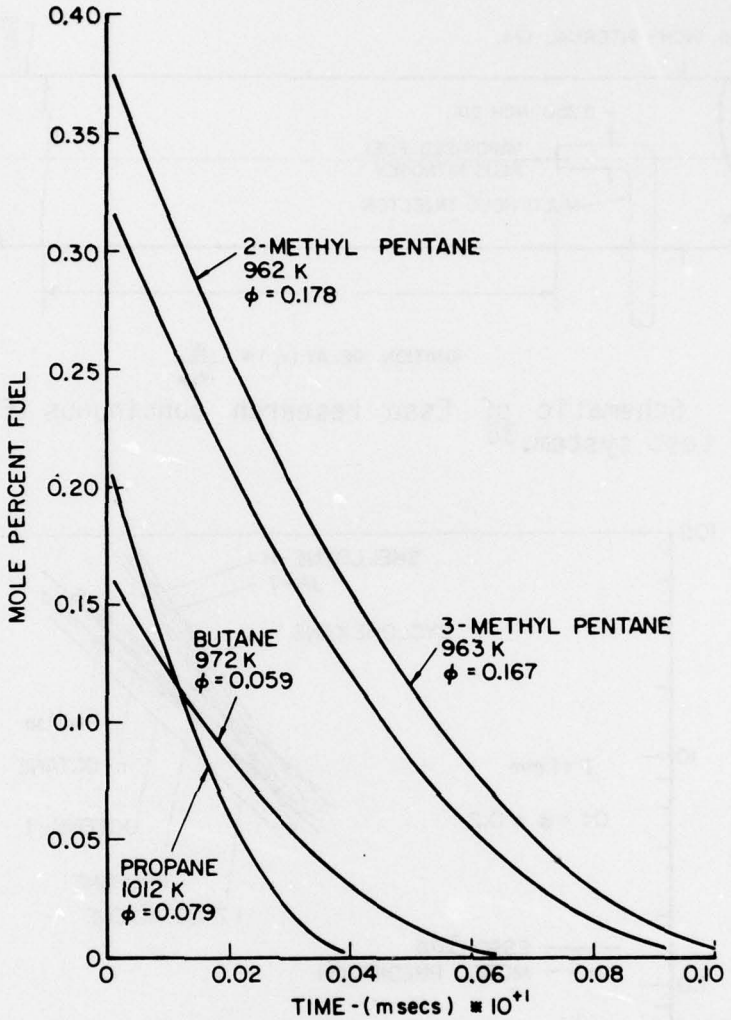


Fig. 14 Fuel disappearance vs time predicted by Edelman global reactions for conditions shown in Figs. 1-6.

Figure 14 presents a summary of fuel disappearance predicted by the subglobal reaction step of the quasiglobal model for the oxidation of the pure fuel under the initial conditions corresponding to Figs. 2, 3, 5, and 6. As a first approximation, constant (initial) reaction temperature and oxygen cocentration were assumed, and the global reaction expression employed by Engleman et al.[38] was employed.

Complete fuel disappearance was predicted in all cases within reaction times less than 10^{-2} msec, i.e., less than about 10^{-2} cm of the flow reactor duct. Relaxing the constraints used for this first approximation will result in even more rapid fuel disappearance. Predicted fuel disappearance could be brought into approximate agreement with

experiment by multiplying the reported overall frequency factor by a number the order of 10^{-3} to 10^{-4}.

Comparisons using the complete quasiglobal model (expression 4, Table 2 and the reaction set of Table 3) show similar disagreement.[53] It would appear that the global rate expressions reported in all of the articles[34,36-40] either are stated incorrectly, or that the agreement between experimental and numerical comparisons used to establish and corroborate the models was fortuitous. In either case, other quasiglobal models[45-48] developed from this literature are in error. This problem has been referred to the originators for further clarification.

Furthermore, there appear to be some potentially serious inadequacies in the mechanism shown in Table 3 for predicting carbon monoxide oxidation over wide ranges of temperature and pressure. Westbrook et al.[3] recently have shown that, without the inclusion of the hydroperoxyl radical and hydrogen peroxide (Table 4) reactions, carbon monoxide oxidation in the flow reactor cannot be modeled satisfactorily. Without these additional reactions, the carbon monoxide oxidation time under flow reactor conditions is significantly too short (factor of 4 to 5). The role of the HO_2 in the mechanism is not one of direct reaction with carbon monoxide but as a moderator of the concentration of O and OH radicals through competition of

$$M + H + O_2 \rightarrow HO_2 + M$$

with

$$H + O_2 \rightarrow OH + O$$

This competition slows the rate of chain branching and decreases the superequilibrium concentrations of the radicals OH and O. The fact is that these reactions often are overlooked and remain of equal importance at higher temperatures as the reaction pressure is increased. For example, with $M = N_2$, the rates of conversion and approximately of equal value at 1 atm, 1000 K; 10 atm, 1500 K; and 60 atm, 2000 K. Indeed, additional calculations using the mechanism shown in Table 5 confirm that, at 1500 K, the same relative importance of HO_2 and H_2O_2 chemistry just shown is apparent at 10 atm pressure.[53] Thus the use of a limited CO-H_2 mechanism in practical combustion modeling may overpredict significantly the rates of CO and H_2 conversion and the maximum (nonequilibrium) concentrations of OH and O radicals produced, and underpredict the characteristic time at which maximum radical overshoot is achieved. Indeed, the latter errors may cause

difficulty in predicting Zeldovich NO_x production in real combustion systems.

Summary and Future Needs

Although the Edelman and Fortune model for hydrocarbon oxidation appears to have several serious deficiencies, the concept upon which it is developed is quite appropriate for combustion modeling. Correct modeling of carbon monoxide/hydrogen oxidation in detail can estimate both the major energy release step of alkyl-hydrocarbon oxidation, and the radical intermediates (OH, O, H) necessary to predict the Zeldovich NO_x production and quenching of carbon monoxide. By adding elementary SO_2/SO_3 chemistry, the mechanism also could define the SO_2/SO_3 conversion that occurs during dilution or cooling of combustion gases. However, a global model for CO oxidation coupled with partial equilibrium might be sufficient for calculation of the Zeldovich NO_x production when one is concerned only with long residence times at high temperature. But the more difficult problem is how to predict empirically the ignition delay period for the carbon monoxide conversion. From the qualitative hydrocarbon oxidation description assembled earlier, it is apparent that the initiation of CO_2 formation and the formation of soot percursor species coincides with the oxidation of olefins formed from the initial hydrocarbon and not with that of the initial hydrocarbon itself. These two conversion steps may indeed have different temperature and concentration dependences, and thus we have suggested[53] that accurate modeling of hydrocarbon oxidation over the required temperature range will necessitate empirical prediction of each of these hydrocarbon conversion processes: the conversion of primary fuel to olefins, and the conversion of olefins to CO. Flow reactor experiments can provide the necessary data for construction of the models at temperatures in the vicinity of 1000 - 1200 K; however, other experimental techniques at higher temperatures and other pressures will be required to extend the models over the required ranges of parameters. The introduction of dye laser instrumentation to shock tubes should permit development of information somewhat similar to that currently available from the flow reactor.

Global rate expressions of ethane recently have been determined[5] and provide some further support for this proposed modeling approach. In the case of ethane oxidation, the subglobal expressions of the quasiglobal model would be

$$C_2H_6 \rightarrow C_2H_4 + H_2$$

$$C_2H_4 + O_2 \rightarrow 2CO + 2H_2$$

Table 5 Carbon Monoxide oxidation mechanism including HO_2 and H_2O_2 chemistry[3] {rate constants $k_f = AT^n \exp(-E/RT)$}[a]

Reaction	A	n	E
$OH + CO = CO_2 + H$	1.5×10^7	1.3	-0.765
$H + O_2 = OH + O$	2.19×10^{14}	0	16.79
$H_2 + O = OH + H$	1.82×10^{10}	1	8.9
$O + H_2O = OH + OH$	6.76×10^{13}	0	18.36
$H + H_2O = OH + H_2$	9.33×10^{13}	0	20.37
$O + H + M = OH + M$	1.0×10^{16}	0	0
$O + O + M = O_2 + M$	5.01×10^{15}	-0.25	0
$H_2 + M = H + H + M$	2.19×10^{14}	0	96.0
$O_2 + H_2 = OH + OH$	7.94×10^{14}	0	44.7
$H_2O + M = H + OH + M$	2.19×10^{16}	0	105.1
$CO + O + M = CO_2 + M$	5.89×10^{15}		4.10
$CO + O_2 = CO_2 + O$	3.16×10^{11}	0	37.6
$H + O_2 + M = HO_2 + M$	1.51×10^{15}	0	-1.00
$O + OH + M = HO_2 + M$	1.0×10^{17}	0	0
$HO_2 + O = O_2 + OH$	5.0×10^{13}	0	1.0
$H + HO_2 = OH + OH$	2.51×10^{14}	0	1.90
$\cdot + HO_2 = H_2 + O_2$	2.51×10^{13}	0	0.70
$\cdot + HO_2 = H_2O + O_2$	5.01×10^{13}	0	1.00
$HO_2 + HO_2 = H_2O_2 + O_2$	1.0×10^{13}	0	1.00
$H_2O_2 + M = OH + OH + M$	1.2×10^{17}	0	45.50
$H + H_2O_2 = HO_2 + H_2$	1.7×10^{12}	0	3.78
$CO + HO_2 = CO_2 + OH$	1.0×10^{14}	0	23.00
$H_2O_2 + OH = H_2O + HO_2$	1.0×10^{13}	0	1.80

[a]Dimensions are kcal, K, moles-cm^{-3}, atm, sec; reverse rate constants k_r are obtained from k_f and the equilibrium constant k_c.

Table 6 Calculations of the ethane oxidation regimes as functions of temperature and mole fraction of oxygen ($\alpha = k_{10}/K_{11}\ [O_2]$)

	Temp. K	1000	1200
Lean regime:	$\alpha \leq 2.2$, $X^{\circ}_{O_2}$	≥ 0.05	≥ 0.95
Stoiochiometric and fuel-rich regime:	$\alpha \leq 5.5$, $X^{\circ}_{O_2}$	≤ 0.02	≤ 0.38

It would found that two distinct regimes requiring different global rate expressions exist: a fuel-lean regime for which $\alpha \leq 2.2$, and a stoichiometric and fuel-rich regime for which $\alpha \geq 5.5$. The parameter α is defined by

$$k_{10}/K_{11}\ [O_2]_o$$

where reactions (7) and (8) are

$$C_2H_5 \rightarrow C_2H_4 + H \qquad (7)$$

$$C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2 \qquad (8)$$

The fact that two regimes exist is believed to be a result of a shift in the primary branching reaction from

$$H_2O_2 + M \rightarrow 2OH + M$$

in the lean regime to

$$H + O_2 \rightarrow OH + O$$

in the stoichiometric and fuel-rich regime. This shift is produced by the relative ratio of the two primary sources of H and HO_2 (which lead to H_2O_2), reactions (7) and (8).

The existence of two different sets of global reaction rate expressions for paraffin and olefin conversion which apply over different ranges of would appear at first sight to be a complicating factor. However, if one uses available values[3] of rates constants for reactions (7) and (8) and further assumes that reaction (7) is indeed at its high-pressue limit, it is found that, under most practical conditions, the ethane oxidation proceeds primarily in the stoichiometric and rich regime (see Table 6). For that regime, the

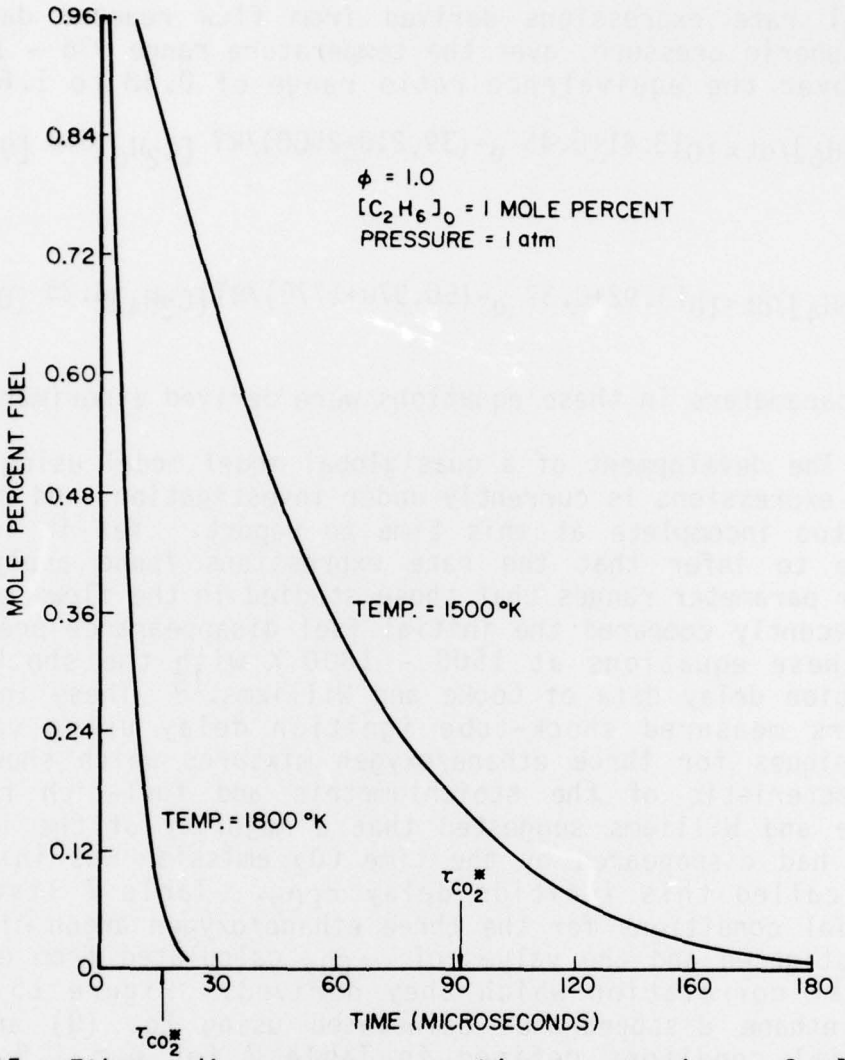


Fig. 15 Ethane disappearance vs time; comparison of global prediction[5] and experiments.[15]

Table 7 Comparison of ignition delays based on CO^2 emission[15] [ethane disappearance calculated using Eq. (9)]

Mixture	ϕ	$X^{\circ}_{C_2H_6}$	$X^{\circ}_{O_2}$	X°_{Ar}	τ_{CO_2}, 1500 K	μ sec 1800 K	$\tau_{C_2H_6}$, 1500 K	μ sec 1800 K
1	0.5	0.00625	0.4375	0.95	61.4	18.7	145	26
2	1.0	0.0111	0.0389	0.95	90.6	...	180	...
3	2.0	0.0182	0.0318	0.95	147	...	225	...

global rate expressions derived from flow reactor data at atmospheric pressure, over the temperature range 976 - 1155 K and over the equivalence ratio range of 0.38 to 1.6, are

$$-d[C_2H_6]/dt = 10^{13.41\pm0.45}\, e^{-(39{,}210\pm2500)/RT}\, [C_2H_6]^{0.8}\, [O_2]^{0.75} \quad (9)$$

and

$$-d[C_2H_4]/dt = 10^{11.92+0.37}\, e^{-(50{,}970+1770)/RT}\, [C_2H_4]^{0.25}\, [O_2]^{0.85} \quad (10)$$

All parameters in these equations were derived experimentally.

The development of a quasiglobal model model using these rate expressions is currently under investigation, and results are too incomplete at this time to report. Yet it is possible to infer that the rate expressions found apply over wider parameter ranges that those studied in the flow reactor. We recently compared the initial fuel disappearance predicted by these equations at 1500 - 1800 K with the shock-tube ignition delay data of Cooke and Williams.[15] These investigators measured shock-tube ignition delay using various techniques for three ethane/oxygen mixtures which should be characteristic of the stoichiometric and fuel-rich regime. Cooke and Williams suggested that a majority of the initial fuel had dispapeared by the time CO_2 emission was initiated and called this ignition delay τ_{CO_2}. Table 7 lists the initial conditions for the three ethane/oxygen argon mixtures investigated and the values of τ_{CO_2} calculated from experimental correlation which they derived. Figure 15 shows the ethane disappearance caluclated using Eq. (9) and the initial conditons defined in Table 7 for ϕ = 1.0. The pressure was assumed to be at 1 atm, and the temperature was assumed to be constant at 1500 or 1800 K. The global rate expression derived in the flow reactor successfully predicts a fuel disappearance time within a factor of 2 of the CO_2 emission ignition delay. The reaction times are nearly 10^3 shorter at the shock-tube temperatures, and the agreement is probably as good as can be expected without experimental shock-tube chemical profile information. Agreement actually may be better than indicated, since the temperature should rise slightly during the fuel decay, and some fuel may remain when CO_2 emission begins. It is worth noting from Table 7 that the total disappearance time for ethane is so short that, in most conventional combustion systems, the fuel would have disappeared long before gas temperatures approaching 1800 K could be reached. Thus, knowledge of hydrocarbon disappearance correlations extending to near 1800 K may be adequate for

most practical combustion modeling. Additional data also will be required to establish any pressure dependence not already appearing in the concentration terms of rate equations.

In comparison to the combustion chemistry of aromatics, the oxidation and pyrolysis kinetics of alkyl hydrocarbons are relatively well understood. However, the qualitative understanding that we have gained has not yet been exploited fully in developing semiempirical mechanisms that successfully predict both qualitative and quantitative behavior except in weakly coupled gross quantities. The currently available "quasiglobal" models have been shown to have several limitations, particularly the published values for the overall global rate expressions, poorly defined rate parameters, and limited detailed mechanisms for H_2 and CO oxidation. It is suggested that more strongly coupled parameters than ignition delay and NO_x emissions should be used in the future to corroborate model validity. It appears that we must begin to employ our new technology to add to our qualitative and quantitative knowledge of high-temperature oxidation through the use of resonant dye laser techniques in instrumentation capable of data acquisition over the necessary ranges of pressure, temperature, and equivalence ratio (shock tubes and flow reactors). Finally, we should be aware of the effects of turbulence and how it might be incorporated in generated semiempirical models for comparison with more simple reacting turbulent systems (stirred reactors, etc.).

Acknowledgments

In preparing this paper, the authors have drawn upon their research support by the Air Force Office of Scientific Research under Grant No. 74-2604, the National Science Foundation/Research Applied to National Need under Grant No. AER-75-09538, and the Conservation Research and Technology/ Division of the Energy Research and Development Administration under Grant No. EC-17-S-02-4272. Much of the experimental work was performed by Richard Cohen as part of his Ph.D. thesis.

References

[1]Edelman, D. and Allara, D. L., "The Use of Large-Scale Chemical Models in the Elucidation of Reaction Mechanism" Fifteenth International Symposium on Combustion, Paper 88, Tokyo, Japan, Aug. 25-31, 1974 (not published in Symposium Proceedings).

[2]Golden, D. M., "Pyrolysis and Oxidation of Aromatic Compounds," published elsewhere in this volume.

[3]Westbrook, C. K., Creighton, J., Lund, C., and Dryer, F. L., "A Numerical Model of Chemical Kinetics of Combustion in a Turbulent Flow Reactor," Journal of Physical Chemistry (to be published).

[4]Olson, D. B. and Gardiner, W. C., Jr., "An Evaluation of Methane Combustion Mechanisms," Symposium on Reaction Mechanisms, Models, and Computers, American Chemical Society, New Orleans, La., March 20-25, 1977 (to be published).

[5]Cohen, R., "The High Temperature Oxidation and Pyrolysis of Ethane," Ph.D. dissertation, Dept. of Aerospace and Mechanical Sciences, Princeton Univ., July 1977; also Aerospace and Mechanical Sciences Rep. T-1338.

[6]Dryer, F. L., "The High Temperature Oxidation of Carbon Monoxide and Methane in a Turbulent Flow Reactor," Air Force Office of Scientific Research, Scientific Rep. TR-72-1109, March 1972.

[7]Dryer, F. L. and Glassman, I., "High Temperature Oxidation of CO and CH_4," Fourteenth International Symposium on Combustion, The Combustion Institute, Pittsburgh, Pa., 1973, pp. 987-1003.

[8]Colket, M. B., III, "High Temperature Pyrolysis and Oxidation of Acetaldehyde," Ph. D. dissertation, Dept. of Aerospace and Mechanical Sciences, Princeton Univ., 1975; also Aerospace and Mechanical Sciences Rept. 1270-T.

[9]Colket, M. B., III, Naegeli, D. W., and Glassman, I., "High Temperature Pyrolysis of Acetaldehyde," International Journal of Chemical Kinetics, Vol. 7, 1975, pp.223-247.

[10]Glassman, I. and Eberstein, I. J., "Turbulence Effects in Chemical Reaction Kinetics Measurements," AIAA Journal, Vol. 1, June 1963, pp. 1424-1426.

[11]Orr, C. R., "Combustion of Hydrocarbons Behind a Shock Wave," Ninth International Symposium on Combustion, Academic Press, New York, 1963, pp. 1034-1045.

[12]Levinson, G. S., "High Temperature Preflame Reactions of n-Heptane," Combustion and Flame, Vol. 9, 1959, pp. 63-72.

[13]Burcat, A., Lifshitz, A., Scheller, K., and Skinner, G. B., "Shock Tube Investigation of Propane-Oxygen-Argon Mixtures," Thirteenth International Symposium on Combustion, The Combustion Institute, Pittsburgh, Pa., 1971, pp. 745-755.

[14]Burcat, A., Scheller, K., and Crossley, R. W., "Shock Tube Ignition of Ethane-Oxygen-Argon Mixtures," Combustion and Flame, Vol. 18, 1972, pp. 115-123.

[15]Cooke, D. F. and Williams, A., "Shock Tube Studies of Methane and Ethane Oxidation," Combustion and Flame, Vol. 24, 1975, pp. 254-256.

[16]Walker, R. W., "A Critical Survey of Rate Constants for Reactions in Gas-Phase Hydrocarbon Oxidation," SPR Chemical Society, Reaction Kinetics, Vol. 1, 1975, pp. 161-211.

[17]Hawthorne, R. D. and Nixon, A. C., "Shock Tube Ignition Delay Studies of Endothermic Fuels," AIAA Journal, Vol. 4, March 1966, pp. 513-520.

[18]Fristrom, R. M. and Westenberg, A. A., Flame Structure, McGraw-Hill, New York, 1965, pp. 350-351.

[19]McNesby, J. R., Drew, C. M., and Gordon, A. S., "Mechanism of the Decomposition of Primary and Secondary n-Butyl Free Radicals," Journal of Chemical Physics, Vol. 24, 1956, p. 1260.

[20]Jackson, W. M. and McNesby, J. R., "Phtolysis of Acetone - d_6 in the Presence of 2,2 - Propane d_2," Journal of the American Chemical Society, Vol. 83, 1961, p. 4891.

[21]Jackson, W. M. and McNesby, J. R., "Thermal Isomerization of Isoproply1-1,1,1-d_3 Radicals," Journal of Chemical Physics, Vol 36, 1962, pp. 2272-2275.

[22]Jackson, W. M., McNesby, J. R., and Darwent, B. deB., "Reaction of Methyl-d_3 Radicals with Isobutane, Isobutane-2-d, and Propane," Journal of Chemical Physics, Vol. 37, 1962, pp. 1610-1615.

[23]Jachimowski, C. J., "An Experimental and Analytical Study of Acetylene and Ethylene Oxidation Behind Shock Waves," Combustion and Flame, Vol. 29, 1977. pp. 55-66.

[24]Glassman, I., Dryer, F. L., and Cohen, R., "Combustion of Hydrocarbons in an Adiabatic Flow Reactor: Some Considerations and Overall Correlations of Reaction Rate," Joint Meeting of the Central and Western States Section of the Combustion Institute, San Antonio, Texas, April 21, 22, 1975.

[25]Levy, A. and Weinberg, F. J., "Optical Flame Structure Studies: Examination of Reaction Rate Laws in Lean Ethylene-Air Flames," Combustion and Flame, Vol. 3, 1959, pp. 229-253.

[26]Bellan, J. R. and Sirignano, W. A., "A Theory of Turbulent Flame Development and Nitric Oxide Formation in Stratified Charge Internal Combustion Engines," Combustion Science and Technology, Vol 8, 1973, pp. 51-68.

[27]Elgohobashi, S., Spalding, D. B., and Srivatsa, S. K., "Prediction of Hydrodynamics and Chemistry of Confined Turbulent Methane-Air Flames with Attention to Formation of Oxides of Nitrogen," NASA CR-135179, CHAM 961/2, NASA Lewis Research Center, June 1977.

[28]Howard, J. B., Williams, G. C. and Fine, D. H., "Kinetics of Carbon Monoxide Oxidation in Post Flame Gases," Fourteenth International Symposium on Combustion, The Combustion Institute, Pittsburgh, Pa., 1973, pp. 975-986.

[29]Matula, R. A., Gangloff, H. L., and Malonsy, K. L., "Ignition Delay in Hydrocarbon Systems," Symposium on Hydrocarbon Combustion Chemistry, American Chemical Society, Div. of Petroleum Chemistry, Dallas, Texas, April 1973.

[30]Seery, D. J. and Bowman, C. T., "An Experimental Study of Methane Oxidation Behind Shock Waves," Combustion and Flame, Vol 14, 1970, pp. 37-47.

[31]Bowman, C. T., "An Experimental and Analytical Investigation of the High Temperature Oxidation Mechanism of Hydrocarbon Fuels," Combustion Science and Technology, Vol. 2, 1970, pp. 161-172.

[32]Westbrook, C. K. and Chang, J. S., "A Theoretical Study of Flame Propagation Through Stratified Media," Central States Section Meeting on the Combustion Institute, NASA Lewis Research Center, Cleveland, Ohio, March 28-30, 1977.

[33]Appelby, W. G., Avery, W. H., Meerbott, W. K., and Sartor, A. F., "The Decomposition of n-Butane in the Presence of Oxygen," Journal of the American Chemical Society, Vol. 75, 1953, pp. 1809-1814.

[34]Edelman, R. B. and Fortune, O. F., "A Quasi-Global Chemical Kinetic Model for Finite Rate Combustion of Hydrocarbon Fuels with Application to Turbulent Burning and Mixing in Hypersonic Engines and Nozzles," AIAA Paper 69-86, New York, Jan. 20-22, 1969.

[35]Nixon, A., et al., "Vaporizing and Endothermic Fuels for Advanced Engine Applications," Shell Development Co. Reps., Pt. I, AFAOL-TR-67-114, Pts. II and III, APL-TDR-64-100, 1964-1967.

[36]Siminski, V. J. and Wright, F. J., "Experimental Determination of Ignition Delay Times in Subsonic Flows," Vol. I; and Edelman, R., Economos, C., and Fortune, O., Vol. II, "Kinetics Modeling and Supersonic Testing," Vol. II, AFAPL-72-74, Air Force Aero Propulsion Lab., Air Force Systems Command, TR. Wright-Patterson Air Force Base, Ohio, Feb. 1972.

[37]Edelman, R. B., Fortune O., and Weilerstein, G., "Some Observations on Flows Described by Coupled Mixing and Kinetics," Emissions from Continuous Combustion Systems, edited by W. Cornelius and W. G. Agrew, Plenum Press, New York, 1972, pp. 55-106.

[38]Engleman, V. S., Bartok, W., Longwell, J. P., and Edelman, R. B., "Experimental and Theoretical Studies of NO_x Formation in a Jet Stirred Combustor," Fourteenth International Symposium on Combustion, The Combustion Institute, Pittsburgh, Pa., 1973, pp. 755-765.

[39]Edelman, R. B., "The Relevance of Quasi-Global Kinetics Modeling as an Aid in Understanding the I.C. Engine Process," Workshop on the Numerical Simulation of Combustion for Application to Spark and Compression Ignition Engines, A. A. Boni, Chairman, Science Applications Inc., La Jolla, Calif., Oct. 1975, Appendix 4.1B.

[40]Edelman, R. B. and Harsha, P. T., "Current Status of Laminar and Turbulent Gas Dynamics in Combustors," Invited Survey Paper, Central States Section Meeting of the Combustion Institute, NASA Lewis Research Center, Cleveland, Ohio, March 28-30, 1977.

[41]Edelman, R. B., private communication, Sept. 1977.

[42]Mellor, A. M., "Current Kinetic Modeling Techniques for Continuous Flow Combustors," Emissions from Continuous Combustion Systems, Plenum Press, New York, pp. 23-53.

[43]Hammond, D. C., Jr. and Mellor, A. M., "Analytical Predictions of Emissions from and Within an Allison J-33 Combustor," Combustion Science and Technology, Vol. 6, 1973, pp. 279-286.

[44]Marteney, P. J., "Analytical Study of the Kinetics of Formation of Nitrogen Oxide in Hydrocarbon-Air Combustion," Combustion Science and Technology, Vol. 1, 1970, pp. 461-469.

[45]Roberts, R., Aceto, L. D., Kollrack, R., Teixeira, D. P., and Bonnell, J. M., "An Analytical Model for Nitric Oxide Formation in a Gas Turbine Combustor," AIAA Journal, Vol. 10, June 1972, pp. 820-826.

[46]Kollrack, R. and Aceto, L. D., "Nitric Oxide Formation in Gas Turbine Combustors," AIAA Journal, Vol. 11, May 1973, pp. 664-669.

[47]Herrin, J., private communication, Sept. 1977.

[48]Mador, R. J. and Roberts, R., "A Pollutant Emission Prediction Model for Gas Turbine Combustors," AIAA Paper 74-1113, San Diego, Calif., Oct. 21, 1974.

[49]Kollrack, R. and Aceto, L. D., "The Effects of Liquid Water Additions in Gas Turbine Combustors," Journal of the Air Pollution Control Association, Vol. 23, 1973, pp. 116-121.

[50]Aceto, L. D. and Kollrack, R., "Primary Zone Carbon Monoxide Levels for Gas Turbines, Part I - Premixed Combustion," AIAA Journal, Vol. 12, April 1974, pp. 463-465.

[51]Aceto, L. D. and Kollrack, R., "Part II - Liquid Fuel Combustion," AIAA Journal, Vol. 12, April 1974, pp. 465-467.

[52]Adelman, H. G., Browning, L. H., and Pefley, R. K., "Pretested Emissions from a Methanol and Jet Fueled Gas Turbine Combustor," AIAA Journal, Vol. 14, 1976, pp. 793-798.

[53]Westbrook, C. L., Chang, J. S., and Dryer, F. L., unpublished work, 1977.

DISCUSSION

DR. R. B. EDELMAN (Science Applications, Inc.): I would like to compliment Dryer on the progress he is making in measuring product species histories under controlled conditions. As I see it, his data, at least for some conditions of practical interest, can be useful in developing models for finite rate oxidation of hydrocarbons. Although the 1-atm, fuel-lean mixtures ratios of the experiments, are limited in terms of many practical applications, they do provide a data

Table 1 Extended C-H-O Chemical kinetic reaction mechanism $k_f = AT^b \exp(-E/RT)$

Reaction	A Long chain	A cyclic	Forward b	E/R Long chain	E/R cyclic
1) $C_nH_m + \frac{n}{2}O_2 - \frac{m}{2}H_2 + n\,CO$ [a]	6.0×10^4	2.08×10^7	1	12.2×10^3	19.65×10^3
2) $CO + OH = H + CO_2$	5.6×10^{11}		0	$.54^3 \times 10^3$	
3) $CO + O_2 = CO_2 + O$	3×10^{12}		0	25.0×10^3	
4) $CO + O + M = CO_2 + M$	1.8×10^{19}		-1	2×10^3	
5) $H_2 + O_2 = OH + OH$	1.7×10^{13}		0	24.7×10^3	
6) $OH + H_2 = H_2O + H$	2.19×10^{13}		0	2.59×10^3	
7) $OH + OH = O + H_2O$	5.75×10^{12}		0	$.393 \times 10^3$	
8) $O + H_2 = H + OH$	1.74×10^{13}		0	4.75×10^3	
9) $H + O_2 = O + OH$	2.24×10^{14}		0	8.45×10^3	
10) $M + O + H = OH + M$	1×10^{16}		0	0	
11) $M + O + O = O_2 + M$	9.38×10^{14}		0	0	
12) $M + H + H = H_2 + M$	5×10^{15}		0	0	
13) $M + H + OH = H_2O + M$	1×10^{17}		0	0	
14) $O + N_2 = N + NO_2$	1.36×10^{14}		0	3.775×10^4	
15) $N_2 + O_2 = N + NO_2$	2.7×10^{14}		-1.0	6.06×10^4	
16) $N_2 + O_2 = NO + NO$	9.1×10^{24}		-2.5	6.46×10^3	
17) $NO + NO = N + NO_2$	1.0×10^{10}		0		
18) $NO + O = O_2 + N$	1.55×10^9		1.0	1.945×10^4	
19) $M + NO = O + N + M$	2.27×10^{17}		-0.5	7.49×10^4	
20) $M + NO_2 = O + NO + M$	1.1×10^{16}		0	3.30×10^4	
21) $M + NO_2 = O_2 + N + M$	6.0×10^{14}		-1.5	5.26×10^4	
22) $NO + O_2 = NO_2 + O$	1×10^{12}		0	2.29×10^4	
23) $N + OH = NO + H$	4×10^{13}		0	0	
24) $H + NO_2 = NO + OH$	3×10^{13}		0	0	
25) $CO_2 + N = CO + NO$	2×10^{11}		-1/2	4×10^3	
26) $CO + NO_2 = CO_2 + NO$	2×10^{11}		-1/2	2.5×10^3	

[a] $\frac{dC_{C_nH_m}}{dt} = -A\,T^b\,p^{0.3}\,C_{C_nH_m}^{1/2}\,C_{O_2}\exp -\frac{E}{RT}$; $[C]=\frac{gm\ moles}{cc}$, $[T]={}^oK$, $[P]=atm.$, $[E]=\frac{cal}{mole}$

base which taken together with modeling can improve our understanding of the oxidation of hydrocarbon fuels. Because of the potential importance of these data, I want to encourage him to make his more recent results available to us. In this regard it is of the utmost importance to document the initial conditions and the details of the experimental facility. This should include a description of the method of fuel/air preparation, the reactor geometry, and the initial pressure, temperature, and velocity. A fair degree of detail is required since, to my knowledge, most of his experiments have been carried out at very low fuel/air ratios that produce temperature rises on the order of only 10% or less of the "initial" temperature (the first recorded temperature along the reactor length).

A question which puzzles me relates to the importance Dryer has given to the hydroperoxy radical, HO_2, at temperatures in the range of 1000° to 1500 °K. HO_2 is a radical gobbler and is involved in the so-called quenching reactions at low temperatures. Thus, HO_2 is extremely important in the low-temperature (below 1000 °K) ignition and oxidation process for hydrogen and hydrocarbons. Since HO_2 (like H_2O_2) is so highly unstable in the higher temperature range, I wonder if he could provide substantiation for the importance he associates with HO_2 in this high-temperature range.

Regarding our quasiglobal kinetics model, Dryer has raised a question pertaining to the reported values of the rate parameters for the partial oxidation step that have appeared in our past publications. An error has been propagated in the literature, and Table 1 gives all the correct rate constants for the entire quasiglobal mechanism. I want to emphasize that this particular set of constants for the initial partial oxidation (or subglobal) step (reaction 1) is based on the data obtained from a plug flow reactor used by EXXON Research and Engineering Company and reported in the following document: Siminski, V., Wright, F. J., Edelman, R. B., Economos, C., and Fortune, O., "Research on Methods of Improving the Combustion Characteristics of Liquid Hydrocarbon Fuels," AFAPL-TR-72-24, Vol.'s I and II, Feb. 1972. The data are comprised of ignition delay times for aliphatic and cyclic type hydrocarbons at 1-atm pressure for fuel-lean mixtures.

I want to make it clear that the various predictions that have been published and presented are correct. To indicate the kinds of predictions that can be made with this model, I want to go through several types of applications we have made using our quasiglobal model.

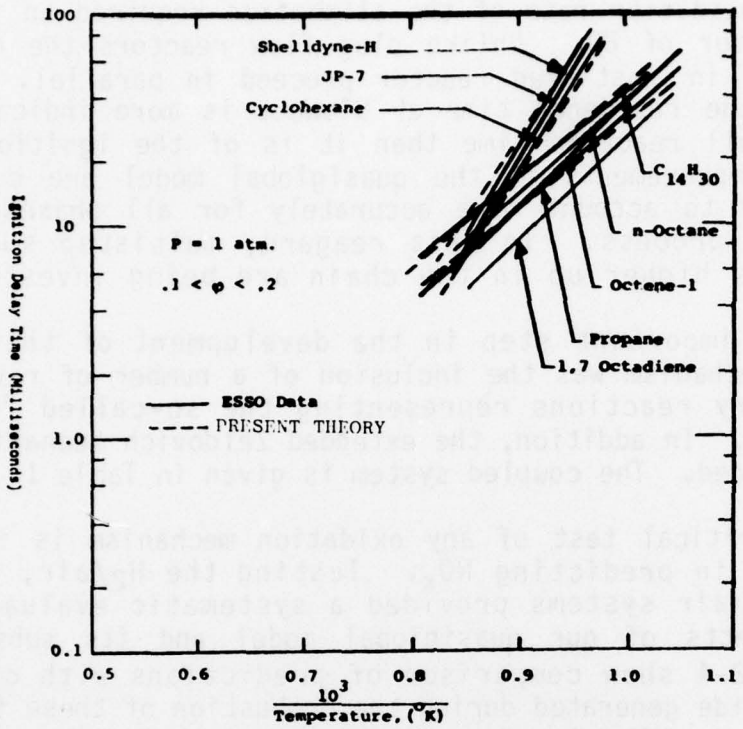


Fig. 1 Ignition delay time (msec).

Figure 1 shows ignition delay time data obtained by Siminski. This work is reported in the aforementioned reference. The grouping of the aliphatics and of the alicyclics is important to note. Some of the alicyclics are of particular interest to the Air Force because of their high volumetrics heating values. The behavior of these hydrocarbons is, of course, relevant to the combustion of coal and shale derived of fuels. Our predictions, shown in Fig. 1, using the quasi-global model, seem to reinforce the value of relatively simple modeling of hydrocarbon fuels for which little detail is currently available.

Figure 2 of Lefebvre's paper shows the blowout curve for well-stirred reactors burning propane. The solid lines represent the bounds of data as reported by several experimenters in the Combustion Institute Proceedings. The experiments were performed on aliphatic hydrocarbons in jet stirred reactors based on the type originally developed by Longwell. These reactors are very well mixed, and their performance suggests that kinetics is the controlling mechanism over wide ranges of operating conditions. The comparison of these data with our predictions is quite favorable. However, the pre-exponential constant in the expression for the subglobal

partial oxidation rate of the aliphatics required an increase of a factor of 80. Unlike plug flow reactors the chemical reactions in a stirred reactor proceed in parallel. Consequently the residence time at blowout is more indicative of the overall reaction time than it is of the ignition delay time. Improvements in the quasiglobal model are currently under way to account more accurately for all phases of the reaction process. In this reagard, multistep subglobal reactions higher up in the chain are being investigated.

One important step in the development of the quasiglobal mechanism was the inclusion of a number of reversible elementary reactions representing the so-called "WET CO" mechanism. In addition, the extended Zeldovich mechanism also was included. The coupled system is given in Table 1.

A critical test of any oxidation mechanism is its performance in predicting NO_x. Testing the H_2/air, CO/air, and C_3H_8/air systems provided a systematic evaluation of many aspects of our quasiglobal model and its subsystems. Figures 2-4 show comparison of predictions with data for nitric oxide generated during the combustion of these fuels in EXXON's jet stirred reactor. The pressure level was 1 atm, and the residence times were in the 1-2 msec range. The agreement for the hydrogen and CO-air systems is excellent. It is worth noting that for the CO-air system a very small amount of hydrogen was added to the CO to provide flame stabilization. Our simulation required exactly the same amount of the H_2 to be added to the CO. Otherwise we predicted blowout. The prediction for the propane/air system was not so good (Fig. 4). We show a variety of predictions for different assumptions. Although bound nitrogen is really not relevant to propane, it is worth noting the effect of assuming 0.1% N in the fuel by weight. The sensitivity is apparent. The results, in general, show the apparent need to account for additional mechanisms, such as HC and HCN species and reactions, particularly in the fuel-rich regions.

In many practical systems the fuel is injected in the form of a spray. Furthermore, liquid water injection also has played a role in combustion systems and has been considered for NO_x control. Figure 5 shows a comparison of our predictions with data for NO_x reduction using water injection. The data were obtained from a jet engine combustor tested at Pratt and Whitney Aircraft. The water was injected through a 10 width slit. The agreement, assuming 10 size droplets in the calculations, is quite good. This result raises an interesting question regarding two-phase flow in intense backmixed regions. Although the gas-phase components in a

well-designed combustor will tend to be perfectly mixed, the spray generally will not be mixed to the same degree. This is due to the spectrum of sizes and velocities of the droplets generated at their point of injection. The larger droplets will follow ballistic trajectories governed by their initial momentum and low drag whereas only the very small ones will tend to follow the turbulent fluctuations and diffuse like any of the gas-phase components. In general, a residence time distribution must be taken into account in the modeling of the combustion of multiphase systems. In terms of the comparison I have just shown (Fig. 5) it might be that we have demonstrated that the droplets are indeed small (perhaps even smaller than 10μ) and that for practical purposes the water was vaporized on injection. Note that the computed result, assuming steam injection, is practically identical to the 10 size droplet injection result. Thus, although one must be careful about generalizing these results, I should point out that these calculations represent the first of their kind. The only prior results are in the form of linear empirical correlations. They predict unrealistically high NO_x reductions when the water-to-fuel weight ratios are above about 40%.

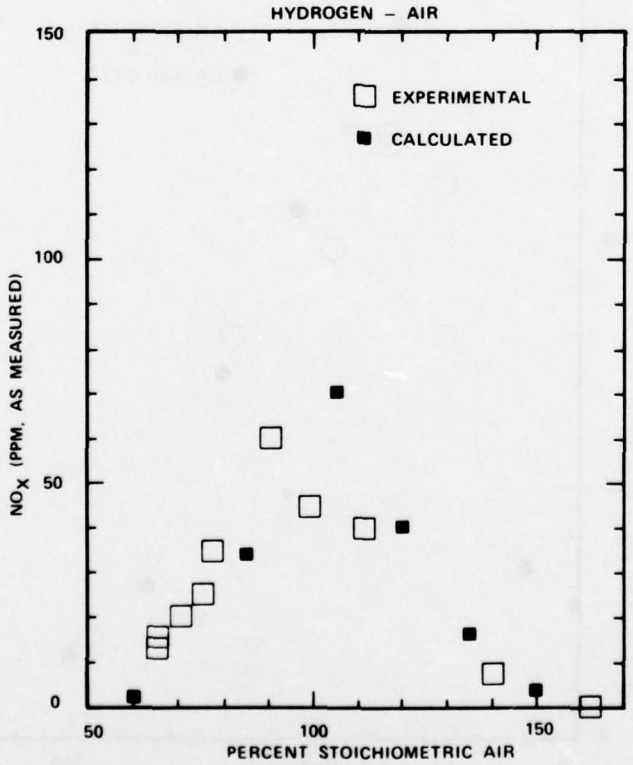


Fig. 2 Comparison of stirred reactor theory with experimental data for NO_x emissions from an H_2/air jet stirred reactor.

I would like to conclude by stressing several points: 1) The first pertains to the modeling of the chemical kinetics of alternative fuels combustion. It appears that quasiglobal modeling can provide relevant information on a near-term time scale. 2) Relatively simple characterizations of the combustion process make it feasible to treat the real problems of combustor design and performance when aerodynamics and chemical kinetics are coupled -- that is, computational time can be a controlling factor severely limiting the utility of large chemical kinetic shcemes. 3) Basic kinetics and mechanism studies on the pyrolysis and oxidation of aromatics and on soot formation should proceed in support of engineering model development. 4) Although aerodynamic coupling, including turbulence and mixing, was not discussed in this workshop, I must emphasize its relevance to many of the basic experimental facilities that are ostensibly designed and reported to be kinetically controlled. Like kinetics, turbulence is some way off from being fully understood. Nevertheless, modeling of turbulence and of the interaction of turbulence with chemistry has progressed to a point where accounting for the coupling

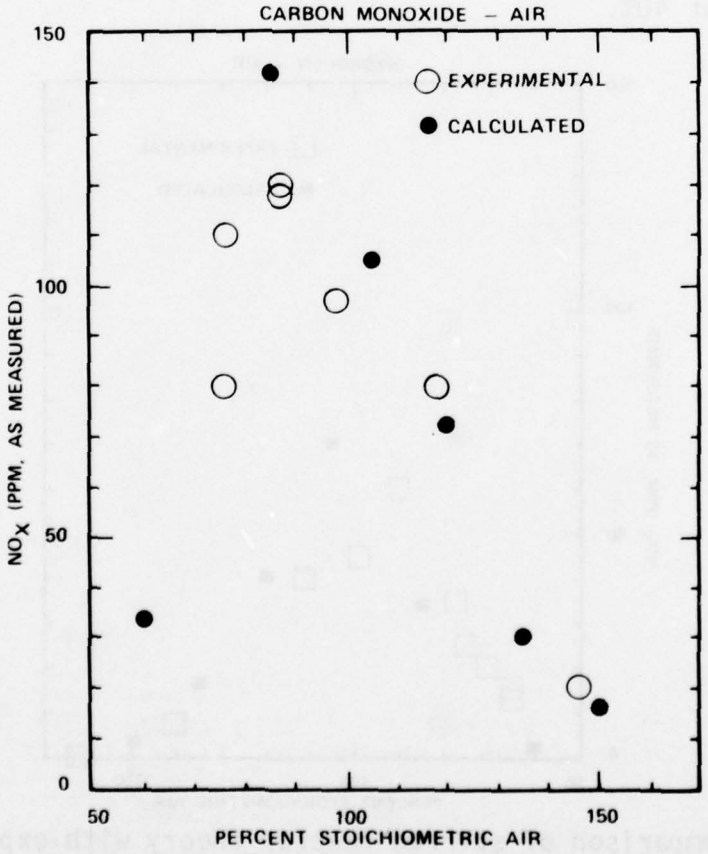


Fig. 3 Comparison of stirred reactor theory with experimental data for NO_X emissions from a CO/H_2 jet stirred reactor.

can be done. We can now hope to do a more in-depth job of interpreting experimental results as well as doing more realistic modeling of practical combustors. Of course, advances in the application of numerical methods and computer capability play crucial roles in the development of practical models.

DR. R. B. KLEMM (Brookhaven National Labs): You made some general comments about the importance of HO_2 reactions, especially in certain regimes. In particular, you indicated that the formation of CO_2 was influenced by the reaction of HO_2 with CO. Are you able to estimate the rate constant for that reaction from your data? If, so, what is the value you derive and how does it compare with direct measurements?

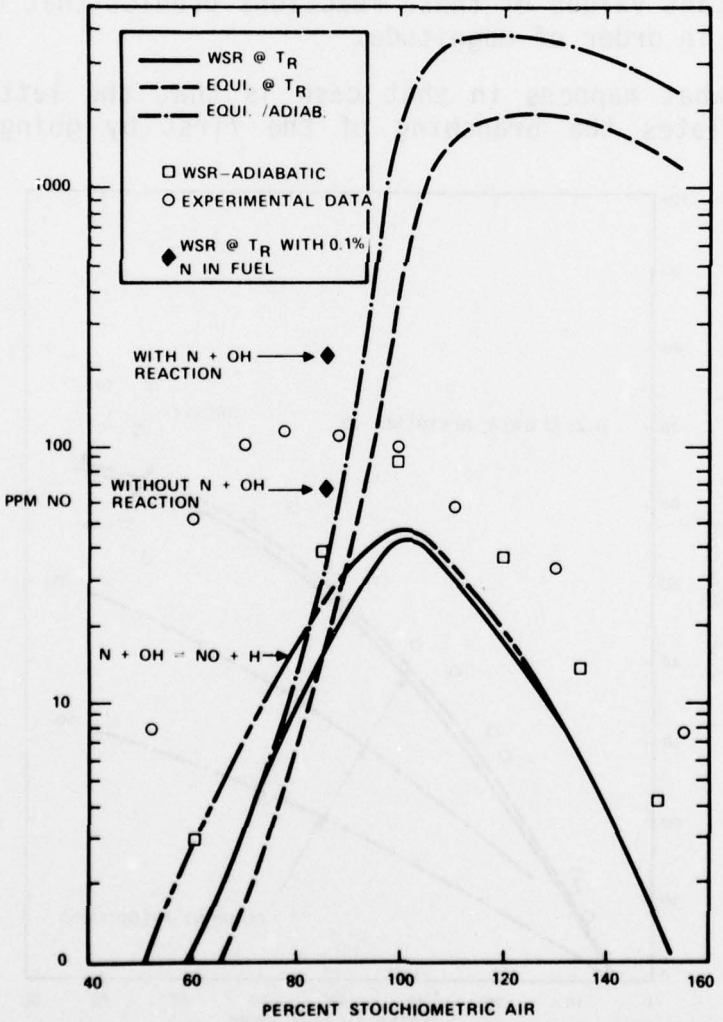


Fig. 4 Comparison of stirred reactor theory with experimental data for NO_x emissions from A C_3H_8/air jet stirred reactor.

DR. DRYER: In the 16th Combustion Symposium, in a paper by Colket et al., you will find an estimate of this reaction rate constant which was derived from studies of acetaldehyde oxidation in a flow reactor. The value so determined supports the suggested high activation energy for the CO + HO_2 reaction. We are currently looking at other approaches to estimate this reaction rate constant.

Let me answer the questions asked by Dr. Edelman on HO_2. The reason that I have concluded that HO_2 is important at much higher pressures is because of the competition between $H+O_2$ -> OH+O and $H+O_2+M$ -> HO_2+M. If one raises the pressure, obviously the second reaction becomes faster. It is still in the fall-off region because of the simple molecular structure. At 1500 K, if one raises the pressure to 10 atm, the current rate constant values of these reactions predict that the rates are equal in order of magnitude.

Now what happens in that case is that the latter reaction modulates the branching of the first by going through

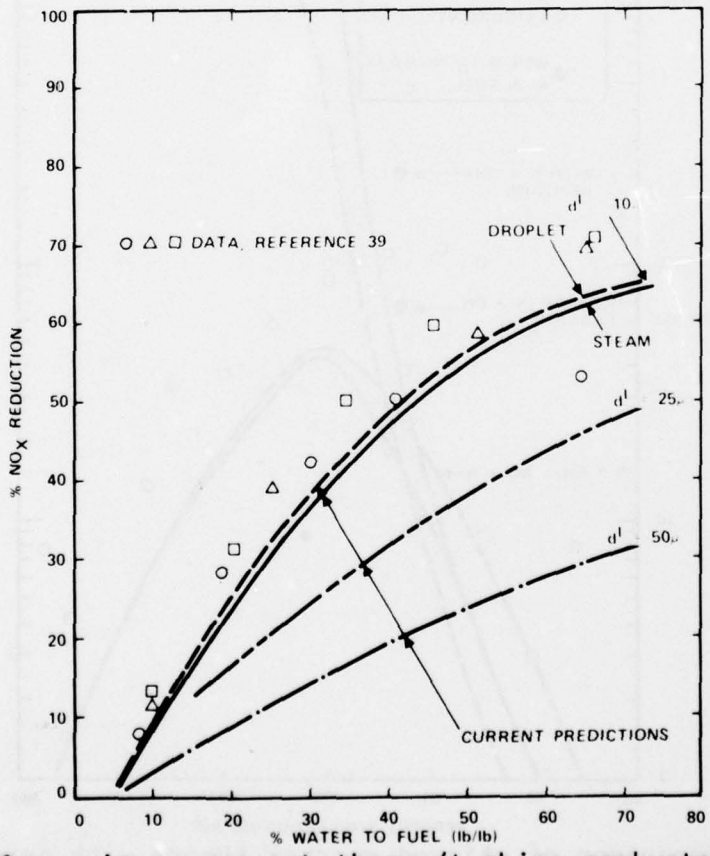


Fig. 5 Comparison, present theory/turbine combuster data -- effect of water and steam injection upon NO_X reduction.

HO_2 plus H, and HO_2 plus HO_2, to form peroxide, which then decomposes to form hydroxyl. That decomposition will be very fast at those high temperatures, but nonetheless we find that the OH, O, and H concentrations are reduced in the analytical calculation when the HO_2 reactions are included.

At 1 atm, we consequently find that we cannot predict the carbon monoxide oxidation at flow reactor temperatures. When the HO_2 reactions were neglected, the predicted consumption rate of CO_2 was about a factor of three to fast.

Now, I would also like to make some general comments. If it has been interpreted from my discussion that the quasiglobal approach is a bad one, that is an improper interpretation. I beleive that a concept similar to quasiglobal modeling -- that is, in some what combining the detailed hydrogen-oxygen and CO mechanisms with empirical models for hydrocarbon oxidation -- is a very important approach. Let me explain why. In terms of quenching reactions of CO, one needs to know the hydrogen-oxygen mechanism and how OH, O, and H vary as the temperature is quenched by dilution in order to predict CO quenching in many practical combustion systems.

The second important segement of including those systems is modeling combustion in which the residence times are very short and NO is produced. There, superequilibrium concentrations of O atoms produced through the hydrogen-oxygen mechanism become very important.

Now, the third area in which the hydrogen-oxygen mechanism is important is in the determination of SO_2 - SO_3 conversion which occurs in quenching of fuels that are burning sulfur. When one quenches the CO oxidation, there is nothing around to react with O atoms. CO does not react with O atoms very well. So there is a superequilibirum concentration, if you will, of O atoms built up upon quenching of the CO-hydrogen-oxygen mechanism which are available to react with SO_2 and form SO_3. Thus, to predict the SO_2-SO_3 ratio during quenching properly, one needs to include the hydrogen-oxygen mechanism.

Now, the one criticism I do have of the "quasiglobal" concept is I believe that we should be looking at modeling the hydrocarbon oxidation with more than one simple, single-step reaction.

If one starts to talk about soot formation, what one is interested in is soot precursor species production. The soot precursor species production comes from the olefin.

It does not come from the paraffin in the case of alkane oxidation. Let us reconsider Fig. 8 of my paper. What we are interested in here is the production of acetylene. You will note that acetylene occurs in the oxidation reaction of the hydrocarbon after the olefin oxidation, which in turn follows the paraffin disappearance. So to relate properly the time at which soot precursor species start to develop, one has to predict when the olefin oxidation occurs. Thus, I believe that some sort of "quasiglobal" model is the way to go, but the way to go is in modeling the overall hydrocarbon oxidation with at least two steps. The two steps that I see are: 1) the conversion of the paraffin to olefin species, which we can predict in ratios based upon elementary reaction chemistry and hydrogen; and 2) the olefin going to carbon monoxide and hydrogen. Those two steps would be combined with the full elementary reaction set composed of the $H_2/O_2/CO$ reactions, including HO_2.

Now this leaves one further step that can be done as detailed development comes along, and in particular detailed development on acetylene oxidation and its production from ethylene. Since we can get more detailed information on that mechanism and there is quite a bit already in existence on acetylene, but very little on the production of acetylene from olefin, we can then add that to the empirical model and predict, hopefully from acetylene production, a correlation for the rate of formation of soot precursor species. I believe we should approach the soot formation problem along these lines rather than with a single-step reaction.

DR. EDELMAN: We are just underway on a Department of Energy program with EXXON Engineering and Research Company to develop an understanding of the relationship between the properties of alternative fuels and their combustion characteristics. Our approach to the chemical kinetics aspects of this problem involves extensions of our original quasiglobal mechanism. It is gratifying to see that Dryer's data seem to support what we had already believed to be necessary in more realistically modeling the important reactions early in the "oxidation" process. The advanced modeling includes a multiple-step subglobal scheme bridged to a detailed set of reversible reactions. This modeling provides for a manufacturing process that includes, for example, olefins from paraffins, prior to the formation of soot. Pyrolysis, soot formation, and soot oxidation are included in the overall oxidation mechanisms.

DR. B. S. HAYNES (University of Gottingen): I just wanted to make a brief comment about the appearance of hydro-

carbons in the burned gases of flat flames. When you make a premixed flat flame fairly rich, hydrocarbons suddenly start breaking through beyond the critical stoichiometry. The only hydrocarbons that you actually see there, until you get a lot richer, are methane and acetylene. Of those, acetylene is usually the more important, but it also decays in the burnt gases faster than methane.

DR. DRYER: The acetylene produced is a function of the olefin oxidation.

DR. HAYNES: I believe that too. If you go quite a bit richer, then you start to see things like propylene and butane. They do look to be correlated.

DR. DRYER: I would also suggest that the methane is a function of the methyl radicals that do not burn very well.

DR. D. GARVIN (National Bureau of Standards): I agree that quasiglobal modeling is the way things are going to go, but you still want the chemical kinetics data in order to see that you model is going the right way.

There is a crucial point on which I hope people will comment later -- namely, how good does this global model have to be for what purposes? Because if the case is that a factor of two, a factor of three, or a factor of four is considered good agreement, then this will simplify the amount of work that has to be done to provide good laboratory data. However, if the statements that have been made so far are merely to convince people that modeling is getting someplace, but it is not yet good enough for the engine designer, then the kineticists need to know that. Modern rate data can be good to plus or minus 20% -- really no better than that over a wide range. I am being optimistic when I say that.

Suppose you put 50 chemical reactions into a model and do sensitivity studies. If the rate constants were all good to plus or minus 20%, you would have <u>at least</u> a 50% error bar on your model output. Now in an atmospheric modeling, to take a case in which sensitivity studies have been made, the errors on the rate constants range from 20% to a factor of 3. As a result, the models are rated as good to a factor of four. You may be faced with similar cases in the combustion model, but if a factor of four is good enough, then probably the kineticist can help fairly rapidly. If you want a factor of 50%, then a great deal of kinetics work will have to be done to help out.

DR. DRYER: I am glad you brought that problem up again because I would like to re-emphasize again what you said and what I said. I do not believe that there is any way that quasiglobal models can be successfully developed unless they are developed in hand with good qualitative experimental data -- and I mean qualitative data, not detailed chemical kinetic data -- and the development of good reliable chemical kinetic information for detailed reactions. Both of these things will be necessary.

DR. GARVIN: How good do you want the kinetic data to be?

DR. DRYER: I believe that for most NO_x productions in practical systems, as Dr. Blazowski showed, at the high inlet temperatures, which is what we are striving for, early NO formation from kinetic overshoot concentrations is not an important problem. That means we probably can be off somewhat in predicting in positions where flame temperatures are reached. So, in the sense of NO_x emission modeling, probably we do not need such an accurate system. In the sense of how heat release affects the fluid mechanics in combustion systems, I believe we need a reasonably accurate system. I would say a factor of two to four is probably as good as we are going to do now. Maybe we will have to be satisfied with that.

In the case of soot formation, we are going to have to refine the model considerably before we can get anywhere near predicting that problem. I am not even too hopeful that in the long run the problem is going to be capable of analytical prediction.

DR. GARVIN: What you have said is that the numerical values of the rate constants are much less important than knowing what the chemistry is that is going on. If the kineticists can tell you that, you can build your quasiglobal model.

DR. DRYER: No, we actually need to know a little bit more than that. We need rate data. For example, in the case of estimating what the ratios of the various olefins which are formed from the alkane species, I need to know what the primary, secondary, and tertiary attack rates are.

DR. GARVIN: Dr. Golden can estimate that for you.

DR. DRYER: That is right, but that is my point.

DR. GOLDEN: Not with aromatics.

DR. DRYER: With aromatics, no information exists on how the ring structure breaks.

DR. GARVIN: All right, let us get to work on the aromatics, and we can all avoid experiments.

LIQUID-PHASE REACTIONS OF VAPORIZING HYDROCARBON FUELS

Alexander Vranos*
United Technologies Research Center, East Hartford, Conn.

Abstract

The objective of this study was to explore chemical and physical interactions that occur during surface vaporization of hydrocarbon fuel. Hydrocarbon product distributions were determined from the decomposition of air-saturated, n-hexadecane vaporizing from a heated surface into a stream of heated nitrogen carrier gas. Surface temperature was varied over the range 482°-313°C. Hydrocarbon product distributions are described over most of the range of experimental conditions by a radical chain mechanism. It is found that liquid-phase reactions play a more important role as temperature decreases. The fraction of fuel decomposed, as hydrocarbon product, was found to increase with increased surface and carrier gas temperature. On the other hand, oxygenated products consisting primarily of C_{16} hydroperoxides, alcohols, and ketones decrease as temperature increases. Oxidation reactions occur primarily in the liquid phase, and product turnover occurs at about 400°C. Heat-transfer effects strongly influence product distributions and product levels. Further work is needed to explore the effects of the nature of the surface, heat-transfer rate, oxygen concentration, and fuel properties on the extent of fuel decomposition and the nature of the products formed.

Introduction

Fuel vaporization and heating processes are important in a number of powerplant applications. In liquid-fueled combustors, the rate of vaporization and the conditions under which vaporization is realized strongly affect combustor performance. In gas turbine combustors and in prototype residential oil burners, it has been demonstrated that improved performance and lowered emissions result when fuel is vaporized prior to injection into the combustor. The use

* Consulting Scientist.

of alternate hydrocarbon fuels will impose conflicting requirements on the combustion system, however, since these fuels may exhibit accelerated decomposition upon heating,[1] resulting in the formation of deposits on vaporizer or precombustion reactions can alter fuel characteristics and lead to the formation of pyrolysis products that are subsequently difficult to burn. Detailed data describing the chemical effects attending vaporization are needed in order to understand the practical implications of these precombustion processes. Such data are not available, however, even for simple systems. Therefore, basic information on critical parameters that influence chemical and physical changes in vaporizing fuels will provide technology for more efficient combustors and for combustors that can burn a wider variety of fuels.

A considerable amount of work has been done on thermal stability of fuels under Navy and Air Force sponsorship which provides useful background for studying chemical effects in fuel vaporization. Important variables affecting the thermal stability of aircraft fuels have been identified in studies of fuel cooling of supersonic aircraft components. It has been shown that fuel stability is affected strongly by temperature, hydrocarbon composition, certain oxygen, nitrogen, and sulfur compounds, dissolved oxygen, and the nature of the heated surface. The physical state (vapor or liquid) of the fuel is also important. Although a significant body of empirical data has been generated on deposit formation rates (a measure of fuel decomposition rates), detailed mechanistic data are lacking, and these studies have been confined mostly to the liquid phase. In vaporizing systems, the relative importance of certain variables may be modified. For example, recent tests at United Technologies Research Center (UTRC) confirmed the importance of dissolved oxygen in deposit formation. As in liquid-phase heating experiments, deposits from vaporizing No. 2 fuel oil were reduced substantially when the oil was deoxygenated. In contrast to liquid-phase heating experiments, however, it was found that deposits decreased when surface temperature was increased. Similar results have been reported by Morgenthaler.[2] This result is attributed to the fact that the rates of certain liquid-phase polymerization and condensation reactions do not keep pace with the rate of liquid-phase removal.

Direct injection of liquid fuel into the combustor can lead to the formation of solids through either liquid- or vapor-phase reactions. In gas turbines, these solids can lead to combustor wall deposits, degradation of combustor performance, and/or erosion of turbine components. Also, it

has been observed in industrial furnaces that heavy oil combustion leads to droplet residues that require an exceedingly long time to burn. The nature of these residues depends upon the heating cycle of the droplet and whether it has been exposed to an inert or oxidizing atmosphere.[3] Because of the higher environmental temperatures and the absence of surfaces, the nature of the pyrolysis reactions and the initiation mechanism in the combustor environment may be significantly different from those in the vaporizer environment. Fundamental data also are needed, therefore, to understand pyrolysis kinetics in vaporizing droplets.

The purpose of this paper is to present some new results from an exploratory study of the decomposition of surface vaporized fuel. Reaction products have been measured by direct sampling of the vaporizing fluid and at the exhaust of a simple vaporizer. Hydrocarbon and oxygenate measurements are used to provide insight into the extent of liquid- and vapor-phase decomposition and the interactions between chemical and heat-transfer processes. In order to understand the important of physical processes, a single-component fuel, n-hexadecane (air-saturated), is being studied initially. Hexadecane was selected as a study fuel because of its boiling point and simple molecular structure. Future tests are planned with multicomponent fuels.

Experimental

A schematic of the vaporizer cross section is shown in Fig. 1. The vaporizer consisted of three separate sections: the lower heating section, the vaporizing section, and the upper heating section. The vaporizing section was placed in close contact with the lower heating section and was heated by conduction. The upper heating section served to preheat the carrier gas. The upper section also has two sight ports, which allow illumination and observation of the working surface. A third port was used to admit a cooled sampling probe. With the exception of the stainless-steel gas manifold wall and flanges, the vaporizer was made entirely of copper. All surfaces were nickel-plated. The carrier gas entered the vaporizer cavity through 48 0.34-mm holes located uniformly around (and above) the vaporizing surface. Temperatures of the vaporizing surface and upper heating section were controlled separately by the use of two LFE model 238-13 temperature controllers and two 2500-W Vectrol power controls. One 0.95- x 7.6-cm 100-W heater was used to heat the upper section, and three 1.27- x 5.1-cm 250-W resistance heaters were used to heat the lower section. Temperatures were held to $\pm$ 0.5°C during a run. Nitrogen carrier was

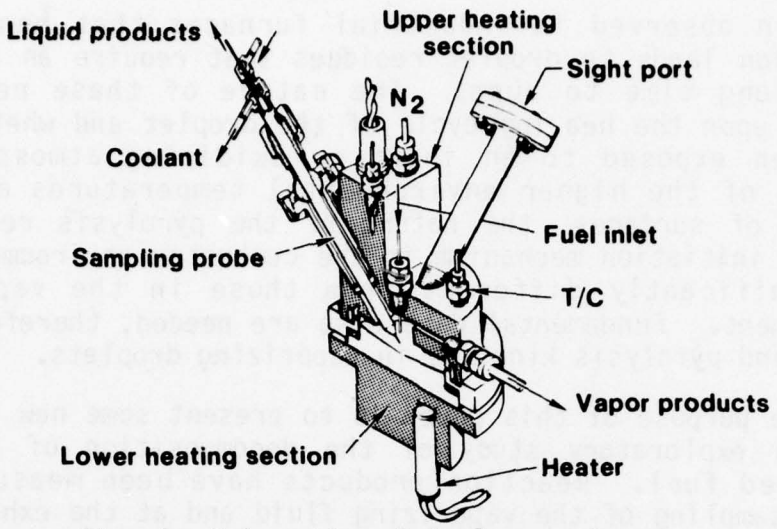


Fig. 1 Schematic of fuel vaporizer.

preheated in the upper heating section and fed to the gas manifold through two 0.32- x 8.57-cm holes. The carrier gas emerged at the approximate upper section temperature, as determined by thermocouples located in the gas manifold and upper section. Surface temperatures were measured by locating seven 0.5-mm chromel-alumel thermocouples 0.25 cm below the surface at distances of 0.35, 1.11, and 1.75 cm from the center of the disk at five azimuthal locations. Spatial surface temperature variations within a 1.11-cm radius, a radius that always circumscribed the liquid radius, did not exceed $\pm$1°C. Upper surface temperatures also were measured and agreed closely with carrier temperature. The fuel was admitted to the surface through a 1.2-mm stainless-steel hypodermic tube at a point approximately 0.6 cm above the surface; boiling occurred on the surface. Minimum needle diameter was chosen to provide fuel injection without dripping and excessive fuel pressure. Steady flow of fuel was insured by use of a Greer Hydraulics hydraulic piston accumulator fitted with Buna-N "O" rings and teflon seals. The piston was pressurized with air. The fuel injector was held in place by an air-cooled, silicon rubber teflon-backed septum. Reactor effluent gas composition measurements verified that no interfering by-products were introduced by septum decomposition. The carrier flow and temperature were maintained sufficiently high so that condensation and refluxing of vaporized products was precluded within the reactor. This was confirmed by visual observation using a glass upper section. Upon leaving the reactor, the products entered a glass-sampling line with bypass. Nitrogen quench gas at ambient termperature was injected through hypodermic tubing

into the reactor effluent at the reactor exhaust. The bypass line was used until steady reactor conditions were achieved. At this point, the reactor effluent was diverted to an air condenser and sample collection system. When steady conditions were attained in the condenser, vapor and liquid samples were collected. Samples of the vaporizing fluid also were obtained directly by means of a convectively cooled, 0.12-mm-i.d. x 0.51-mm-o.d. stainless-steel sampling probe. The probe body was contained in a waterjacket maintained at 46°C, and the tip of the probe extended 2.5 mm from the body. In this way, only the probe tip entered the vaporizing fluid. Sample flow was maintained sufficiently low (about 25% of fuel flow) so that the puddle size remained essentially constant during sampling.

One of the concerns in this experiment was possible change in dissolved oxygen level during fuel transfer as a result of leakage or preheating of the fuel. In order to insure that the partial pressure of oxygen (0.21 atm) was not exceeded during the run by leakage of pressurized air into the fuel, the accumulator was leak-checked by pressurizing the cylinder with methane on the high-pressure side and air on the delivery side. Using methane as a tracer, it was determined that no signficant leakage occurred across the seal. The fuel feed line also was fitted with a transparent loop section at the uppermost point in order to verify the absence of trapped air in the line. Heat-transfer calculations indicated negligible preheating of the fuel prior to injection. The hexade-

Table 1 Test conditions

T_s,°C	T_{N_2},°C	N_2 flow, cm^3/min	Fuel flow, cm^3/min	Surface
482	482	1275	1.5	Ni
416	416	1275	1.5	Ni
	282			
371	371	1275	1.5	Ni
	282	1275	1.5	Ni
	259	3000	1.5	Ni
319	319	1275	1.5, 6	Ni
	235			
313	235	1275	1.5	Ni, C

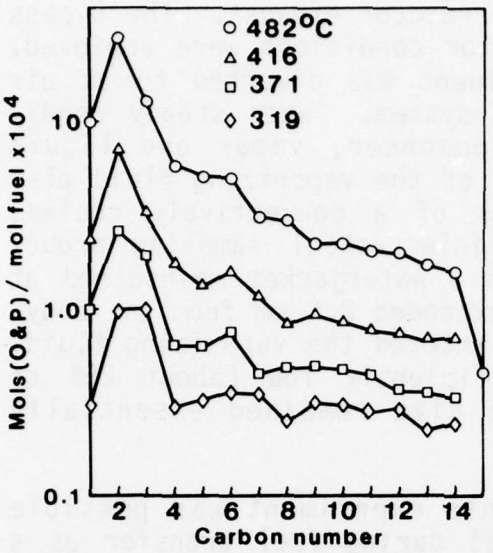


Fig. 2 Measured hydrocarbon product distributions.

cane was air-saturated by bubbling air through the hexadecane at 1 liter/min for a period of 1 h prior to testing. Dissolved oxygen level was not measured; however, the solubility of oxygen in hexadecane at a partial pressure of 0.21 atm is estimated to be 600 ppm by mole. The fuel used in these studies was olefin-free, 99.6% n-hexadecane obtained from Eastman Kodak. The fuel contained about 1000 ppm of one major polar impurity, tetradecanol, which was removed with silica gel. Analytical details are given in the Appendix.

Discussion

Hydrocarbon Product Distributions

Test conditions for hydrocarbon measurements are given in Table 1. Primary variables were surface and carrier gas temperatures, and most tests were conducted with a nickel surface. Since surface deposits were observed to form during the course of testing, a limited number of tests were conducted with a model surface of pure graphite in order to evaluate the effect of surface type on extent of decomposition and product distributions. Overall decomposition rate was accelerated by graphite, but product distributions did not change.[4]

Hydrocarbon product distributions were determined for most of the conditions shown in Table 1. All significant hydrocarbon products were identified and found to consist of C_1-C_{15} n-paraffins and 1-olefins. Hydrocarbons heavier than hexadecane were not found. Product distributions for "isothermal" tests, i.e., equal surface and carrier gas

temperatures, are shown in Fig. 2, where the total moles of olefin and paraffin formed per mole of fuel vaporized are shown as a function of carbon number. It is seen that, as temperature increases, the total amount of fuel reacted increases, and the proportion of lower molecular weight components increases. It also is found that the fraction of fuel decomposed is very small, 0.22% at the highest temperature studied (483°C). For this reason, C_{15} compounds were not always measured because of low concentration. Although the composition measurements represent conditions at the reactor exhaust and thus reflect the integrated effects of vapor- and liquid-phase reactions, oxidation reactions, and physical processes within the reactor, it is possible to assess qualitatively the relative importance of some of these factors from detailed analysis of the hydrocarbon product distributions. This has been done, primarily, by applying the principles of the Rice-Kosiakoff radical chain mechanism of hydrocarbon cracking to the interpretation of the data. Oxygenate measurements support the conclusions derived from the hydrocarbon study.

Description of the Chain Mechanism

The Rice-Kosiakoff mechanism has been applied previously with great success to the description of vapor-phase cracking of lighter hydrocarbons to C_9.[5] The mechanism is reviewed briefly in subsequent paragraphs; however, the reader is referred to the original paper[6] or to an excellent review article by Fabuss et al.[7] for full details. According to Rice and Kosiakoff, hydrocarbon cracking proceeds by a radical chain mechanism wherein the parent molecule undergoes hydrogen abstraction by attacking radicals followed by radical isomerization and C-C bond rupture into smaller molecules and radicals. Thus, in the chain decomposition of hexadecane, primary and secondary hexadecyl radicals are formed first; they then isomerize to form an equilibrium distribution and then decompose according to fixed rules to form olefins and smaller radicals. If, after one decomposition step, the first radical set abstracts hydrogen from the parent molecule, the cycle is completed and the process is called a one-step decomposition.[11] If, however, the radical set decomposes again before becoming stabilized by hydrogen abstraction, the process is called a two-step decomposition, etc. The theory predicts that only n-paraffins and 1-olefins are formed. It is found that the olefin content of the distribution increases rapidly with the number of decomposition steps. Theoretical product distributions have been computed by Fabuss et al. for hexadecane decomposing at 649°C for four decomposition steps and less. The results are shown in Figs.

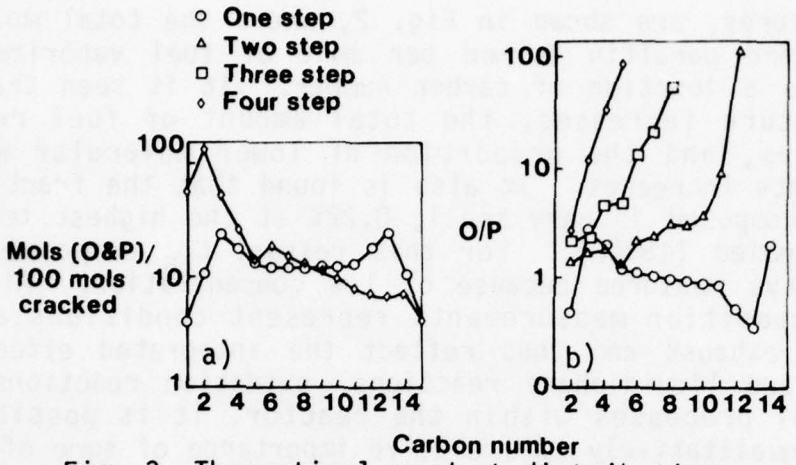


Fig. 3 Theoretical product distributions.

3a and 3b in the form of total carbon and olefin/paraffin ratio distributions, respectively. Take together, Figs. 3a and 3b completely specify the olefin and paraffin distributions. The total carbon distributions (Fig. 3a) clearly show that increasing the number of decomposition steps leads to increased production of lower molecular weight products, but it is seen that the olefin/paraffin ratio (Fig. 3b) provides an even more sensitive indication of the number of decomposition steps. The actual number of decomposition steps achieved depends upon temperature and the molar density of the fuel. It would be expected that increased molar density would lower the number of decomposition steps and hence lead to increased paraffin content. This effect has been demonstrated in tests at elevated pressures and provides further confirmation of the theory.[8] Accordingly, the presence of liquid-phase reactions should provide increased paraffin levels if the theory is valid in the liquid phase. Under these conditions, the olefin/ paraffin ratio should approach unity.

Comparison of Theory and Experiment

The experimental results can be explained, for the most part, in terms of the chain mechanism previously described. The effect of simultaneous vapor- and liquid-phase pyrolysis reactions can be seen by comparing these results with the data of Voge and Good,[9] who studied the vapor-phase pyrolysis of n-hexadecane. These authors measured the vapor-phase, oxygen-free pyrolysis of n-hexadecane in a packed bed reactor at 500°C. The data of Ref. 9 agreed generally with the predictions of the chain mechanism, although, as a result of secondary reactions, the product composition was found to be more complicated than that predicted by the theory;

branched paraffins, diolefins, and aromatics were observed. The extent of conversion was greater than 30%, more than two orders of magnitude greater than that found in this study. Despite differences in physical apparatus, extent of conversion, and oxygen level, it is found that the vapor-phase cracking data and the results of this study are remarkably similar at comparable temperature levels when total carbon distributions are compared. In addition, total carbon

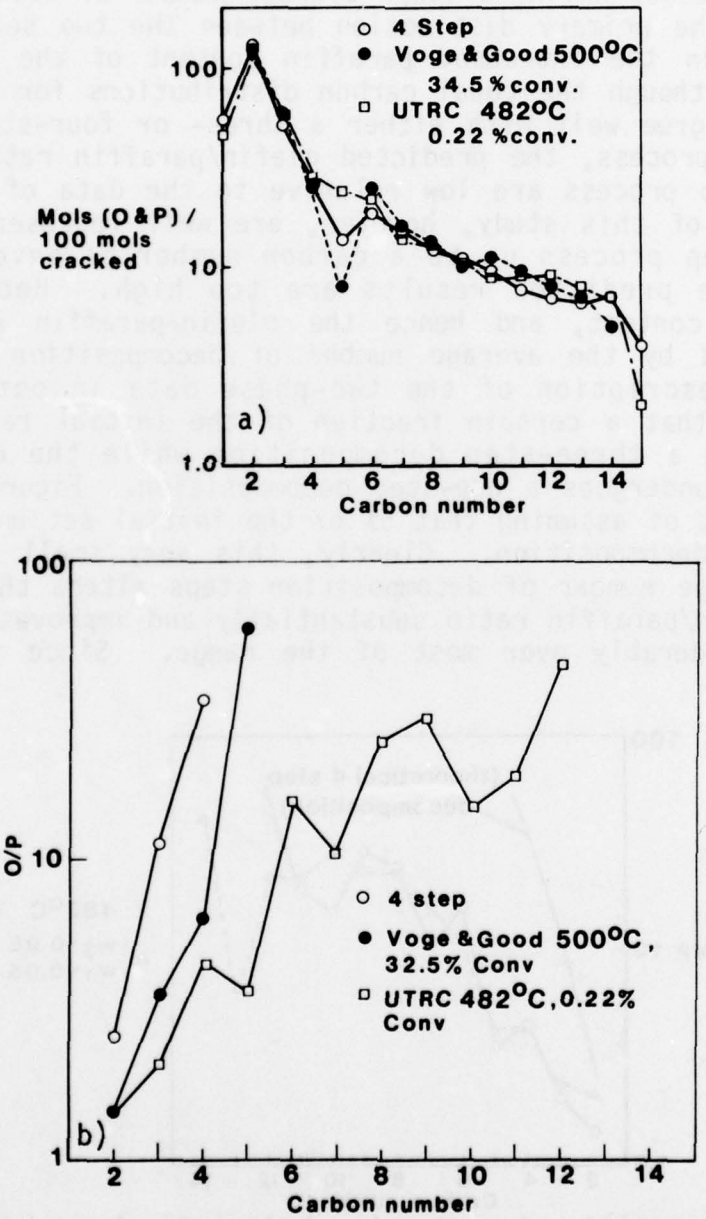


Fig. 4 Comparison of measured and theoretical product distributions.

distributions for both sets of data are in good agreement with either a three- or four-step decomposition process. The experimental results are shown in Fig. 4a and compared with a predicted four-step decomposition process. Differences between the two sets of data become more apparent when olefin/paraffin ratios are compared, reflecting primarily the extent of liquid-phase reactions. When the data are compared in this way, as in Fig. 4b, it is seen that the olefin/paraffin ratio distribution for the two-phase data is consistent with a process having a lower average number of decomposition steps. The primary distinction between the two sets of the data is in the increased paraffin content of the two-phase data. Although the total carbon distributions for both sets of data agree well with either a three- or four-step decomposition process, the predicted olefin/paraffin ratios for a three-step process are low relative to the data of Ref. 13. The data of this study, however, are well represented by a three-step process up to a carbon number of seven, after which the predicted results are too high. Because the paraffin content, and hence the olefin/paraffin ratio, is determined by the average number of decomposition steps, a better description of the two-phase data is obtained by assuming that a certain fraction of the initial radical set undergoes a three-step decomposition while the remaining fraction undergoes a one-step decomposition. Figure 5 shows the result of assuming that 5% of the initial set undergoes a one-step decomposition. Clearly, this very small change in the average number of decomposition steps alters the predicted olefin/paraffin ratio substantially and improves the data fit considerably over most of the range. Since the total

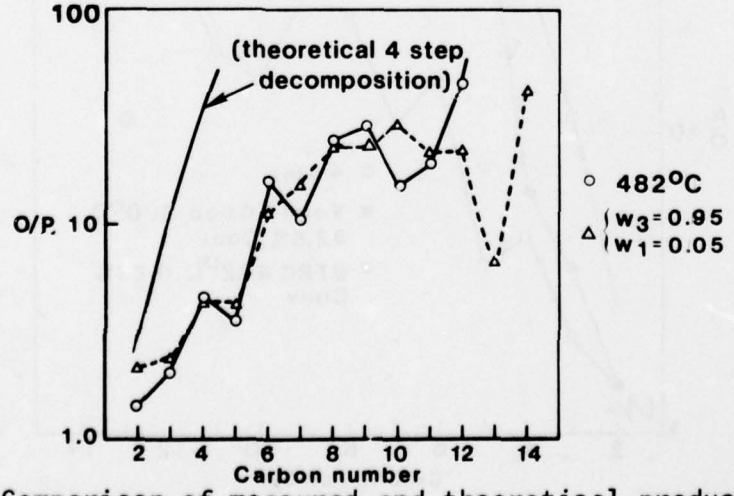


Fig. 5 Comparison of measured and theoretical product distributions.

carbon distribution is not very sensitive to the number of decomposition steps, it is found further that the predicted total carbon distribution is not changed by introduction of a 5% one-step weighting factor. At lower temperatuare, 415°C, a comparison of measured and predicted distributions indicates that nearly the same weighting factors apply as at the higher temperature. In order to conserve space, these data are not shown. Inspection of the total carbon distribution indicates that a slight increase in the one-step weighting factor would improve the agreement between measured and predicted values; however, a better fit of the olefin/paraffin distributions results by retaining the assumption that 5% of the reacted fuel undergoes a one-step process. No attempt has been made to obtain a "best fit" of the data at either temperature, since the general dependence of the weighting factors on operating conditions became evident as more data were examined. Physically, one can conclude that the lower olefin/paraffin ratio and lower average number of decomposition steps in both cases is due to the presence of liquid-phase reactions. This can be seen by comparing estimated liquid- and vapor-phase reaction rates.

The number of decomposition steps depends upon the relative rates of radical decomposition and abstraction and, hence, upon the temperature and molar density of the fuel. Assuming a liquid-phase density of 2.5 moles/liter and a mean vapor density of 2.3×10^{-3} moles/liter, it is possible, using gas-phase rate parameters, to estimate relative rates of radical decomposition and abstraction in the liquid and vapor phases. Typical rate parameters are $A = 10^{13.6}$ sec^{-1}, $E = 29.3$ kcal for butyl radical decomposition[10] and $A = 10^{11.7}$ cm^3/mole-sec, $E = 10.6$ kcal for abstraction of secondary hydrogen by ethyl radical.[11] Results are shown in Table 2 for liquid hexadecane and for the vapor hexadecane/nitrogen system. Table 2 shows that one-step reactions are highly favored in the liquid phase, whereas multistep reactions are favored in the vapor phase.

Table 2 $\dot{R}_D/\dot{R}_A$

T,°C	Liquid	Vapor + Nitrogen
288 (nucleate boiling point)	1.86×10^{-3}	2.05
319	4.84×10^{-3}	5.32
371	1.7×10^{-2}	18.7

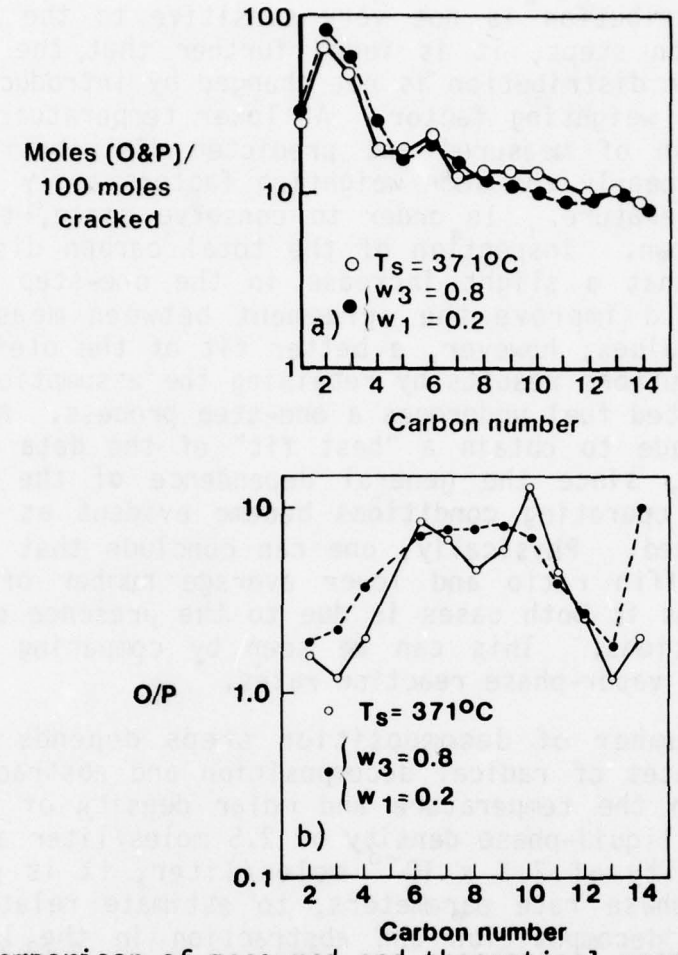


Fig. 6 Comparison of measured and theoretical product distributions.

The data indicate that as system temperature decreases the relative contribution of liquid-phase reaction increases (Fig. 9). This probably occurs because the average liquid temperature does not vary as much as the system temperature. Therefore, the effect of reduced temperature is to increase the relative importance of liquid-phase reactions and simultaneously lower the average number of decomposition steps. The data fits confirm this. A comparison of measured and predicted distributions at 371°C indicates that the one-step weighting factor increases substantially relative to that obtaining at higher temperatures, and the average number of radical decomposition steps decreases. It is found that at 371°C the olefin fraction is considerably lower at higher carbon numbers, and an excellent fit of the data is obtained by assuming that 20% of the reacted fuel undergoes a one-step process. The results are shows in Figs 6a and 6b. Data obtained at reduced carrier temperature are consistent with

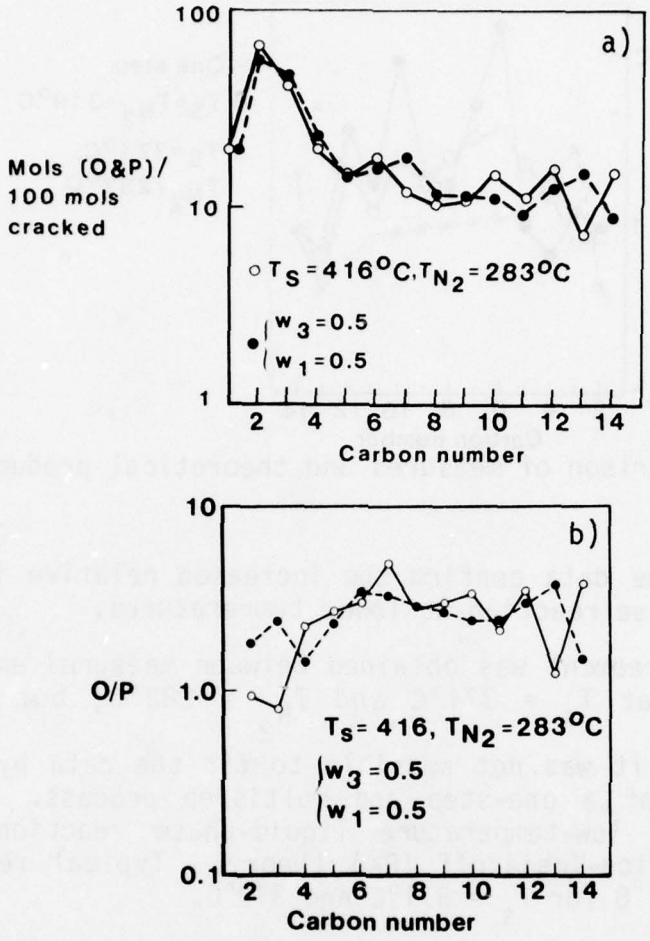


Fig. 7 Comparison of measured and theoretical product distributions.

the preceding results. A series of tests was conducted with carrier gas temperature reduced relative to surface temperature, thereby accentuating the effect of liquid-phase reactions. Suppression of vapor-phase reactions was effective in all cases (Fig. 9), and, at the lowest temperatures studied (T_s = 313°C and T_{N_2} = 235°C), it is believed that reaction occurred entirely in the liquid phase. Product distributions are consistent with lower gas temperature, as shown in Figs. 7a and 7b. At a surface temperature of 416°C and a gas temperature of 282°C, it is seen that an excellent fit of the data results if the one-step component is increased to 50%. At lower surface temperature, 371°C, and a carrier temperature of 282°C, it is found that the one-step component increases to approximately 80%, and, at the lowest temperature studied, the total carbon distrbution is described roughly by a one-step process as shown in Fig. 8.

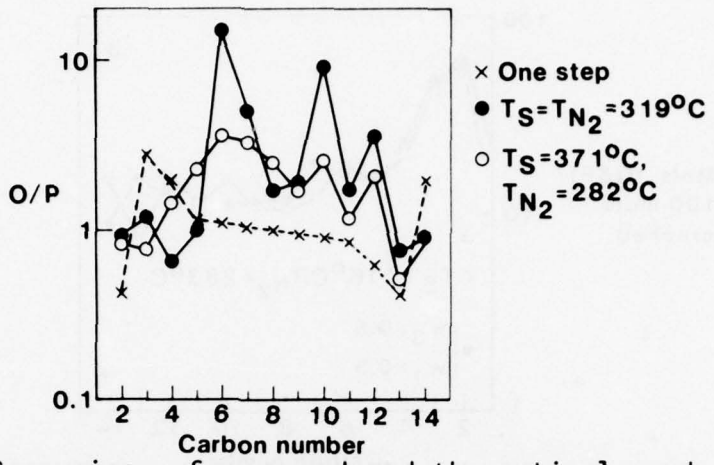


Fig. 8 Comparison of measured and theoretical product distributions.

Therefore, the data confirm the increased relative importance of liquid-phase reaction at lower temperatures.

Fair agreement was obtained between measured and predicted values at T_s = 371°C and T_{N_2} = 282°C, but at lower temperatures it was not possible to fit the data by a simple combination of a one-step and multistep process. Thus, it appears that low-temperature liquid-phase reactions do not conform to Rice-Kosiakoff (RK) theory. Typical results are shown in Fig. 8 for T_s = 371°C and 319°C.

In order to determine the validity of the assumed one-step liquid-phase decomposition process, the vaporizing liquid was sampled directly with a cooled sampling probe. Four samples were taken from the outermost edge of the liquid over the surface temperature range 288°-427°C. The data indicate that the conclusions derived from the reactor exhaust measurements are qualitatively correct, namely, that one-step pyrolysis kinetics are obeyed at sufficiently high liquid temperature. It is found that at 427°C the liquid-phase hydrocarbon distribution conforms approximately to RK theory, whereas at lower temperatuares (below 328°C), the data deviate from theory. Results are shown in Table 3. At 427°C, the only significant deviation occurs at carbon number 14 and is due to high paraffin level. High tetradecane level implies preferential formation of primary hexadecyl radicals, perhaps as a result of surface-initiated reactions. At lower temperatures, paraffin levels are high at all carbon numbers. The possibility of paraffin formation by alkoxy scission has been examined, but attendant aldehyde formation was very low, and this mechanism probably is not important. Nevertheless,

deviations from pyrolysis theory must be attributed partly to simultaneous oxidation reactions. These are discussed in subsequent paragraphs.

Oxygenates

C_{16} oxygenates, consisting of ketones, alcohols, and hydroperoxides, were found to comprise the major fraction of oxygenates. Table 4 shows a product distribution for T_s = 291°C and T_{N_2} = 233°C. C_{16} oxygenates can be used to represent total oxidation decomposition during vaporization, particularly in the liquid phase.

The hydrocarbon distributions imply that oxidation reactions become more important relative to pyrolysis reactions at lower temperatures. The oxygenate measurements confirm that this is true. It is found, for example, that not only relative but absolute levels of total C_{16} alcohols, ketones, and hydroperoxides increase as temperature decreases. Figure 9 shows the dependence of total C_{16} oxygenates and total hydrocarbon products on surface and carrier gas temperature. Data are presented for two conditions, equal surface and carrier temperatures and surface temperature higher than carrier temperature. It is seen that either increased surface or carrier temperature increases hydrocarbon product levels but decreases oxygenate levels. The effect is more pronounced in

Table 3 Liquid phase hydrocarbon analysis

Carbon number	Theoretical O/P one-step	O/P, T_s = 427°C	O/P av. of three samples
8	1.00	1.1	...
9	0.94	1.0	0.68
10	0.91	1.3	0.56
11	0.86	0.94	0.33
12	0.52	0.49	0.21
13	0.36	0.28	0.17
14	2.1	0.25	0.12

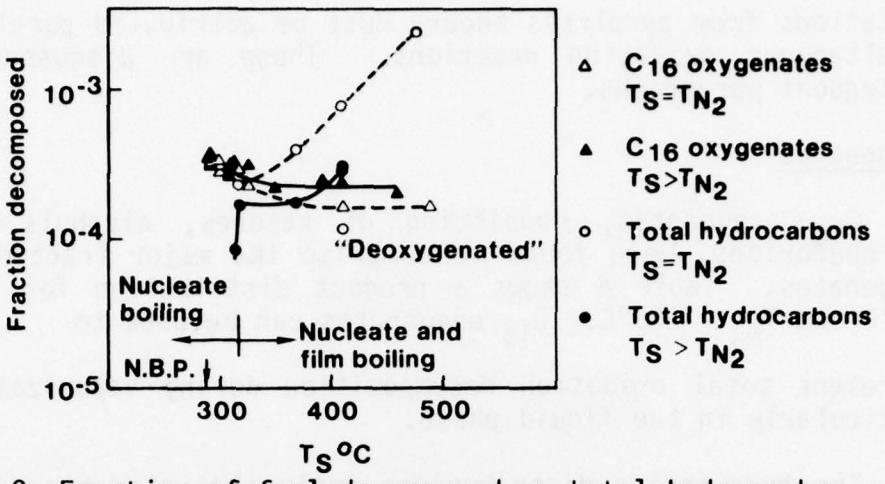


Fig. 9 Fraction of fuel decomposed as total hydrocarbon product or C_{16} oxygenates.

the nucleate boiling mode. If the hydrocarbon data are extrapolated to 288°C, the lowest temperature at which oxygenates were measured, it is seen that very low hydrocarbon levels are predicted, and the products are mostly oxygenates. Although the data show that total C_{16} oxygenates are not influenced strongly by carrier temperature, thereby indicating that oxidation reactions occur primarily in the liquid phase, hydrocarbon products are influenced by carrier temperature, thereby indicating that pyrolysis reactions occur in both phases. (In order to verify that oxygenates were not influenced by nitrogen temperature at reduced surface temperature, a series of tests was conducted wherein nitrogen temperature was varied from 170° to 288°C, whereas the surface was maintained at 288°C. Oxygenate composition was not influenced by nitrogen temperature. Thereafter, nitrogen temperature was maintained at 233°C. At surface temperature above 480°C, some heating of the nitrogen was noticed due to convective heat transfer from the working surface to the carrier gas.) Furthermore, the data show that liquid-phase oxidation and pyrolysis occur at equal rates at about 400°C. It will be recalled that this is the approximate temperature below which the hydrocarbon product distributions were found to deviate from the predictions of Rice-Kosiakoff theory. Product turnover will depend upon the reactions $R + O_2 \rightleftharpoons RO_2$.[12] In many instances, these reactions are near equilibrium,[12] and, since, the equilibrium constant decreases as temperature increases, hydrocarbon formation is favored by higher temperature. Assuming that product turnover occurs when $[RO_2]/[R] \approx 1$,[12] estimated values of $[RO_2]/[R]$ for the conditions of these tests indicate that the maximum temperature for product

Table 4 Product distribution

Product	Concentration, ppm (mole)	Rel. mole%
C_{16} ketones	165	40.2
C_{16} alcohols	97	23.7
C_{16} hydroperoxides	107	26.1
"cyclics"[a]	41	10

[a] "Cyclics" have not been identified completely; mass spectrometric analysis of these compounds indicates probable ring structure and molecular weight ranging from 212-184. Gas chromatograph/infrared analysis indicates strong absorption at 1090 cm^{-1}, a value near that of dibutyl ether (1130 cm^{-1}). Cyclics are probably substituted cyclic ethers. A mean molecular weight of 198 ($C_{13}H_{26}O$) has been assumed.

turnover, based on initial oxygen partial pressure in the liquid, is about 500°C. Also, no significant oxidation should occur in the vapor phase. Both of these observations are consistent with the data. Thus the hydrocarbon distributions may conform to RK theory whenever $[\dot{R}O_2]/[\dot{R}] < 1$.

To date, the program has shown a number of interesting chemical and physical interactions that occur during surface vaporization of fuel. Further discussion can be found in Ref. 13, where it is shown that heat-transfer effects strongly influence product levels and behavior of particular oxygenates. Before control strategies can be devised to minimize the formation of surface deposits and residues, additional experiments are needed to elucidate the role of the nature of the surface, heat-transfer rate, oxygen concentration, and fuel properties on the rate and products of decomposition.

Conclusions

Hydrocarbon measurements from surface-vaporized n-hexadecane indicate that pyrolysis kinetics describe the hydrocarbon product distributions at sufficiently high system temperature. Liquid-phase and oxidation reactions become more important at lower temperature. Deviations from theory at lower temperature are attributed primarily to liquid-phase oxidation reactions, but surface reactions also may be impor-

tant. Heat-transfer effects strongly influence product distributions and product levels. Further work is needed to explore the effects of the nature of the surface, heat transfer, oxygen concentration, and fuel properties on the extent of fuel decomposition and the nature of the products formed.

Appendix

Hydrocarbon analysis was performed using an HP 5830-A gas chromatograph with sample splitter and Perkin Elmer (0.5 mm i.d.) SCOT columns. Three columns were used: 30-m Squalane, 15-m Carbowax 20M, and 15-m DC-550. Initial hydrocarbon identifications were based upon published retention volume data. Hydrocarbon identifications then were confirmed by comparison with retention volumes of pure components. Agreement between measured retention volumes and published data was very good; in particular, the tabulated data of Polyscience Corporation[14] gave very satisfactory agreement. Peak areas were integrated electronically with the HP 5830-A digital processor/integrator. Response factors for C_1-C_6 hydrocarbons were determined from standard mixtures obtained from MG Scientific. Little difference in response factors was found for olefins and paraffins in this range. The system was calibrated carefully to insure that material balances were correct when hydrocarbons were analyzed with splitters and SCOT columns. Measured weight fractions, as determined by gas chromatography, agreed closely with standard mixtures for most components. However, at low concentrations, measured C_{12}-C_{13} component concentrations in hexadecane were always higher than the known values. Correction factors were found to be a function of concentration. Therefore, standard mixtures were prepared in the concentration range 20-500 ppm, to include the range of the data, and C_{12}-C_{13} component concentrations were corrected accordingly.

Oxygenates were measured either directly in the oxidized samples or in a methanol/isopropanol extract of the sample. Initial identifications were made on extracted materials in order to eliminate interferences from hydrocarbon products. Oxygenates first were isolated on silica gel and then extracted with methanol after stripping of nonpolar materials with hexane. The methanol then was evaporated to produce a concentrated product. Because of low product levels, the samples were allowed to sit on silica gel overnight in order to insure absorption by the silica gel. Since in some cases it subsequently was desirable to reduce the volume of methanol by a factor of 1000/1, interferences from solvent impurities, silica gel impurities, and entrained silica gel had to be eliminated. In order to eliminate interferences from solvent

impurities, chromatoquality solvents were used, and these were either distilled further or treated with purified silica gel before use. Silica gel was washed with methanol and distilled water to remove organic and inorganic impurities prior to use. This procedure also removed small pieces of silica gel which, at times, escaped filtration and contaminated the sample. The silica gel was reactivated by baking at 150°C for 4 hr.[15] The methanol extract was filtered with 5-μ PTFE filters (Millipore). Occasionally, large sample volume reduction caused formation of two-phase mixtures because of the presence of dissolved hexadecane in methanol. When this occurred, the sample was evaporated further, and isopropanol was added until a single-phase mixture was obtained.

Preliminary identifications of heavy alcohols, ketones, and aldehydes were indicated by removal with boric acid, benzidine, and FFAP precolumns, respectively.[16] Individual identifications were made by comparison with retention volumes of known compounds. Aldehydes were confirmed by comparison with known compounds on two different columns, Carbowax 20 M and DC-550. Hexadecanone-3 and hexadecanone-2 initially were identified by comparison with retention volumes of known compounds on Carbowax 20 M. Hexadecanones 4-8 were not resolved on Carbowax 20M, but all hexadecanones were confirmed by mass spectrometry. Hexadecanols were identified in a similar manner. A JEOL-D-100 mas spectrometer, interfaced to a Dohrmann gas chromatograph, was used for this purpose. Oxygenates were separated in the chromatograph by a packed, glass, Carbowax 20M column prior to mass spectrometric analysis. Reduction of C_{16} ketones to alcohols also was accomplished in MeOH solution and in hexadecane/isopropanol using $NaBH_4$ in order to insure that the hexadecanones did not obscure the presence of other oxygenates. Extracted oxygenates were measured using 180-cm x 2.0-mm glass columns. Apiezon L was used for aldehydes, light alcohols, and ketones, and Carbowax 20M was used for C_{16} alcohols and ketones. Quantitative analysis of oxygenates in hexadecane was possible using a 0.5-mm x 25-m, wall-coated Carbowax 20M column, which effectively resolved the C_{16} ketones from the hexadecane. A 2.0-mm x 180-cm packed column was unsuccessful in this regard, and column overloading occurred after several 0.25-μl injections, despite the fact that injector temperature was 300°C. Since the oxidized samples also contained C_{16} hydroperoxides, and the hydroperoxide decomposed in the gas chromatograph inlet to form alcohols and ketones, it was necessary to reduce hydroperoxides to alcohols with triphenylphosphine prior to analysis. This technique yielded ketones directly, and alcohols were found by difference (total alcohols in reduced

sample minus hydroperoxides). The effectiveness of the triphenylphosphine procedure was confirmed using t-butylhydroperoxide, which was reduced completely in this way. Hydroperoxides were measured using the method of Boss et al.[17]

References

[1] Reynolds, T. W., "Thermal Stability of Some Aircraft Turbine Fuels Derived from Oil Shale and Coal," NASA TM X-3551, June 1977.

[2] Morganthaler, J. E., Proceedings of the API Research Conference on Distillate Fuel Combustion, Paper CP62-8, 1962.

[3] Masdin, E. G. and Thring, M. W., "Combustion of Single Droplets of Liquid Fuel," Journal of the Institute of Fuel, June 1962, p. 351.

[4] Vranos, A., "Decomposition of Vaporizing n-Hexadecane," Combustion and Flame, Vol. 30, 1977, p. 151.

[5] Doue, F. and Guiochon, G., "The Mechanism of Pyrolysis of Some Normal C_6 to C_9 Alkanes," Journal of Physical Chemistry, Vol. 73, Sept. 1969, pp. 2804-2809.

[6] Rice, F. O. and Koskiakoff, A. J., "Thermal Decomposition of Hydrocarbons, Resonance Stabilization and Isomerization of Free Radicals," Journal of the American Chemical Society, Vol. 65, 1943, p. 590.

[7] Fabuss, B. M., Smith, J. O., and Satterfield, C. N., "Thermal Cracking of Pure Saturated Hydrocarbons," Advances in Petroleum Chemistry and Refining, Vol. LV, Interscience, New York, 1964, p. 157.

[8] Fabuss, B. M., Smith, J. O., Lait, R. I., Boranyi, A. S., and Satterfield, C. N., "Rapid Thermal Cracking of n-Hexadecane at Elevated Pressure," Industrial Engineering Chemistry, Process Design and Development, Vol. 1, 1962, pp. 293-299.

[9] Voge, H. H. and Good, G. M., "Thermal Cracking of Higher Paraffins," Journal of the American Chemical Society, Vol. 71, 1949, p. 593.

[10] Benson, S. W. and O'Neal, H. E., " Kinetic Data on Gas Phase Unimolecular Reactions," National Bureau of Standards, NSRDA NBS 21, 1970, p. 576.

[11] Trotman Dickenson, A. F. and Milne, G. S., "Tables of Bimolecular Gas Reactions," National Bureau of Standards NSRDS NBS 9, 1967, p. 71.

[12] Benson, S. W., " Effects of Resonance and Structure on the Thermochemistry of Organic Peroxy Radicals and the Kinetics of Combustion Reactions," Journal of the American Chemical Society, Vol. 87, May 1965, p. 972.

[13] Vranos, A., "Oxidation and Pyrolysis Products from Vaporizing n-Hexadecane," ASME Winter Annual Meeting, Atlanta, Ga., 1977.

[14] A Guide to the Analysis of Hydrocarbons by Gas Chromatography, 2nd ed., Polyscience Corp. 1969.

[15] Maaron, D., Recent Analytical Developments in the Petroleum Industry, Wiley, New York, 1974, pp. 121-135.

[16] Bierl, B. A., Beroza, M., and Ashton, W. T., "Reaction Loops for Gas Chromatography," Mikrochimica Acta, Vol. 637,1969.

[17] Boss, B. D., Hazlett, R. N., and Shepard, R. L., "Analytical Chemistry, Vol. 45, 1973, p. 2388.

DISCUSSION

DR. C. T. BOWMAN (Stanford University): All of your data were taken above the normal boiling point, or so it seems. Do you think that the types of reactions discussed in your paper can occur to any extent in a fuel which is at, or just slightly below, its normal boiling point, which might be the more normal condition for droplets that are burning in combustors?

DR. VRANOS (United Technologies Research Center): I think it is a matter of how high the boiling point is. The experiments of Masdin and Thring, conducted some time ago, indicate that liquid phase reactions occur during the vaporization of heavy oil droplets. The end result of these liquid phase reactions is the formation of a carbonaceous solid phase. Obviously, initial droplet size, fuel composition, and the presence of surfaces all will influence the extent of liquid phase decomposition. The competition between vaporization and liquid phase reactions of high boiling components is very important.

DR. BOWMAN: What is the relationship between these liquid phase reactions and soot formation.

DR. VRANOS: It may be that the rate of vapor phase decomposition is increased by the vaporization of free radi-

cals from liquids of high boiling point. As a result, fo the case of simple vaporization into a nonoxidizing atmosphere, secondary vapor phase reactions of pyrolysis products could lead to the early formation of solid phase. For the case of droplet combustion at large flame standoff distances, it is not difficult to imagine that increased pyrolysis might occur on the rich side as a result of this additional radical source and that this enhanced pyrolysis eventually might be manifested as gas phase soot.

DR. D. M. GOLDEN (SRI International): It seems to me, in looking back at the literature, that, although you have looked through the combustion literature, you have ignored a large organic oxidation literature in this temperature range and perhaps a little bit lower. I really am not involved with it, but I am aware of it, because some of my colleages at SRI have conducted a study for many years on oxidation of organic compounds. There was an international symposium in San Francisco in 1967, and there are several ACS books about it. So there is a lot of oxidation of organic compounds at these temperatures in liquids.

DR. VRANOS: I am familiar with much of the oxidation literature. In this experiment, oxidation reactions are important at low temperature and in the liquid phase. One of the points that I want to make is that the oxidation in this case is confined, primarily, to oxidation of C_{16} radicals. Oxygenates with lower carbon number are found at trace levels. Apparently, lower molecular weight hydrocarbon radicals are vaporized before combining with oxygen. Ketones are the predominate species at low temperature, indicating that ketones may be formed partly by termination reactions. The origin of ketones is under investigation.

DR. C. MOSES (Southwest Research Institute): What is the time scale involved in your experiments? Of course, the reactions that are involved in cenosphere formation in the combustor have to occur in a very short time period while droplets still exist. How does that relate to the time scale of your experiments?

DR. VRANOS: We are not attempting to simulate any particular situation at the moment. Rather, we are conducting experiments to identify critical parameters in the decomposition of vaporizing fuels. The presence of surface certainly influences the results so that droplet vaporization is not being simulated. Furthermore, droplet evaporation times are typically on the order of milliseconds. In this experiment, the time of contact between the liquid and a surface varies

from 1/3 of a second up to a second, depending on the boiling rate. The vapor phase residence time is 300 msec.

DR. B. T. WOLFSON (AFOSR): I am going to relate some results from a program that I support at USC which is concerned with selective vaporization or distillation of heavier hydrocarbons as they are influenced by hot surfaces.

From what I recall, this study shows that there are three different types of vaporization mechanisms. Depending on the way that vaporization occurs, there are also selective components that are given off, similar to a distillation still. Under the right conditions and upon hitting the right surface, there is a great influence of heat-transfer mechanisms. The mechanisms intereact in different ways, depending on the way that the droplets vaporize. Also, there is a considerable amount of pyrolysis which is directly fed into the formation of soot.

DR. VRANOS: We have conducted experiments with No. 2 oil which I have not discussed here. Although the experiment is not original, it has been repeated in order to see if the results were true. We vaporized No. 2 oil from a heated surface and found, that as surface temperature decreased, the amount of deposit formed increased very rapidly. In the film boiling regime, no deposit formed at all.

There is a correlation between that result and our hexadecane results because we find that the oxidation reactions become more important as temperature decreases. I think oxidation reactions are very important in the formation of polymers.

DR. R. N. HAZLETT (Naval Research Laboratory): We looked at fuels flowing as liquids over a heated metal specimen for a different reason. It was to look at the thermal oxidative stability of fuels. We have done some analyses similar to those by Dr. Vranos just with the dissolved oxygen (60 ppm). We have followed the oxygenated compounds and the pyrolysis to smaller paraffins and olefins over the temperature range 200°-540°C.

We also looked at a stain which is formed on the metal specimen. This may not be too far removed from soot formation in the vapor phase. However, we operate at high pressure, so that we are keeping the fuel or the hydrocarbon in the liquid regime. We find the stain forms during periods when we think there are high free radical concentrations. For instance, at the temperature that the peroxides are decomposing, we see an increase in stain with a pure hydrocarbon like normal dodecane, a material similar to hexadecane. With certain fuels where we

have a complex mixture, we seem to associate the stain with the oxidation reactions--in other words, where the peroxide is being formed. Again, this is a regime of high concentration of free radicals. So we feel that there is some correlation with solid formation and different types of free radical reactions that are occurring.

DR. S. W. BENSON (University of Southern California): Have you explicitly considered isomerization mechanisms for the pyrolysis?

DR. VRANOS: Isomerization has been included. I just did not discuss it.

DR. BENSON: A second comment has to do with the lifetime of the hydroperoxides that are formed. I think, if you will look at them closely, you will find that in the liquid phase the lifetime is of the order of tenths of seconds. So the fact that you are seeing some indicates something about the lifetime in the high-temperature regimes--those that will give aldehydes, alcohols, and all the rest.

I doubt very much that you can account for much of your product in terms of termination mechanisms because the radical concentrations you will get in the liquid phase are much too low to give you a considerable product from termination processes.

DR. VRANOS: High ketone levels are a puzzle at the moment. As mentioned before, ketone levels increase with decreasing temperature even at temperatures below the boiling point. This would be consistent with a low-temperature termination mechanism, especially if there are large temperature gradients within the liquid. Certainly, there are other ways in which ketones can be formed.

DR. BENSON: You will get those just from the decomposition of hydroperoxides. In other words, once you form the hydroperoxide, it cleaves into Alkoxy, and hydroxyl radicals. The Alkoxy immediately cleaves into a ketone or aldehyde, depending on where it is.

DR. VRANOS: In this case, we have an unbranched molecule, so the alkoxy radical would cleave into an aldehyde, not a ketone. We find ketones, not aldehydes, and the ketones are not scission products.

DR. I. GLASSMAN (Princeton University): Since more of us have begun to work in this field of carbon formation, I would like to suggest a convention of terminology to use, so that it becomes clear what we are talking about. May I make the simple suggestion that we refer to cenospheres as that carbon which forms from the liquid reactions that take place and that we use the word soot for carbon particles which form through homogeneous nucleation processes that take place in flames?

Chapter IV - Pollutant Emissions Considerations for Alternative Fuel Combustion

PRECEDING PAGE NOT FILMED
BLANK

ROLE OF AROMATICS IN SOOT FORMATION

James D. Bittner* and Jack B. Howard+
Massachusetts Institute of Technology, Cambridge, Mass.

Abstract

Soot formation would be one of the most important combustion problems encountered in a shift to alternative fuels having higher aromatic content than conventional petroleum-based fuels. Studies with different types of fuels in both laboratory flames and larger scale combustors show that aromatics are stikingly the most prone to form soot. Although the mechanism by which aromatics enhance soot formation is not well established, the role of the intact aromatic ring as a building block in rapid soot formation appears to be important, Hypotheses based on both radical and ionic polymerizations have been advanced to account for this role. With regard to the retardation of soot formation from aromatics, ring rupture in benzene pyrolysis is promoted by high temperatures, and fuel-rich oxidation of aromatics also can lead to ring rupture. There is much need for information on pyrolysis and oxidation reactions of aromatics at high temperatures and on the interactions between nonaromatic and aromatic fuel components.

Introduction

Soot and polycyclic aromatic hydrocarbons (PAH) associated with incomplete combustion generally are recognized as potential pollution problems.[1] Some of the PAH produced in flames and adsorbed on soot particles are known to be carcinogenic. The particle size range of soot (0.1 to 10 μm) allows it to be ingested easily deep into the lungs[2,3] and makes it especially resistant to control by particle collection technology.[4] Control of the soot and PAH emissions from the combustor, through the retardation of formation and assurance of burnout, places constraints on the important NO_x control strategy of staged combustion. The primary combustion in a fuel-rich atmosphere leads to increased soot and PAH formation that requires longer residence times for burnout in the lower temperature, oxygen-rich second stage. Aside from the

*Research Assistant, Department of Chemical Engineering.
+Professor, Department of Chemical Engineering.

PRECEDING PAGE NOT FILMED
BLANK

environmental aspects, soot formation in turbine combustors limits operating conditions by causing overheating of the combustion chamber from enhanced flame radiation and by the formation of carbonaceous deposits that cause fuel spray distortion and turbine damage when they break loose.

These problems of soot formation in combustion systems will become increasingly important when conventional petroleum-based fuels have to be supplemented by coal and coal-derived liquids. Because of their higher aromaticity, coal and liquid fuels derived from coal are much more prone to sooting. Strong economic incentives exist to learn how to burn fuels of high aromatic content without soot formation. As an example, if coal is the major source of liquid fuel in the future, elimination of the restrictions on aromatic content could reduce refining costs by as much as 20% of the heat of combustion of the syncrude processed.[5]

The control of soot and PAH emissions can be achieved either by the suppression of the formation of these species, by the enhancement of burnout once they are formed, or by a combination of these approaches. In order to determine the proper combustion modifications to reduce the formation, it is important to know the effects of temperature, local compositions, and residence times on the precursors of soot and PAH. In order to design for the proper temperature, residence time, and excess air required to insure the burnout, knowledge of the amounts of soot and PAH, the particle size distribution, and the oxidation kinetics is required. In either approach, knowledge of the important (controlling) features of the mechanisms of soot and PAH formation is necessary. It is especially important to understand the role of aromatic species in the mechanism, since studies of pure compounds in simple laboratory systems and studies of practical fuels and mixtures of practical fuels with aromatics in practical combustors demonstrate the increased propensity of aromatic fuels to form soot. This brief review focuses on the effect of fuel type, specifically aromatic contents on soot formation, and discusses the role of the aromatic nucleus in terms of possible mechanisms of soot formation.

Effect of Fuel Type

Reported studies of the effect of fuel type on soot formation which were performed with practical combustors are mainly in the area of turbine combustors. Most available information addresses older engine systems in which the fuel was injected through pressure atomizing nozzles and the combustors had fuel-rich zones. As mentioned previously,

three problems associated with soot formation arise as the H/C ratio (which correlates well with percent aromatics) of the fuel is decreased[5]: 1) smoke emissions under high-power conditions; 2) overheating of the combustion chamber from flame radiation; and 3) formation of solid carbonaceous deposits, which cause fuel spray distortion and turbine damage when deposits become detached.

Shirmer[6] studied particulate emissions and flame radiance in a laboratory-scale combustor designed to give good correlation with aircraft turbine combustors in fuel evaluation studies. He found that both flame radiance and exhaust smoke correlated well with hydrogen content. The H/C ratio was shown to be a better indicator of burning quality than is the ASTM smoke point or the luminometer number performance test.[7] The H/C ratio does not place undue emphasis on a fuel quality such as a high luminometer number, from which no actual benefit in terms of gas turbine performance is realized. Butze and Ehlers[8] investigated the performance of a single-can JT8D combustor using a number of fuels exhibiting wide variations in hydrogen content. They found that liner temperatures and smoke increase sharply with decreasing hydrogen content of the fuel. Recently, Blazowski[9] reported the results of a study of the effects of decreased fuel hydrogen content on a T56 series III single combustor. Fuel hydrogen content was varied from 12.7 to 14.5 wt% (corresponding to fuel aromatic content 45 to 11% by volume) by blending xylene with JP-4 fuel. Again, reductions in fuel hydrogen content resulted in substantially increased combustor liner temperatures and smoke emissions.

The effect of fuel type on soot formation in flames has been studied in several types of simple laboratory systems, including laminar diffusion flames, laminar premixed flames, and well-stirred reactors. The use of laminar diffusion flames to characterize the tendency of different fuels to form soot was reported first by Kewley and Jackson[10] in 1927. They used the height to which a flame in a wick lamp could be adjusted without emitting smoke from the tip as a measure of the burning quality of kerosines used for illumination. Minchin[11] in 1931 used the reciprocal of the flame height in a similar lamp as a measure of the tendency to smoke. Variations of this simple experiment have been used to study many different fuel types, and a standard "smoke point" test has been developed for evaluating aviation turbine fuels.[7] From the works of Minchin,[11] Clark et al.,[12] Hung,[13] and Schalla and McDonald,[14] in which over 75 hydrocarbons were studied, the following order emerges on the basis of increasing tendency to form soot in laminar diffusion flames: n-

alkanes <isoalkanes <alkenes and cycloalkanes <alkynes <benzene and alkyl benzenes <napthalenes.

Since practical fuels usually are not pure hydrocarbons, it is instructive to study the effect of mixture compsoition on the sooting tendency. Minchin[11] studied mixtures of aromatic, naphthene, and paraffin classes of hydrocarbons of a similar boiling range prepared from crude oils. He found the tendency to smoke (as measured by the reciprocal of the flame height) of an aromatic-paraffin mixture to be directly proportional to the volume percent of aromatics. Similar results were obtained for naphthene-paraffin mixtures. Hunt[13] studied pure aromatics mixed with n-dodecane in a wick lamp. For sec-butylbenzene and α-methyl naphthalene, the smoke point (defined as the height of the flame at which soot is emitted from the tip) dropped drastically in a nonlinear manner with increasing percentage of aromatic.

In studies of premixed laminar flames, only the effect of fuel type on the sooting limit under conditions near the adiabatic flame temperature has been investigated extensively. The soot limit is defined as the ratio of fuel to oxidizer in the unburned gas mixture at which the yellow luminosity of carbon particles is just detectable. The most extensive study is that of Street and Thomas,[15] who studied many premixed hydrocarbon-air flames burning in their own combustion products on a burner surrounded by a Pyrex tube to prevent oxygen enrichment from the atmosphere. They observed the following ranking of hydrocarbons on the basis of mixture strength (actual air as a fraction of stoichiometric) at which soot appeared in the flame (in order of increasing tendency to form soot): acetylene <alkenes <isoalkanes <alkanes <benzene and alkyl benzenes <alkyl naphthalenes.

Grumer et al.[16] studied yellow-tipping of Bunsen burner flames and defined the yellow-tip limit as the fuel-air composition of the stream in the burner port for which yellow is just perceptible anywhere above the port. For large port diameters and high flow rates, the yellow-tip limit became independent of velocity and port diameter. Radial diffusion of oxidizing species from the surrounding diffusion flame was considered negligible for these conditions. These constant yellow-tip limits agreed fairly well with the data of Street and Thomas, although the order of alkanes and alkenes was reversed. Grumer et al. found (in order of increasing tendency to form soot) acetylene <alkanes <alkenes <monocyclic aromatics.

Miller and Calcote[17] recently studied nine hydrocarbon-air flames on a premixed burner shielded by a rich propane-air

flame and found that flames about 10 to 20% richer than those of Street and Thomas could be burned without sooting. However, the order of increasing tendency to soot of the compound classes was similar: acetylene <alkanes <monocyclic aromatics.

To summarize qualitatively these three studies on laminar premixed flames, alkanes required from 15 to 30% more air than did acetylene on a stoichiometric basis to burn without soot formation. Aromatics required 35 to 65% more air than did acetylene.

A third laboratory system that has been used very little to study soot formation, but one that offers some unique opportunities to studiy the chemistry of the process without heat- and mass-transfer limitations, is the well-stirred reactor. Wright[18] measured the soot limits of 34 fuels in such a system. For cases where comparison could be made with the premixed flame data of Street and Thomas,[15] the well-stirred reactor could be operated with about 10 to 20% less air without forming soot. Again, nonaromatics could be burned substantially richer than aromatics without forming soot.

The effect of flame structure and the inherent effects of heat and mass transfer on the soot formation process are illustrated dramatically by the switch in the order of the tendency to soot of acetylene (and other alkynes) relative to alkenes and alkanes in going from diffusion flames to premixed flames. In laminar diffusion flames, molecular diffusion controls the rate of fuel and oxygen mixing. Since the main oxidation reactions are very fast relative to diffusion rates, sharp concentration and temperature gradients exist, and pyrolysis and soot formation reactions occur in a very fuel-rich atmosphere. Although heat and reactive species such as free radicals and ions diffuse toward the fuel-rich zone, oxidation reactions are slow compared to the pyrolysis reactions in the soot formation zone. In premixed flames, pyrolysis and soot formation reactions occur simultaneously with oxidation reactions. Rapid oxidation of the fuel and pyrolysis products can either prevent the occurrence of or remove precursors of soot. Therefore, simplistically, the change in relative positions of the hydrocarbons reflects the reactivity of the fuel in the oxidation reactions relative to that in the pyrolysis and soot-forming reactions.

The laminar premixed flame ideally is a plug flow reacting system, but it is not free of heat- and mass-transfer effects, since the preferential diffusion of the hydrogen radicals and molecular hydrogen can alter the local H/C and O/C ratios. However, in the well-stirred reactor, the effects

of heat and mass transfer are minimized by providing maximum backmixing. Chemical reactor theory indicates that intermediates or products (such as soot precursors and soot) produced by reactions of higher kinetic order than the oxidation process should be reduced by backmixing.

Although the studies in the laboratory systems just discussed cannot provide the means to predict whether soot will be formed or emitted in more complex systems when changes are made in fuels composition, they have had utility. As mentioned previously, the smoke point from laminar diffusion flame measurements has been used as a parameter to correlate effects of fuel type on soot emissions from more complex systems. The premixed laminar flames and well-stirred reactor studies provide performance limits for avoiding soot formation based solely on fuel chemistry. More importantly, these studies indicate that, when burning adiabatically in the extremes of well-mixed systems and systems with molecular diffusion-controlled mixing, aromatics form soot at fuel equivalence ratios [(fuel/air)/(fuel/air)stoichiometric] in the first case and at fuel flow rates in the second case which are lower than nonaromatics.

The discussion of premixed flames and well-stirred reactors has addressed only the effect of fuel type on the sooting limit. Little work has been done to quantify the effect of fuel type on the amount of soot produced, the soot particle size distribution, or compositions of the PAH associated with the soot under well-defined conditions. Wright[19] reported soot concentrations in both a flat premixed flame and a well-stirred reactor for several fuels under near-adiabatic conditions. In order to produce similar soot concentration in the well-stirred reactor, alkenes had to be burned at fuel equivalence ratios from 25 to 85% higher than did benzene. In premixed flat flames, alkenes formed 20 to 80% less soot than did benzene when the former were burned at fuel equivalence ratios 25 to 80% higher than those of the benzene. The effect of backmixing on soot production was demonstrated by the observation that soot concentrations in the well-stirred reactor were reduced to less than 10% of those in the premixed flat flame. MacFarlane et al.[20] measured soot limits and soot production in premixed laminar and turbulent flames of C_5 and C_6 hydrocarbons with air at pressures up to 20 atm. The fuel equivalence ratio at the soot limit for benzene was lower than for all other hydrocarbons. Benzene produced several times more soot than the other hydrocarbons under similar conditions of fuel equivalence ratio, pressure, and injection velocity. An increase in injection velocity which resulted in a transition from a laminar flat flame to a

turbulent flame had little or no effect on the soot limit but reduced the amount of soot formed at equivalence ratios greater than the soot limit in the case of all hydrocarbons. These two studies demonstrate two points. First, alkanes and alkenes produce much less soot than does benzene under a wide range of pressures, fuel equivalence ratios, and degrees of backmixing. Second, even in premixed systems, backmixing has a significant effect on the amount of soot formed.

From the few studies that have reported electron-microscope analysis of the soot formed from different fuels, no discernable trends in the variations of particle size with fuel type were evident.[20-22] Similarly, the literature contains few reports of the effects of fuel aromaticity on the quantities or structures of PAH's extractable from soot. Prado et al.[21] reported a larger total mass of PAH in the fuel-rich zone of a turbulent diffusion flame when burning benzene than when burning kerosene, which contained about 17 wt% monocyclic armoatics. It also was noted that concentrations of PAH with methyl and phenyl groups were much lower in the kerosene flame than the benzene flame. Homann and Wagner,[23] in studies of premixed laminar acetylene-oxygen and benzene-oxygen flames, reported PAH concentrations about 100 times larger in the benzene flames for the same carbon-to-oxygen ratio.

Role of Aromatics in Soot Formation Mechanisms

The studies just cited establish the fact that aromatics form soot more readily (i.e., at lower fuel flow rates in laminar diffusion flames or lower fuel equivalence ratios in premixed systems) and more profusely (i.e., in larger quantities) than nonaromatics when both types of fuels are burned under similar conditions in a wide variety of systems. The following disucssion centers on the chemical role of aromatics in soot formation. It does not include the roles of physical properties such as volatility and viscosity which affect atomization and droplet or spray evaporation, although these may be important variables with regard to the mixing process that has been shown to be important in soot formation.

A framework for discussion of the role of aromatics in soot formation is provided by the following brief summary of the mechanistic picture of soot formation which emerges from the literature. More detailed discussions of the chemistry and physics of the process are available in reviews by Palmer and Cullis,[24] Gaydon and Wolfhard,[25] Street and Thomas,[15] and Homann.[26]

Soot formation in hydrocarbon flames has been studied for over a century, but the understanding of the process remains inadequate. As shown already, the extent of soot formation exhibits a complicated dependence upon the type of flame or combustion system, type of fuel, pressure, temperature, and other factors.

Soot particles are usually chainlike aggregates of approximately monodisperse spherical units. The spheres contain domains of considerable order consisting of approximately hexagonal-plane structure similar to that of graphite. The diameter of the spheres is usually about 100 to 500 Å.[24] The solid material consists of carbon and hydrogen; the atomic C/H ratio increases from about 1 to 8 as the particles age in the flame. The very young particles are largely polymeric; it now appears that the number of domains of high order per spherical unit is comparable to the number of young or primary particles agglomerated in each spherical unit.[27]

The details and consistent occurrence of the preceding structure indicate that soot formation involves the following steps: nucleation, formation of spherical units (about 250-Å size) by agglomeration and surface growth, and chaining of spherical units by coagulation. An acceptable model of soot formation must explain all three steps. In premixed flames, particles apparently nucleate within a narrow region of the reaction zone of the flame near the location of the peak concentration of radical, atomic, and ionic species and then grow by surface reactions and agglomeration while they traverse the remainder of the flame zone. Attempts to derive a mechanism of soot formation traditionally have focused upon chemical steps that might lead from molecules, radicals, or ions to soot particles, and possible reasons for the strong effect of flame conditions or fuel type on the amount of soot formed. Several mechanisms have been proposed, each designed to explain certain aspects of the literature data, but none of them are free from serious shortcomings.

A summary of many mechanisms that have been proposed to explain soot formation in flames is depicted in Fig. 1, an earlier version of which was given by Street and Thomas.[15] Since soot particles contain many more carbon atoms and a much lower H/C ratio than the fuel molecules, soot formation must involve both aggregation and dehydrogenation. The extreme routes, the C_2 route and the saturated polymer route, are unlikely to occur under typical combustion conditions. The C_2 route may be important at temperatures around 3000K. At lower temperatures, around 700K, and long reaction times the saturated polymer route might occur. But in the range

1200-2200K most mechanisms can be represented by the central portion of Fig. 1. Acetylene, biphenyl, polycyclic aromatic hydrocarbons, polyacetylenes, radicals of these hydrocarbon classes, and hydrocarbon ions all have been proposed as important intermediates in either nucleation of soot particles or surface growth.

Any general mechanism that purports to be applicable to a variety of fuels must explain the propensity of aromatics to form soot relative to nonaromatic fuels. It then is instructive to speculate on the effect of a substantially increased percentage of aromatics in fuels of an alkene and alkane base.

The first question that arises is: What are the immediate reactions of the aromatic ring? The answer will depend, of course, upon the local residence time, temperature, and chemical environment. The reaction products and intermediates of the pyrolytic decomposition of benzene have received considerably more attention than those of benzene-rich flames. Stehling et al.[28] studied benzene pyrolysis in a flow reactor at 973-1173K and benzene concentrations of 8×10^{-4} g-mole/liter and observed hydrogen, biphenyl, tar, and carbon as the major products. Kinney and Slysh[29] studied benzene pyroly-

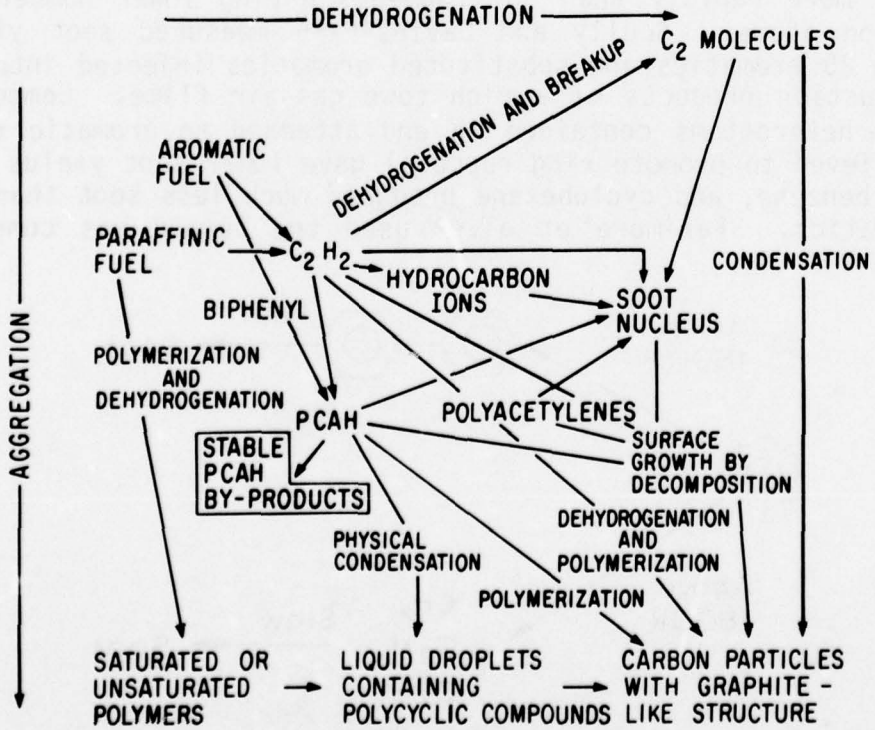
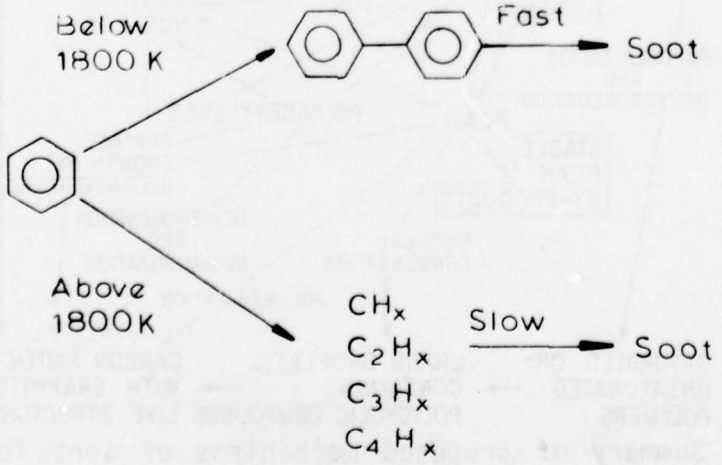


Fig. 1 Summary of proposed mechanisms of soot formation.

sis at 1473K and benzene concentrations of 0.8 to 3 x 10^{-5}g-mole/liter in a flow system. Under these conditions, benzene decomposed according to first-order kinetics, and acetylene, diacetylene, and hydrogen were the main primary decomposition products with smaller amounts of biphenyl. More recently, Asaba and Fujii[30] studied the pyrolysis of benzene (1400-1900K and 10^{-3} to 10^{-4}g-mole benzene/liter) in a shock tube. They found, even at high temperatures and at concentrations of benzene closer to flame conditions than those studied by Kinney and Slysh, that the primary pathway for benzene disappearance was through the biphenyl pathway rather than ring rupture to acetylene and diacetylene. Graham et al.[31] studied the formation of soot from the pyrolysis of benzene in a shock tube at tempertures from 1600-2300K and benzene concentrations of 0.5 to 1.0 x10^{-4}g-mole/liter. A maximum in the conversion of benzene to soot at 1800K was explained by the dual pathway for soot formation from aromatics illustrated below. Support for this type of behavior in benzene pyrolysis comes from the multistep reaction mechanism proposed by Asaba and Fujii.[30] Their mechanism, when using Graham et al's. benzene concentrations, quantitatively predicts a change at 1500-1600K as the temperature is increased from the biphenyl pathway to the ring rupture pathway as the main means of benzene disappearance. Two studies support the assumption that benzene rings form soot more rapidly than do fragments having lower numbers of carbon atoms. Scully and Davies[22,32] measured soot yields from 25 aromatics and substituted aromatics injected into the combustion products of a rich town gas-air flame. Compounds with heteroatoms contained in and attached to aromatic rings (believed to promote ring rupture) gave lower soot yields than did benzene, and cyclohexane produced much less soot than did aromatics. Fenimore et al.[33] used the burned gas composi-



tions of premixed flames to correlate carbon/oxygen ratios at the sooting limits of different fuels burned on a flat flame burner under conditions giving the same peak temperature. They found benzene in the burned gas to be 17 times more effective (after allowance for the greater carbon content) in promoting soot formation than was acetylene or methane, which are the major hydrocarbons in the burned gas of nonaromatic fuels.

According to the foregoing benzene pyrolysis literature, possibilities may exist for reducing the sooting and PAH forming tendencies of aromatics if ring rupture can be promoted. Presumably, reactions other than the unimolecular decompositions,

$$C_6H_6 \longrightarrow C_6H_5 + H$$

$$C_6H_5 \longrightarrow C_4H_{3E} + C_2H_2$$

which have been proposed as leading to ring rupture in pyrolysis systems, operate in systems containing oxygen. The effect of oxygen in benzene pyrolysis also was studied by Fujii and Asaba[34] in a shock tube. Oxygen in the proportion $O_2/C_6H_6 = 1/10$ resulted in an order-of-magnitude increase in acetylene production over the case of pure pyrolysis.

Since most fuels have both aromatic and nonaromatic components, it is difficult to predict from separate studies of pure aromatic and pure nonaromatic fuels how the aromatic ring will behave in a mixture and the subsequent effect on soot and PAH formation. Stehling et al.[28] found, in the pyrolysis of benzene-acetylene mixtures in a flow reactor (973-1173K), that the rate of disappearance of benzene was accelerated by the presence of acetylene. At the same time, the rate of acetylene disappearance was not affected by the presence of benzene. The effect on carbon formation was not measured, but hydrogen production was accelerated. Studies of carbon formation from mixtures of cyclohexane and benzene injected into the burned gases of a rich town gas-air flame show that the effects of the pure components are not additive, and the presence of cyclohexane appears to inhibit soot formation from benzene.[22]

Although the scope of this paper does not allow an extensive discussion of oxidation and pyrolysis mechanisms of armoatic compounds, it can be inferred from the studies just cited that a more complete picture of the kinetics and mechanisms of both oxidation and pyrolysis of aromatics in the

presence of nonaromatics is essential for the determination of the soot-forming tendency of fuels with increased aromatic content.

If it is assumed, as the preceding evidence suggests, that it is the intact aromatic ring that promotes soot formation, the question arises as to the mechanistic role of the aromatic ring in this process. Numerous authors have proposed a progressive polymerization of aromatic rings beginning with biphenyl through large polycyclics and on to the polybenzoid stto structure.[31,34-39] Such a process would go through stages of polycyclic aromatic hydrocarbons that do not have aliphatic, olefinic, or acetylenic side chains. These PAH without side chains are believed to be relatively unreactive in flames. Homann[40] observed that in premixed benzene flames two classes of PAH were formed in the oxidation zone. Grouped into one class were PAH without side chains such as naphthalene, anthracene, phenanthrene, and pyrene, whose concentrations of the species belonging to the other class of compounds, which included phenylacetylene, indene, methyl naphthalene, and biphenyl, reached maxima in the oxidation zone and decreased near the point where soot formation began. D'Alessio et al.,[41] in a study of atmospheric premixed methane-oxygen flames, also observed two classes of PAH with behavior similar to that which Homann observed. To the contrary, Crittenden and Long[42] measured concentrations of PAH in sooting premixed acetylene-oxygen and ethylene-oxygen flames and found that all PAH concentrations went through maxima in the oxidation zone. They concluded that all PAH, even those without side chains, could be intermediates in soot formation.

In any case, some ring rupture occurs from the oxidative and pyrolytic reactions in flame systems. Thus, Smith et al.[43,44] proposed that soot is a copolymer of benzene and acetylene. Through such a mechanism of polymerization of benzene and primarily two- and four-carbon fragments of benzene, PAH with side chains are formed. Homann and Wagner[23] have detected species above 250 amu which they believe to have carbon rings with side chains. These species have very low concentrations in acetylene-oxygen flames and pass through a maximum shortly after the oxidation zone, where carbon forms. Similar species are detected in benzene flames. These species were proposed to act as soot nuclei. In the same study, much larger concentrations (100 X) of PAH within the oxidation zone were observed in benzene flames than in acetylene flames. Independent of the type of aromatic molecules which is reactive, a free radical polymerization mechanism is thought to be responsible for soot formation, and the propensity

of aromatics to form soot is attributed to the higher concentrations of the larger "building blocks" available to the hydrocarbon radicals.

A theory that has received increasing attention has been that of nucleation by hydrocarbon ions. Bartholome and Sachse[45] first suggested that electrostatic effects may be important in the coagulation of soot particles. Weinber et al.[46-49] demonstrated that electrical fields applied to flames can alter dramatically the lumosity and soot formation in flames. It was concluded that, in the presence of the fields, charge attachment by diffusing ions was the main charging mechanism for the carbon particles collected from the flame. Miller[50] detected mass spectrometrically natural flame hydrocarbon ions up to mass 150 in acetylene-oxygen diffusion flames, and more recently Vinckier et al.[51] reported evidence of ionic polymerization of acetylene in an oxygen atom-acetylene system. Howard et al.[52-54] demonstrated that soot particles are charged in flames without electrical fields applied and studied the effects of charges on coagulations of the particles. Measurements of charged species and soot particle number concentrations in sooting flames have shown that concentrations of large hydrocarbon ions (probably polycyclic aromatic) are high enough to support the view that ionic nucleation plays an important role in soot formation in flames.[55,56]

A fact that has troubled researchers looking for a single unifying mechanism to explain soot formation (although it is not likely that such a mechanism exists) has been that oxygen is required in the only mechanism of chemi-ionization that has been shown to operate in flames to date.[57] Therefore, production of ions in pyrolysis sytems was assumed to be unlikely. Recently two experimenters, using electric probe techniques, have detected ion currents in pyrolyzing hydrocarbons.[58,59] Identification of the primary chemi-ion or its formation mechanism has not been established.

Another troublesome observation has been that total ionization in nonsooting hydrocarbon flames maximizes at a fuel equivalence ratio near one.[60] Therefore, as fuel equivalence ratio increases, toal ionization would be expected to decrease while soot formation increases. However, Wersborg et al.[55] found that, in flat premixed sooting acetylene-oxygen flames, concentrations of charged species above about 300 amu increased with increasing fuel equivalence ratio and with decreasing cold-gas velocity (the latter causing a decrease in temperature). Although both of these effects would be expected to decrease total ionization and to increase

soot formation, it was postulated that the increase in charged species concentration resulted from increased transfer of charge to the higher molecular weight hydrocarbons. Support for this explanation has come from recent work of Miller and Calcote.[17] The natural flame ions of premixed acetylene-air and benzene-air flames at fuel equivalence ratios just below the soot limit were investigated with a mass spectrometer system. For the acetylene flame, the total ion concentration decreased only 10% as the fuel equivalence ratio increased over the range studied, but the distribution of ion masses shifted dramatically to higher masses. The heavier the ion, the greater was its sensitivity to changes in fuel equivalence ration.

Hydrocarbon ions are attractive as soot nuclei, since ion-molecule reactions are very rapid in comparison to radical-molecule reactions.[61] Thus polymerization of neutral species around a hydrocarbon ion might be expected to be faster than around a radical. The role of aromatics in a mechanism of ionic nucleation is intriguing, since the lower ionization potentials of aromatic structures could result in increased hydrocarbon ion concnetrations. In nonaromatic flames, the production of ionic aromatic strucures would be much slower because of the increased complexity of the pyrolysis reactions required to form the aromatic structure. Indirect support for this again comes from the recent work of Miller and Calcote.[17] Qualitatively, at masses greater than 100 amu the same ions are present in both acetylene and benzene flames, and they appear to be aromatic. From the study of the effects of increasing the fuel equivalence ratio in the acetylene flame, charge transfer to form such ions appears to be rapid, as the concentrations of aromatic neutrals presumably increase with increased fuel equivalence ratio. The increased hydrocarbon ion concentration provides more centers for rapid polymerization of otherwise relatively unreactive neutral species and thereby increases the rate of conversion to soot of lower molecular weight gas-phase hydrocarbon species. An increased production rate of soot also can result from the larger concentration of larger "building blocks" available to the ions, as in the theory based on radical polymerization.

Of mechanistic and modeling importance and of some practical importance is the effect of the increased aromatic content on the particle size distribution of the soot, since the mass rate of carbon burnout for a monodisperse system of nonporous particles varies inversely with the particle diameter. The means by which the mass of soot is increased (nucleation, surface growth, or both) here arises as an

important question. Is nucleation increased through a higher production rate of reactive species (radical or ionic), which then grow by the addition of relatively inert neutral species, or is surface growth increased by the higher production rate of the relatively inert neutral species? Particle studies have attempted to shed light on these processes that control size distributions. In a study of carbon formation from benzene pyrolysis in a flow reactor, LaHaye et al.[62] found the number of spherical units per volume of product gas to be independent of benzene concentration and residence time, and attributed the increased mass to increased surface growth. In studies of low-pressure flat premixed acetylene-oxygen and benzene-oxygen flames at the same C/O ratio, Homann and Wagner[23] found that the high number density of soot particles in benzene-oxygen flames accounts much more for the larger mass of soot than do slightly larger mean particle diameters. This would indicate that nucleating species are more plentiful in benzene flames. Homann and Wagner explain this by the greater overlap of the carbon formation and oxidation zones which occurs in the benzene flame than that in the acetylene flame. Thus radicals (and probably ions) are in greater concentrations at the point of soot formation. In a comparison of flat premixed benzene-oxygen and acetylene-oxygen flames that form the same amount of carbon (i.e., different C/O ratios were used), Homann and Wagner[63] found that, of the carbon in the unburned gas in excess of that at the limit of carbon formation, 5% goes to soot in the acetylene flame, and 30% goes to soot in the benzene flame. The average particle diameter was about 200 Å from the benzene flame. The particle number density in the benzene flame was smaller by about a factor of 2. Although the authors do not give sufficient information to tell what variables (pressure, gas velocities, maximum flame temperature, etc.) were held constant, it appears that surface growth at the limit of carbon formation, 5% goes to soot in the acetylene flame, and 30% goes to soot in the benzene flame. The average particle diameter was about 200 Å from the acetylene flame and about 300 Å from the benzene flame. The particle number density in the benzene flame was smaller by about a factor of 2. Although the authors do not give sufficient information to tell what variables (pressure, gas velocities, maximum flame temperature, etc.) were held constant, it appears that surface growth in the benzene flame is contributing more toward the control of the total mass production rate. From these seemingly conflicting results on particle size distributions, it is difficult to draw general conclusions about the separate roles of aromatics in particle nucleation and surface growth.

Summary

1) Significant differences exist between the soot formation behavior of aromatic and nonaromatic fuels, the former being strikingly the more prone to form soot:

a) In tests with gas turbine combustors, decreases in the H/C ratio of the fuel (or increases in the aromatic content) lead to increases in both smoke emission and liner temperatures, and the H/C ratio is an effective correlating parameter for these effects.

b) In the comparison of aromatic and nonaromatic fuels in laboratory-scale laminar flames, the aromatics form soot at lower fuel flow rates in diffusion flames and at lower fuel equivalence ratios in premixed flames. Aromatics also form quantitatively more soot than do nonaromatics for the same fuel equivalence ratios. Laboratory studies using a well-stirred combustor show that backmixing significantly reduces the rate of soot production compared with the premixed flame case. Thus the diffusion flame and the well-stirred combustor exhibit, for a given fuel, two extremes of sooting behavior which provide limits to be expected from practical systems.

2) The mechanism by which aromatics enhance soot formation is not well established, but the following statements can be made:

a) The intact aromatic ring appears to be essential to high rates of soot formation: i) studies of benzene pyrolysis indicate that ring rupture can be promoted at high temperatures; ii) interactions between nonaromatic and aromatic fuel components are important; and iii) there is a need for information on reactions leading to ring rupture of aromatics in pyrolysis and in fuel-rich oxidation and on the roles of nonaromatics in these mechanisms.

b) The role of the intact aromatic ring in soot formation is uncertain and therefore in need of clarification. Two hypotheses that have been advanced are based on radical and ionic polymerizations. A better understanding of ionic effects would, of course, enhance the potential of control techniques based on the use of electric fields and additives.

References

[1]"Particulate Polycyclic Organic Matter," Rept. by the Committee on Biological Effects of Atmospheric Pollutants, Div. of Medical Sciences, Washington, D.C., 1972.

[2]"Air Conservation," Rept. of the Air Conservation Commission of the American Association for the Advancement of Science, Washington, D.C., Publ. 80, 1965.

[3]Goldsmith, J. R., "Effects of Air Pollution on Humans," Air Pollution, edited by A. C. Stern, Vol. 1, Academic Press, New York, 1962, pp. 335-386.

[4]Friedlander, S. K., "Small Particles in the Air Pose a Big Control Problem," Environmental Science and Technology, Vol. 7, Dec. 1973, pp. 1115-1118.

[5]Longwell, J. P., "Synthetic Fuels and Combustion," Sixteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, Pa., 1977, p. 1.

[6]Shirmer, R. M., "Effect of Fuel Composition on Particulate Emissions from Gas Turbine Engines," Emissions from Continuous Combustion Systems, edited by W. Cornelius and W. G. Agnew, Plenum Press, New York, 1972, p. 189.

[7]"Standard Test Method for Smoke Point of Aviation Turbine Fuels" and "Standard Test Method for Luminometer Numbers of Aviation Turbine Fuels," American Society for Testing Materials, ANSI/ASTM D 1322-75 and ANSI/ASTM D 1740-75, 1975.

[8]Butze, H. F., and Ehlers, R. C., "Effect of Fuel Properties on Peformance of a Single Aircraft Turbojet Combustor," NASA TM-71789, 1975.

[9]Blazowski, W. S., "Combustion Considerations for Future Jet Fuels," Sixteenth Symposiium (International) on Combustion, The Combustion Institute, Pittsburgh, Pa., 1977, p. 1631.

[10]Kewley, J., and Jackson, J. S., "Burning of Mineral Oils in Wick-Fed Lamps," Journal of the Institute of Petroleum Technologists, Vol. 13, May 1927, pp. 364.

[11]Minchin, S. T., "Luminous Stationary Flames: the Quantitative Relationship between Flame Dimensions at the Sooting Point and Chemical Composition, with Special Reference to Petroleum Hydrocarbons" Journal of the Institute of Petroleum Technologists, Vol. 17, Feb. 1931, p. 102-120.

[12]Clarke, A. E., Hunter, T. G., and Garner, F. H., "The Tendency to Smoke of Organic Substances on Burning. Part I," Journal of the Institute of Petroleum Technologists, Vol. 32, May 1946, pp. 627-642.

[13]Hunt, R. A., Jr., "Relation of Smoke Point to Molecular Structure," Industrial and Engineering Chemistry, Vol. 45, March 1953, pp. 602-606.

[14]Schalla, R. L. and McDonald, G. E., "Variation in Smoking Tendency among Hydrocarbons of Low Molecular Weight," Industrial and Engineering Chemistry, Vol. 45, July 1953, pp. 1497-1500.

[15]Street, J. C. and Thomas, A., "Carbon Formation in Premixed Flames," Fuel, Vol. 34, 1955, pp. 4-36.

[16]Grumer, J., Harris, M. E., and Rowe, V. R., "Yellow-Tipping of Bunsen Burner Flames and Related Exchangeability of Fuels in Gas Utility Systems," Industrial and Engineering Chemistry, Vol. 48, Nov. 1956, pp. 2052-2062.

[17]Miller, W. J. and Calcote, H. F., "Ionic Mechanisms of Carbon Formation in Flames," Eastern Section of Combustion Institute 1977 Fall Meeting, United Technologies Research Center, East Hartford, Conn., Nov. 10-11, 1977.

[18] Wright, F. J., "The Formation of Carbon Under Well-Stirred Conditions," Twelfth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, Pa., 1969, p. 867.

[19] Wright, F. J., "Carbon Formation Under Well-Stirred Conditions, Part II," Combustion and Flame, Vol. 15, Dec. 1970, pp. 217-222.

[20] Macfarlane, J. J., Holderness, F. H., and Witcher, F. S. E., "Soot Formation Rates in Premixed C_5 and C_6 Hydrocarbon - Air Flames at Pressures up to 20 Atmospheres," Combustion and Flame, Vol. 8, Sept. 1964, pp. 215-229.

[21] Prado, G. P., Lee, M. L., Hites, R. A., Hoult, D. P., and Howard, J. B., "Soot and Hydrocarbon Formation in a Turbulent Diffusion Flame," Sixteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, Pa., 1977, p. 649.

[22] Scully, D. B., and Davies, R. A., "Carbon Formation from Aromatic Hydrocarbons," Combustion and Flame, Vol. 9, June 1965, pp. 185-191.

[23] Homann, K. H., and Wagner, H. Gg., "Some New Aspects of the Mechanism of Carbon Formation in Premixed Flames," Eleventh Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, Pa., p. 371.

[24] Palmer, H. B., and Cullis, C. F., "The Formation of Carbon from Gases," The Chemistry and Physics of Carbon, Vol. 1, edited by P. L. Walker, Jr., Marcel Dekker, New York, 1965, p. 265.

[25] Gaydon, A. G., and Wolfhard, H. G., Flames, 3rd ed., Chapman and Hall, Ltd., London, 1970, pp. 175-210.

[26] Homann, K. H., "Carbon Formation in Premixed Flames," Combustion and Flame, Vol. 11, Aug. 1967, pp. 265-287.

[27] Wersborg, B. L., Howard, J. B., and Williams, G. C., "Coagulation of Carbon Particles in Premixed Flames," Faraday Symposia of the Chemical Society, No. 7, 1973, pp. 109-119.

[28] Stehling, F. C., Frazee, J. D., and Anderson, R. C., "Mechanisms of Nucleation in Carbon Formation," Eighth Symposium (International) on Combustion, Williams and Wilkins, Baltimore, Md., 1962, p. 744.

[29] Kinney, C. R., and Slysh, R. S., "On the Mechanism of the Carbonization of Benzene, Acetylene and Diacetylene at 1200° C," Proceedings of the Fourth Conference on Carbon, Pergamon Press, New York, 1960, p. 301.

[30] Asaba, T., and Fujii, N., "Shock-Tube Study of High-Temperature Pyrolysis of Benzene," Thirteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, Pa., 1971, p. 155.

[31] Graham, S. C., Homer, J. B., and Rosenfeld, J. L. J., "The Formation and Coagulation of Soot Aerosols Generated by the Pyrolysis of Aromatic Hydrocarbons," Proceedings of the Royal Society of London, Vol. 344, June 1975, pp. 259-285.

[32] Davies, R. A. and Scully, D. B., "Carbon Formation of Aromatic Hydrocarbons II," Combustion and Flame, Vol. 10, June 1966, pp. 165-170.

[33] Fenimore, C. P., Jones, G. W., and Moore, G. E., "Carbon Formation in Quenched Flat Flames at 1600°K," Sixth Symposium (International) on Combustion, The Combustion Institute, Rheinhold Publishing Corp., New York, 1957, p. 242.

[34] Fujii, N., and Asaba, T., "Shock-Tube Study of the Reaction of Rich Mixtures of Benzene and Oxygen," Fourteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, Pa., 1973, p. 433.

[35] Rummel, K., and Veh, P. O., "Die Strahlung Leuchtender Flammen Erster Teil: Schrifttumsgrundlagen, Arbeitshypothesen und Vorversuche," Archiv fur Das Eiesenhuttenwessen, Vol. 14, April 1941, pp. 489-499.

[36] Thorp, N., Long, R., and Garner, F. H., "Carbon Formation in Benzene-Oxygen Diffusion Flames," Fuel, Vol. 30, Nov. 1951, p. 266.

[37] Kinney, C. R., and Delbel, E., "Pyrolytic Behavior of Unsubstituted Aromatic Hydrocarbons," Industrial and Engineering Chemistry, Vol. 46, March 1954, pp. 548-556.

[38] Thomas, A., "Carbon Formation in Flames," Combustion and Flames, Vol. 6, March 1962, pp. 46-62.

[39] Virk, P. S., Chambers, L. E., and Woebcke, H. N., "Thermal Hydrogasification of Aromatic Compounds," Coal Gasification, edited by L. G. Massey, Advances in Chemistry Series No. 131, American Chemical Society, Washington, D.C., 1974, p. 237.

[40] Homann, K. H., "Soot Formation in Premixed Hydrocarbon Flames," Angewandte Chemie (International Edition), Vol. 2, June 1968, pp. 414-427.

[41] D'Alessio, A., DiLorenzo, A., Sarofim, A. F., Beretta, F., Masi, S., and Venitozzi, C., "Soot Formation in Methane-Oxygen Flames," Fifteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, Pa., 1975, p. 1427.

[42] Crittenden, B. B. and Long, R., "Formation of Polycyclic Aromatics in Rich Premixed Acetylene and Ethylene Flames," Combustion and Flame, Vol. 20, June 1973, pp. 359-368.

[43] Smith, S. R., and Gordon, A. S., "Studies of Diffusion Flames. I. The Methane Diffusion Flame," Journal of Physical Chemistry, Vol. 60, June 1956, pp. 759-763.

[44] Gordon, A. S., Smith, S. R., and McNesby, J. R., "Study of the Chemistry of Diffusion Flames," Seventh Symposium (International) on Combustion, Buttersworth, London, England, 1959, p. 317.

[45] Bartholome, E. and Sachsse, H., "Catalytic Phenomena in Aerosols," Zhurnal fur Elektrochemie, Vol. 53, 1949, pp. 326-331.

46 Payne, K. G., and Weinberg, F. J., "A Preliminary Investigation of Field-Induced Ion Movement in Flame Gases and Its Applications," Proceedings of the Royal Society of London, Series A, Vol. 250, 1959, pp. 316-336.

47 Place, E. R., and Weinberg, F. J., "Electrical Control of Flame Carbon," Proceedings of the Royal Society of London, Series A, Vol. 289, 1965, pp. 192-205.

48 Place, E. R. and Weinberg, F. J., "The Nucleation of Flame Carbon by Ions and the Effect of Electric Fields," Eleventh Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, Pa., 1967, p. 245.

49 Mayo, P. J. and Weinberg, F. J., "On the Size, Charge and Number-rate of Formation of Carbon Particles in Flames Subjected to Electrical Fields," Proceedings of the Royal Society of London, Series A, Vol. 319, Oct. 1970, pp. 351-371.

50 Miller, W. J., comments on reference 48, Eleventh Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, Pa., 1967, p. 252.

51 Vinckier, C., Gardner, M. P. and Bayes, K. D., "A Study of Primary and Secondary Chemi-ionization Reactions in Hydrocarbon Oxidations," Sixteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, Pa., 1977, p. 881.

52 Howard, J. B., "On the Mechanism of Carbon Formation in Flames," Twelfth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, Pa. 1969, p. 877.

53 Ball, R. T. and Howard, J. B., "Electric Charge of Carbon Particles in Flames," Thirteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, Pa., 1971, p. 353.

54 Wersborg, B. L., Yeung, A. C., and Howard, J. B., "Concentration and Mass Distribution of Charged Species in Sooting Flames," Fifteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, Pa., 1975, p. 1439.

56 Prado, G. P. and Howard, J. B., "Formation of Large Ions in Sooting Flames," Evaporation Combustion of Fuel Droplets, edited by J. T. Zung, Advances in Chemistry Series, American Chemical Society, Washington, D.C. (to be published).

[57] Miller, W. J., "Ions in Flames - Evaluation and Prognosis," Fourteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, Pa., 1975, p. 307.

[58] Abrahamson, J. and Kennedy, E. R., "Electric Probe Studies in Pyrolyzing Hydrocarbons," Twelfth Biennial Conference on Carbon, The American Carbon Society, 1975, p. 169.

[59] Bowser, R. J. and Weinberg, F. J., "Chemi-ionization during Pyrolysis," Combustion and Flame, Vol. 27, Aug. 1976, pp. 21-32.

[60] Calcote, H. F., "Ions in Flames," Ion-Molecule Reactions, edited by J. L. Franklin, Plenum Press, New York, 1972, p. 673.

[61] Knewstubb, P. F., Mass Spectrometry and Ion-Molecule Reactions, Cambridge Univ. Press, London, England, 1969.

[62] LaHaye, J., Prado, G., and Donnet, J. B., "Nucleation and Growth of Carbon Black Particles During Thermal Decomposition of Benzene," Carbon, Vol. 12, Jan. 1974, pp. 27-35.

[63] Homann, K. H. and Wagner, H. Gg., "Chemistry of Carbon Formation in Flames," Proceedings of the Royal Society of London, Series A, Vol. 307, Oct. 1968, pp. 141-152.

DISCUSSION

DR. B. T. WOLFSON (AFOSR): I want to bring up one important point, and I want to expand on one of the statements that you made pertaining to the utilization of additives for either enhancement or reduction of particle size. All organizations utilizing gas turbine engines are deeply concerned about this. They will be more concerned as we are forced to use alternative fuels.

The point that I wanted to make is that it is not sufficient only to control the particle size. What we are really looking for is reduction in the mass that is emitted. Now, as you point out, there are some additives that can reduce particle size. That is not sufficient. The investigation should encompass not only the mechanisms for reduction in particle size, but also reduction in the mass due to that. In addition, we should obtain a basic understanding of how the additives react.

DR. HOWARD: That is a good point. In fact, additives widely used in the carbon black industry to control the size

of particles and the structure of agglomerates have little effect on the mass of carbon black formed.

DR. I. GLASSMAN (Princeton University): We should be careful in discussing the carbon-hydrogen ratio. Indeed, acetylene is an anomaly; its soot-forming tendency is different than in a premixed flame, is it not? Acetylene does not form carbon as readily as most other compounds in a premixed flame; it forms soot very readily in the diffusion flame.

DR. HOWARD: That is correct.

DR. GLASSMAN: So in that case, I do not think the carbon-hydrogen ratio will hold, will it?

DR. H. F. CALCOTE (Aerochem Research): Before you start making that kind of a comparison, you have to consider the temperature because the temperature in the premixed acetylene flame is very high. That complicates it.

DR. GLASSMAN: That is exactly what I am trying to point out.

DR. HOWARD: Chemical structure clearly is important along with the H/C ratio. The very different behavior of acetylene and benzene in soot formation is a good example of the H/C ration not being the whole story.

DR. GLASSMAN: Exactly. I would like to answer a question directed earlier to Dr. Dryer regarding relative importance of HO_2 and hydroxyl. I believe that we had been thinking along diffusion flame lines, where the HO_2 does not get into the fuel-rich side of the flame, and neither do many O radicals, whereas you can get hydroxyl from reactions of hydrogen atoms with water.

DR. D. M. GOLDEN (SRI International); I just want to amplify this question of H/C ratios because it seems to me that, if you have a simple mixture of benzene and a substituted aromatic compound, then the H/C ratio would be one thing, but the reactivity -- certainly the initial reactivity -- would all be carried by the substituted aromatic. The H/C ratio, by itself, is really not a good parameter. You modified it by saying with composition. At that point, maybe the combination of those two is a reasonable and useful parameter.

DR. HOWARD: I certainly agree that composition is important. Although the H/C ration has served as a useful

working parameter in dealing with data from small combustor rigs, the example given points out difficulties to be expected in any attempt to describe such a complex system with only one parameter.

DR. A. H. LEFEBVRE (Purdue University): As I mentioned earlier, although the chemistry of soot formation is very important in gas turbine combustion, soot formation also depends on the physical properties of the fuel and on combustor design, sometimes to an overriding extent. Thus, one can reduce soot formation very drastically by proper combustor design. For example, I have run a gas turbine combustor at fairly high pressures using benzene fuel, which as you pointed out, has a high tendency to smoke. There was no trace of any smoke whatsoever.

When I consider the problems that alternative fuels will pose for the gas turbine, I am not unduly worried except for one aspect which I shall refer to in a moment. If we take note of the new technologies that are being actively developed, especially in regard to fuel preparation, and I am thinking here of airblast atomization, premixing of fuel and air, prevaporization, etc., and if one adds to these the possibility of staging the combustion process and other techniques which, I believe, will be fully developed by the time we have to use alternative fuels, then I do not really see any serious combustion problems, provided we can get the fuel into the burner. This is the part that worries me, especially in regard to the problem of low thermal stability. This is a point that Professor Longwell and Dr. Blazowski already have touched on, but, surprisingly, it has not been developed here. I believe that, of all the practical problems that alternative fuels will pose, this is by far the most important. If we can persuade the fuel to enter the burner, then I foresee few problems, provided I am allowed to use the new techiques which might result in a slightly longer and more complicated combustor than we have now. The technology is there, and the only problem that causes me concern is that of thermal instability.

KINETICS OF NITRIC OXIDE FORMATION IN COMBUSTION

B. S. Haynes*
Department of Fuel Technology
University of New South Wales, Kensington, N.S.W., Australia

Abstract

A computer kinetic analysis of experimental data for nitrogen species (HCN, NO, and NH_3) in the burnt gases of fuel-rich ethylene flames shows that the NO yield, which is a strong function of temperature and composition of the flame, can be explained in terms of the N-atom reactions:

$$N + OH \longrightarrow NO + H$$

$$N + NO \longrightarrow N_2 + O$$

Under some conditions, it is also necessary to take into account: i) N_2 formation by $NH_i + NH_i$ processes; and ii) the rapid reduction of NO in the presence of hydrocarbons, possibly through processes such as

$$CH_3 + NO \longrightarrow \ldots HCN + H_2O$$

Overall, hot fuel-rich conditions favor the production of N_2 as opposed to NO.

Introduction

Experience with conventional fuels, which in all likelihood will prove valid in "alternatively-fueled" combustion systems as well, has indicated three main processes leading to the formation of nitric oxide.

---

* Presently Research Fellow, Institut für Physikalische Chemie der Universität, Göttingen, Federal Republic of Germany.

A. Zeldovich Mechanism

The kinetics of the extended Zeldovich mechanism[1,2]

$$O + N_2 \rightleftharpoons NO + N$$

$$N + O_2 \rightleftharpoons NO + O$$

$$N + OH \rightleftharpoons NO + H$$

have been studied widely and well reviewed.[3] This mode of NO formation is basically a fuel-lean, high-temperature phenomenon that has been found relatively amenable to control techniques.

B. Prompt NO

The existence of a non-Zeldovich pathway to the fixation of molecular nitrogen, first proposed by Fenimore,[4] was for some years a subject of controversy. The question as to whether excess concentrations of oxygen atoms in and near the primary reaction zone might not, in fact, explain the high rates of NO formation in this region of fuel-rich hydrocarbon flames was resolved largely by the detailed measurements of Iverach[5] and finally settled by the neat experiments of Hayhurst and McLean.[6] The latter showed that traces of hydrocarbon addition to fuel-rich hydrogen-oxygen-nitrogen flames dramatically increase NO production in the flame front. In similar experiments, Hayhurst[7] more recently has shown that the production of prompt NO is proportional to the concentration of N_2, the (hydrocarbon) fuel concentration, and the number of carbon atoms per fuel molecule.

The nature of the hydrocarbon-N_2 interaction is not yet definitely known, although the reaction

$$CH + N_2 \longrightarrow HCN + NH$$

seems a likely candidate. In this case, a rate constant k_a 2×10^{10} cm^3/mole-sec would apply.[8-10] Other reactions that have been considered include:

$$CH_2 + N_2 \longrightarrow HCN + NH$$

$$C_2 + N_2 \longrightarrow 2\ CN$$

The fact that C-N bonds (as HCN) are produced in the flame zone of such flames also has been demonstrated.[10-13] These observations have not yet been linked directly to the

N-N bond rupture because the high concentrations of hydrocarbons in these flames effectively reduce all reactive (non-N_2) nitrogen species to HCN, thus obscuring the nature of any source reactions.

The variation of the extent of hydrocarbon-N_2 reaction with temperature and with stoichiometry is an important consideration in terms of control techniques. In both cases, there is little sensitivity. The sharp fall-off in the amount of prompt NO at $\phi \sim 1.4$[4,5] is deceptive because the total concentration of reactive nitrogen continues to increase with increasing fuel-air ratio, the difference being a result of the growing stability of HCN and NH_3.[13] The question of the postflame distribution of reactive nitrogen among NO, HCN, and NH_3 is discussed, together with the fuel-NO problem, in the following section.

C. Fuel NO

Fuel NO is derived from bound nitrogen introduced with the fuel. This mode of NO formation, which has proved difficult to control with existing techniques, predominates when the nitrogen content of the fuel exceeds a few tenths of a percent, a condition very likely to occur in alternative fuels dervied from, e.g., coal.

In fuel-lean and stoichiometric flames, the conversion of fuel N to NO (and perhaps NO_2) is practically complete and occurs on a time scale comparable to that of the combustion itself. Apart from a few parametric studies,[14] very little examination of the kinetics of this process has been undertaken. Axworthy et al.[15] probed a lean, low-pressure CH_4-O_2-Ar flame that had been seeded with NH_3 or HCN. Because a large fraction of the added N species could not be accounted for in the reaction zone but was recovered later downstream, they concluded that a long-lived intermediate, possibly the OCN radical, may be involved. In ammonia-seeded, low-pressure, fuel-lean CO/O_2 flames, Seery and Zabielski[16] have measured NO and NH_3 concentrations and concluded that the N-atom reactions of the Zeldovich mechanism cannot alone describe the observations and that therefore other species such as NH and NH_2 must be involved.

Under fuel-rich conditions (such as pertain in diffusion flames in general), the conversion of fuel N to NO decreases monotonically with increasing fuel-air ratio.[14] However, it is now apparent[12] that the fuel N not appearing as NO may form HCN and NH_3, as well as the desirable end-product N_2. Quite apart from the noxious characteristics of HCN and NH_3,

consideration of the primary NO yield alone is obviously misleading because both of these species are converted practically quantitatively to NO on being mixed with excess air. Thus, what is of prime importance is the amount of N_2 produced under given conditions.

Results obtained for the distribution of nitrogen in a range of fuel-rich ethylene-air flames after a total reaction time of 10 msec are shown in Fig. 1. Here it is seen that the maximum yield of N_2 achievable is quite high (> 70%) but that this maximum is followed by a steep fall-off even though, based on equilibrium considerations, we should expect conversion to N_2 to keep increasing with fuel-air ratio. In order to understand bettter the conditions leading to increased N_2 production, we shall consider the kinetics of this process in some detail.

Several recent studies[10,13,17-19] of nitrogen chemistry in the burnt gases of fuel-rich hydrocarbon flames have dealt with the behavior of HCN, NH_i (NH_3, NH_2, NH, N), and NO. The sources of this combined nitrogen include the as-yet-unidentified hydrocarbon-N_2 reaction characteristic of these flames (prompt NO), as well as traces of fuel nitrogen species such as pyridine, acrylonitrile, ammonia, or nitric oxide itself added to the unburnt fuel-air mixture; under the fuel-rich conditions chosen (e.g., ethylene-air flames, ϕ >

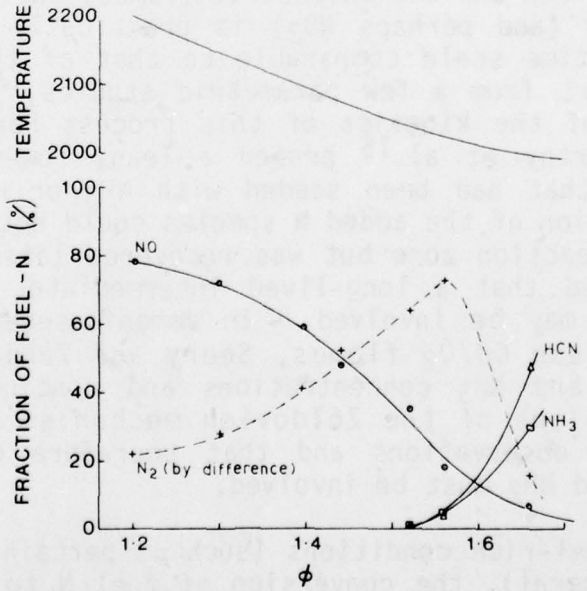
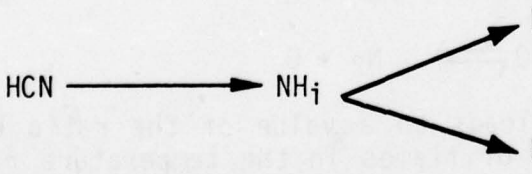


Fig. 1 Distribution of fuel-nitrogen among NO, HCN, NH_i, and N_2 (by difference) in the postflame gases of fuel-rich ethylene-air flames after an elapsed reaction time of 10 msec, as a function of fuel-air equivalence ratio.

1.4, temperature $\sim$ 2000 K), the formation of NO by the Zeldovich mechanism is always negligible. Regardless of the source, only HCN and NO are found just beyond the primary reaction zone, whereas NH_i species appear only further downstream in the burnt gases. These observations apply even to cases where NH_3 is added to the unburnt mixture, and so the nature of the input fuel nitrogen is not decisive in the postflame nitrogen chemistry. This simplification results from the fact that fuel nitrogen is converted quantitatively to HCN in the primary reaction zone of fuel-rich hydrocarbon flames[10] and accounts for the early observations that fuel NO does not depend on the type of the fuel N.

Full descriptions of the experimental observations may be found in Refs. 10 and 17-19. Briefly, HCN decomposes, and NH_i and NO begin to form; under conditions where a large accumulation of NH_i is observed, [NO] grows only slightly with time in the postflame gases, if at all, and the total combined nitrogen ($\Sigma_N = [HCN] + [NH_i] + [NO]$) falls only slowly (indicating slow conversion to N_2). On the other hand, in cases where NH_i reaches only a low concentration, both NO and N_2 formation are much faster. These observations support a mechanism where NH_i is intermediate to the production of NO and N_2, so that the accumulation of NH_i depends on the relative rates of HCN decay (input to NH_i) and NO and N_2 formation (output from NH_i). Experimentally, it also is observed that this accumulation of NH_i is very sensitive to the temperature and composition of the gases, and any mechanism attempting to explain nitrogen chemistry first of all must be capable of describing this feature.

The overall reaction scheme I has been proposed[17-19]:



(reaction scheme I)

The decay of HCN is thought[10,18,19] to occur via the mechanism

$$HCN + H \rightleftharpoons CN + H_2 \quad (1a)$$

$$HCN + OH \rightleftharpoons CN + H_2O \quad (1b)$$

$$HCN + OH \rightleftharpoons HOCN + H \quad (2)$$

$$CN + OH \rightleftharpoons OCN + H \quad (3)$$

where reactions (2) and (3) are rate-controlling.

At temperatures below about 2100 K, reaction (2) dominates ($k_2 = 2 \times 10^{11}$ cm^3/mole-sec). The rate of reaction (3) ($k_3 = 6 \times 10^{13}$ cm^3/mole-sec) depends on the second power of the OH radical concentration, and this reaction dominates at higher temperatures.

The oxycyanogen species such as HOCN and OCN have not been detected, but they are likely intermediates on the basis of thermodynamic and steric considerations.[10,12,19] These species probably give rise to NH_i species through reactions such as:

$$HOCN \rightleftharpoons HNCO \qquad (4)$$

$$OCN + H_2 \rightleftharpoons HNCO + H \qquad (5)$$

$$HNCO + H \rightleftharpoons NH_2 + CO \qquad (6)$$

$$OCN + H \rightleftharpoons NH + CO \qquad (7)$$

Such a mechanism would seem to account plausibly for the observed appearance of NH_i as HCN decomposes.[10,12,13,17-19]

With the assumption that the NH_i system $\{NH_3, NH_2, NH, N\}$ is balanced internally, we have shown that, in the absence of hydrocarbon species, the results are consistent with a mechanism in which NO is both formed and removed by a single species, which is identified as the nitrogen atom N[7]:

$$NH_i + H \rightleftharpoons NH_{i-1} + H_2; \quad i = 3,2,1 \qquad (8a\text{-}c)$$

$$NH_i + OH \rightleftharpoons NH_{i-1} + H_2O; \quad i = 3,2,1 \qquad (9a\text{-}c)$$

$$N + OH \rightleftharpoons NO + H \qquad (10)$$

$$N + NO \rightleftharpoons N_2 + O \qquad (11)$$

This interpretation leads to a value of the ratio $k_{10}/k_{11} = 1.0 \pm 0.2$ in a variety of flames in the temperature range 1950 to 2300 K.

The conclusion by Seery and Zabielski[16] that the N-atom is not the crucial species in an N_3-seeded, fuel-lean CO/O_2 flame is hardly surprising when one considers the abundance of oxidants such as O and O_2 in that system. The direct oxidation of, e.g., NH and NH_2 obviously will complicate the simple scheme given above, and we therefore emphasize that the present discussion is restricted to rather fuel-rich flames ($\phi > 1.5$) from which O and O_2 are effectively absent.

The identification of reactions (10) and (11) as the dominant processes in the NH_i-No interaction is rather surprising in the light of room-temperature data for reactions (12)[20,21] and (13).[21-25] However, given

$$NH + NO \longrightarrow (N_2 + OH) \qquad (12)$$

$$NH_2 + NO \longrightarrow (N_2 + H_2O) \qquad (13)$$

and the uncertainty in the heat of formation of the NH radical, the failure to find evidence for reaction (12) may not be inconsistent (see "Discussion"). Furthermore, it now appears[24,25] that, in the temperature range 200 to 500 K, reaction (13) has a negative "activation energy" of about 4 kJ/mole, so that this reaction could, in fact, be considerably slower at temperatures around 2000 K. Against this stands the evidence of recent flame work by Fenimore[17] in substantial agreement with the room-temperature work, although the undoubted presence of hydrocarbon species in his gases may render Fenimore's analysis of his data invalid (see "Discussion" and Ref. 18).

The objective in what follows is to examine more closely the nature of the NH_i-NO reactions. The proposed mechanism is used to predict the $[NH_i]$ and [NO] profiles resulting from the experimental decay of HCN, and the predicted results are compared with those observed experimentally. In this way, the ability of the model to account individually for the species NO and NH_i can be ascertained.

Measurements of the pertinent species H-atom, NO, HCN and NH_3 in the post-flame gases of atmospheric-pressure premixed ethylene/oxygen/nitrogen flat flames have been made.[18] The species HCN and NH_3 were determined by scrubbing quenched sample gases with 0.1-M NaOH solution and analyzing the solution for dissolved CN^- and NH_3, using specific ion electrodes. Continuous monitoring of NO was provided by a non-dispersive infrared analyzer. The Li/liOH technique was employed for H-atom determinations.

The analysis of four ethylene+fuel-nitrogen/oxygen/nitrogen flames (Table 1) is presented; flames I to III have the same stoichiometry (ϕ = 1.52) but average burned gas temperatures of 2070, 2010, and 1950 K, respectively. Flame IV is slightly more fuel-rich (ϕ = 1.66, T = 2000 K). Although apparently similar, these four flames are markedly different in respects that provide a sensitive test of reaction scheme I. Firstly, the measured downstream concentration of NH_i varies by two orders of magnitude from flame I to flame IV,

Table 1 Summary of flame conditions studied by computer kinetic modeling

Flame	Fuel[a]	Ø	Temp., K	Additive[b] ppm	Data Ref.	Figure
I	C_2H_4	1.52	2070	800 P	18	1
II 62%	C_2H_4/N_2	1.52	2010	700 A	18	2
III 46%	C_2H_4/N_2	1.52	1950	700 A	18	2
IV	C_2H_4	1.66	2000	500 NO	...	...

[a] Oxident is air in all cases.

[b] Equivalent concentration of N species in the burnt gas for the additives P = pyridine, A = ammonia, and NO = nitric oxide.

and both net increase and net decrease of both [NH_i] and [NO] are observed. Also, since the partial equilibrium N-atom mechanism [reactions (8-11)] depends on the cube of the radical (H, OH) concentration, the variation of [OH] by an overall factor of 5 between the flames (as shown in Fig. 2) means that the dependence on the radicals also can be gaged sensitively. Finally, flame IV is notably different from flames I to III in that in this case hydrocarbon species persist beyond the primary reaction zone and exist in significant concentration well into the burnt gases. The results for this flame show that this breakthrough of hydrocarbons, which is a very sensitive function of stoichiometry, causes important interference to reaction scheme I.

The experimental N-species data for flames I to III already have been presented graphically in Figs. 1, 2b, and 2c, respectively, of Ref. 18. In the case of flame IV, the data have not been presented before, but they are qualitatively similar to those of Fig. 1 of Ref. 19.

Method of Analysis

A computer kinetic program GCKP[26] has been used to model the proposed chemical mechanism and predict the profiles of NH_i and NO which are to be compared with the experimental observations. The inputs to the model are the starting conditions for all species, the experimentally observed profiles of HCN, H, and temperature, and the bulk burned gas composition. Since the cold-gas velocities used were 55±5 cm/sec,

and since we are considering only the burnt gas region, the diffusion velocities, even of H atoms, have been neglected.

The starting conditions for the calculations correspond to the composition and temperature at the first sampling point, usually 0.5 to 1.0 msec after the primary reaction zone. For the bulk gas, the equilibrium composition at the measured temperature was used. This was checked by occasional measurements of CO and CO_2 and found to be accurate. For species that were not determined experimentally, the initial concentrations were estimated from related measured species using partial equilibrium approximations and the bulk gas composition: thus $\{O_2, O, OH\}$ from H; CN from HCN; and $\{NH_2, NH, N\}$ from NH_3 and H. The calculated results actually were found to be insensitive to the initial concentrations of the minor species, because the starting transients are removed rapidly and the concentrations of these species are so low anyway.

For the program to model the measured temperature within 1 K throughout the reaction period, allowance has been made in the energy balance for radiant energy losses from the burnt gases. These losses lead to a temperature decline of about 4 K/msec.

The bulk gas composition and the radical pool $\{H, OH, O\}$ are related through the well-known series of reactions

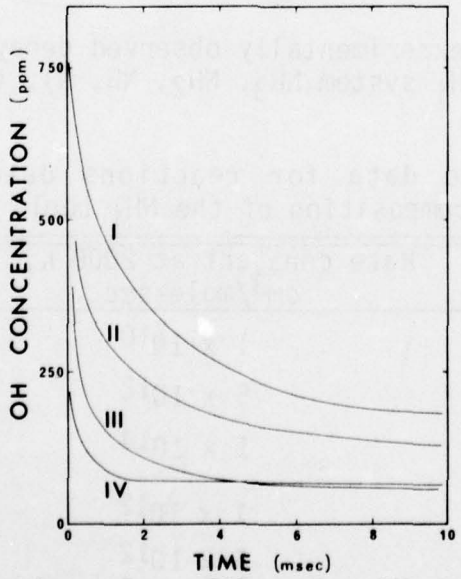


Fig. 2 Concentration of profiles for OH determined from the measured H-atom concentration for flames I to IV described in Table 1.

(14-18). The rate constants for reactions (14-17) are taken from Baulch et al.[27] and for reaction (18) the recommendation of Baulch and Drysdale[28] has been used. Each of the reactions is predicted by the program to be balanced throughout the postflame gases examined [in which case the system (14-17) is overspecified]:

$$H_2 + OH \rightleftharpoons H_2O + H \quad (14)$$

$$H_2 + O \rightleftharpoons H + OH \quad (15)$$

$$H_2O + O \rightleftharpoons OH + OH \quad (16)$$

$$O_2 + H \rightleftharpoons O + OH \quad (17)$$

$$CO + OH \rightleftharpoons CO_2 + H \quad (18)$$

In order to model the approach to overall equilibrium of this system, a recombination reaction must be included; in this case, the process

$$H + H + M \xrightarrow{k_\alpha} H_2 + M$$

has been used. Here k_α represents the effective forward rate constant for the actual processes H + H + M and H + OH + M. The value of k_α is chosen in each case to fit the experimental measurements of [H]; this fit is always within the scatter ($\pm$ 5%) in the experimental data.

To model the experimentally observed decay of HCN (that is, the input to the NH_i system NH_3, NH_2, NH, N), the reactions

Table 2 Kinetic data for reactions determining the composition of the NH_i pool.

Reaction	Rate constant at 2000 K, cm^3/mole-sec	Ref.
(8a)	1×10^{10}	29
(8b)	5×10^{12}	30
(8c)	1×10^{14}	31
(9a)	1×10^{12}	29,32
(9b)	5×10^{12}	31
(9c)	8×10^{13}	31

$$HCN + OH \xrightarrow{k_\beta} HNCO + H$$

$$HCNO + H \xrightarrow{k_\gamma} NH_2 + CO$$

have been used. These reactions represent a summary of the proposed sequence of reactions (1-7). For each flame, k_β is chosen to match precisely the data, and $k_\gamma = 10^{13} cm^3/mole\text{-}sec$. The value of k_β required is substantially constant from flame to flame and is largely insensitive to k_γ in the range $10^{12} < k_\gamma < 10^{14}$ $cm^3/mole\text{-}sec$, as expected if the initial attack on HCN is rate-controlling. As discussed elsewhere,[19] values of k_β of $2 - 4 \times 10^{11}$ $cm^3/mole\text{-}sec$ describe the HCN decay.

With the input to the NH_i pool specified, we now can examine the depletion processes such as reactions (10-13) and thus predict the $[NH_i]$ and [NO] profiles. Firstly, however, we must know something about how the various NH_i {NH_3,

Table 3 Thermodynamic data for the NH_i species

Species	ΔH_f°, kJ/mole	Ref.
NH_3	-46.0 ± 0.5[a]	33
NH_2	168 ± 12	33
	196 ± 8	34
	185 ± 5[a]	35
NH	339 ± 10	33
	343 ± 5	36
	378 ± 15	37
	376 ± 15	38
	377 (ab initio)[a]	39
N	472 ± 4[a]	33

[a]Value taken in this study for the basic data set.

Table 4 Composition of the NH_i $\{NH_3, NH_2, NH, N\}$ pool at partial equilibrium in flame IV, calculated using the basic data set of Table 3

Species	Relative concentration[a]
NH_3	1
NH_2	0.031λ
NH	$0.00083\lambda^2$
N	$0.0022\lambda^3$

[a] $\lambda = [H]/[H]_{eq}$.

Table 5 Summary of cases studied

Case[a]	Flames	Features[b]
A	I,II,III,IV	Basic N-atom model. In each flame, $k_{11} = 2.75$, and k_{10} is adjusted to predict accurately the peak [NO] (see text).
B	I,II,III,IV	Exactly as for case A, except that k_{10} and k_{11} have been doubled.
C	IV	Reaction (13), with $k_{13} = 1.0$, included in basic model to examine possibility of role for this reaction in the fast decay of NO in this flame.
D	III	Shows effects of error in the determination of [H]; conditions as for Case A, with H and OH concentrations 10% higher.
E	IV	Shows effects of error in the measurement of temperature on predicted NH_i concentration; conditions as for case A, with initial temperature 20 K higher.
F	I,II,III,IV	Shows effects of including reaction (13), with $k_{13} = 0.8$, on NH_i accumulation. In each flame, $k_{11} = 2.75$, and k_{10} is adjusted to match the peak experimental NO concentration.

[a]Cases refer to curves in Figs. 3-6 for flame I-IV, respectively.

[b]Units for rate constants = 10^{13} cm^3/mole-sec.

NH_2, NH, N_i species are related to each other, through the reaction sets (8) and (9). Rate constants for this system have been determined experimentally only for reactions (8a) and (9a), and these at room temperature, so that little reliance can be placed on them at flame temperatures. Recourse to calculated rate constants has been made for the remaining reactions; Table 2 summarizes the basic data used for all of these rate constants.

In terms of the thermodynamics of the NH_i species, summarized in Table 3, there is uncertainty in the heats of formation of both NH and NH_2. For our basic data set, we have used the more recent value of $\Delta H_f^o(NH)$ = 376 kJ/mole in preference to the older value of 340 kJ/mole. The data for $\Delta H_f^o(NH_2)$ are less polarized, and the median value of 185 kJ/mole, which we have used here, would seem fairly reliable. The relative concentrations of the NH_i species which apply for partial equilibrium in flame IV, calculated using the basic data set, are shown in Table 4.

To prevent this analysis from becoming bogged down in an elaborate "curve-fitting" routine, we have begun with the simple N-atom mechanism for NH_i depletion suggested in the previous work,[18] that is, reactions (10) and (11). The efficacy of this model is evaluated by comparison of prediction with experiment, and the effects of uncertainties in some parameters are considered. Finally, where deficiencies in the simple model are apparent, we consider what alterations and extensions may be invoked in the model to account for observations reasonably.

Discussion

In terms of reaction scheme I, the NH_i depletion reactions are the only reactions forming and removing NO. Therefore, the ability to predict accurately the behavior of this species is the first test of any model.

A. Behavior of NO

In each of the flames I to III, the experimentally observed behavior of NO can be modeled precisely by the simple scheme of reactions (10) and (11), where N is generated by successive H-atom abstraction from the NH_i species, $NH_3 \longleftrightarrow NH_2 \longleftrightarrow NH \longleftrightarrow N$ [reactions (8) and (9)]. The only variable to which the predicted [NO] was found to be sensitive is the ratio of the rate constants k_{10}/k_{11}; this ratio was adjusted in each case to make the predicted maximum NO concentration agree with that experimentally observed and was found

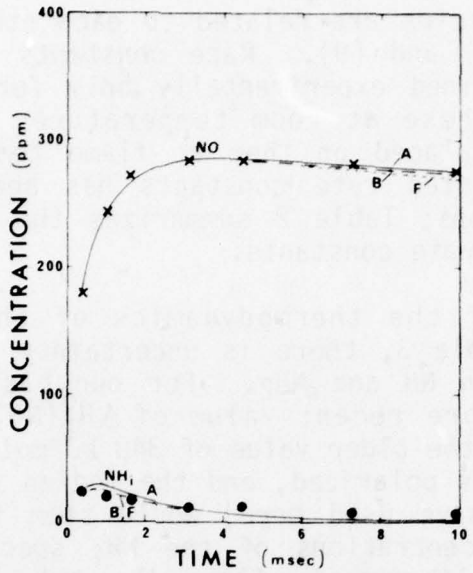


Fig. 3 Comparisons of experimental NO (x) and NH_i (●) concentrations in flame I with values predicted for the modeling cases identified in Table 5.

to be 1.1, 1.1, and 1.0 (±0.1) for flames I to III, respectively. These results, showing the accuracy with which the experimental [NO] is modeled over the entire reaction period, are plotted in Figs. 3-5 for case A+; here a value of k_{11} = 2.75 x 10^{13} cm^3/mole-sec (compatible with the recommendation of Baulch et al.[29]) has been used and k_{10} adjusted to give the appropriate ratio. When both k_{10} and k_{11} are doubled (case B, Figs. 3-5), the difference in the predicted [NO] profile is negligible (within the scatter of the experimental data); this implies a change in the required ratio k_{10}/k_{11} of less than 5%.

The result that the predicted [NO] is practically independent of reasonable values of the rate constants for reactions (10) and (11) (at constant k_{10}/k_{11}) is not unexpected, since NO is formed and removed, respectively, only by these two reactions. Also there is some feedback in the system because faster reactions (10) and (11) deplete NH_i more quickly, thus slowing the reaction rate and resulting in less sensitivity to the changes in reaction rate constants. This effect is accentuated by the fact that, as predicted by the model, the H-atom abstraction reactions (8) and (9) are partly rate-controlling.

Since the predicted [NO] effectively does not depend on the absolute values of k_{10} and k_{11}, it is not surprising

+ Descriptions of parameters used in the individual cases studied are listed in Table 5.

that it also should be quite insensitive to the state of the NH_i system. This is because increasing the N-atom concentration has analytically the same effect as an increase in k_{10} and k_{11}. Thus, the fact that the predicted and measured $[NH_i]$ for cases A and B in Figs. 3-5 show marked differences does not affect the analysis significantly in terms of NO. Uncertainties in heats of formation and rate constants in the NH_i system also may be neglected: for example, the inferred ratio k_{10}/k_{11} remains constant within 10% if a value of $\Delta H_f^o(NH)$ = 340 kJ/mole is used in place of the basic data set value of 376 kJ/mole.

In the case of flame IV, where substantial decomposition of NO occurs, the model is clearly inconsistent, with the experimental results failing to predict the initial rate of decay within a factor of 10 (curves A and B in Fig. 6). The possibility that a reaction such as reaction (13) may play an important role was investigated by including this reaction in the model with $k_{13} = 1 \times 10^{13}$ cm^3/mole-sec (curve C). Now, however, the model is totally at odds with the observed behavior of NO, and it appears that NH_i-NO interactions cannot explain satisfactorily the behavior of NO in this flame; how this deficiency can be rectified in terms of hydrocarbon reactions is discussed later.

B. Behavior of NH_i Species

Having determined that reactions (10) and (11) are sufficient to account for the behavior of NO (in the absence

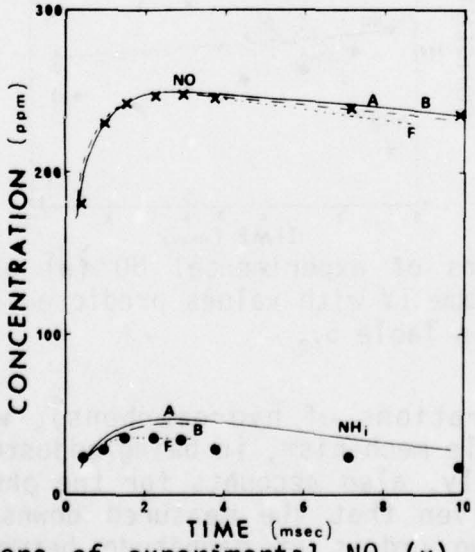


Fig. 4 Comparisons of experimental NO (x) and NH_i (●) concentrations in flame II with values predicted for the modeling cases identified in Table 5.

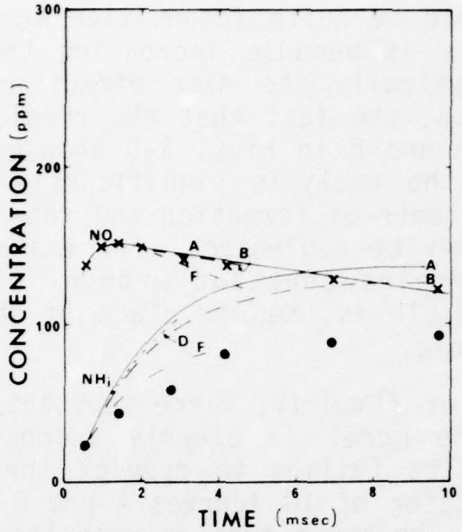


Fig. 5 Comparisons of experimental NO (x) and NH_i (●) concentrations in flame III with values predicted for the modeling cases identified in Table 5.

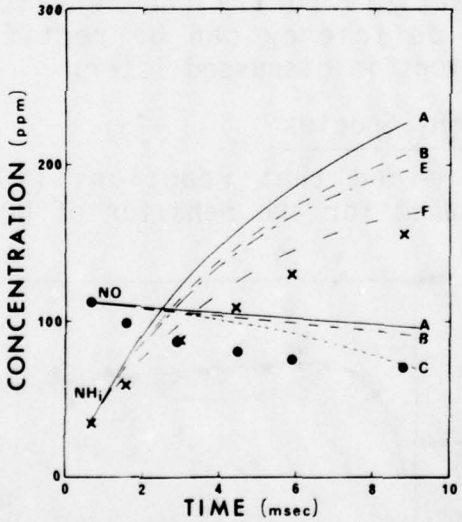


Fig. 6 Comparisons of experimental NO (●) and HN_i (x) concentrations in flame IV with values predicted for the modeling cases identified in Table 5.

of high concentrations of hydrocarbons), we now consider whether this simple mechanism, in being adjusted to predict NO behavior accurately, also accounts for the observed accumulation of NH_i. Given that the measured downstream values of $[NH_i]$ vary by two orders of magnitude between flame I and flame IV, examination of cases A in Figs. 3-5 shows that this model is indeed successful to a large degree.

AD-A061 050 PURDUE UNIV LAFAYETTE IND PROJECT SQUID HEADQUARTERS F/G 21/4
ALTERNATIVE HYDROCARBON FUELS: COMBUSTION AND CHEMICAL KINETICS--ETC(U)
OCT 78 C T BOWMAN, J BIRKELAND N00014-75-C-1143
UNCLASSIFIED SQUID-PU-R2-78 NL

5 OF 5
AD
A061050



END
DATE FILMED
1-79
DDC

In flame I, where only traces of NH_i are detected, measured and predicted profiles are in agreement within 20% for 4 msec into the burnt gases. After that, the predicted $[NH_i]$ falls to 2 ppm at 10 msec, whereas the measured value remains constant at about 8 ppm. This may not be an inconsistent result because of the problems involved in measuring low NH_i concentrations, namely, a long response time for the measuring electrode at low concentrations and an inherent low-level background response.

The relative agreement between predicted and measured NH_i concentrations is within 25% throughout the analyzed reaction time of flame II. The fact that the model correctly predicts the turning point in the $[NH_i]$ profile is also significant. In flames III and IV, significantly more accumulation of NH_i is observed in the burnt gases, and here, too, although overpredicting by up to 50%, the model is seen to be relatively successful.

Based on the results in these four flames, where all of the qualitative and, to a good approximation, the quantitative features of the $[NH_i]$ profiles can be predicted, as can the NO profiles in the absence of hydrocarbons, it is clear that the basic N-atom model does describe most features of the NH_i-NO system. However, this is not a complete description, for, as is shown in the following argument, not all of the quantitative discrepancy between the predicted and measured NH_i profiles, particularly in flames III and IV, can be attributed to experimental error or to uncertainties in the various modeling parameters.

Experimental errors in the measurements of [HCN], [NO], and $[NH_i]$ all are considered less than 5%, so that these may be neglected. Determination of the radical (H-atom) concentration is accurate within 15%, but, as shown in Fig. 6 for case D, even errors of this magnitude have little effect on the predictions. Similarly, although the system is very temperature-sensitive, a temperature change of 20 K (which is greater than the experimental uncertainty of $\pm$ 15 K) cannot improve the prediction radically; see case E, Fig. 6.

Turning to the question of uncertainty in the model, we see first of all that doubling the rate constants k_{10} and k_{11} has little effect on the predictions for NH_i (cases B, Figs. 3-6). This derives from the result that the generation of N atoms by the reaction sets (8) and (9) ($NH_3 \leftrightarrow NH_2 \leftrightarrow NH \leftrightarrow N$) is partly rate controlling; that is, N is not held at its partial equilibrium value because of relatively too rapid depletion by reactions (10) and (11). In fact, the

basic data set used in the calculations predicts that the N-atom concentration is in the range 30 to 80% of its (limiting) partial equilibrium value with respect to NH_3. To improve the performance of the simple mechanism, the rate of generation of N atoms by H-atom stripping from NH_3 must be increased plausibly.

Reactions (8a) and (9a) ($NH_3 \longleftrightarrow NH_2$) offer no scope for improvement, as they always are equilibrated within 10%, independent of reasonable values chosen for the relevant rate constants and thermodynamic properties. The major hold-up in the system comes from the reactions (8c) and (9c) ($NH \longleftrightarrow N$), with lesser contributions from reactions (8b) and (9b) ($NH_2 \longleftrightarrow NH$), but the fact that these reactions already are tending toward a balance means that the net rate is relatively insensitive to changes in the rate constants. Since the rate constants used for these reactions (Table 2) are approaching the collision limit anyway, only negligible improvement in the prediction is foreseeable.

When the low value of $\Delta H_f^o(NH)$ = 340 kJ/mole is used in the computations, the partial equilibrium concentration of NH is increased by an order of magnitude, and reactions (8c) and (9c) ($NH \longleftrightarrow N$) are more nearly balanced. The overall result, however, remains substantially unaltered because reactions (8b) and (9b) ($NH_2 \longleftrightarrow NH$) are now less likely to be balanced, and the two effects offset one another to a large extent. Thus it is concluded that, even though the discrepancies between predicted and measured $[NH_i]$ are relatively small and uncertainty in some of data relatively large, the simple N-atom mechanism cannot account completely for the behavior observed. Therefore we must consider the possibility of other reactions occurring as well.

The obvious candidates for consideration are reactions (12) and (13). For the high value of $\Delta H_f^o(NH)$ used, reaction (12) is found to have negligible effect on the accumulation of NH_i species. Although this reaction may be more important if $\Delta H_f^o(NH)$ is lower, this question will not be considered further here, and the discussion will deal only with the possibility of a role for reaction (13).

When reaction (13) is used to bring about a reduction in the NH_i concentration predicted for flames III and IV, values of $k_{13} \sim 10^{13}$ cm^3/mole-sec are required to match the experimental results, as shown by curves F in Figs. 5 and 6. Such values of k_{13} would be consistent with room-temperature estimates for this rate constant,[21-25] but they are higher than the detailed kinetic analysis of Ref. 17 would suggest.

In fact, it is apparent from the figures that, although NH_i is reasonably well modeled here, the predicted behavior of NO is now in poor agreement with the experimental results. The peak NO concentration can be modeled by judicious choice of k_{10} to match k_{11} and k_{13}, but then the predicted rate of decay of NO after the peak is more than twice that observed experimentally. Moreover, the value $k_{NO\text{-forming}}/k_{NO\text{-removing}}$ is no longer a constant in flames I to III. Similar results are obtained in flames I and II, although the magnitude of the effect on NH_i and the discrepancy with NO are less in both cases. These comparisons cannot be made in flame IV, because the behavior of NO is not governed by NH_i reactions alone. Thus, *although in individual cases the predicted* $[NH_i]$ profile can be forced to fit the experimental results by inclusion of reaction (13), this does not produce consistent results, and we conclude that this reaction does not play an important role in the NH_i-NO interaction in these flames.

Because the NH_i-NO processes such as reactions (10-13) alone do not seem to be able to explain fully the observed rate of NH_i removal, we surmise that some other process also is occurring. The formation of N-N bonds by NH_i-NH_i reactions would seem a likely explanation, and this interpretation is supported by the fact that shock-tube pyrolysis of NH_3 at temperatures above 2000 K leads to significant decomposition, and N_2 formation results.[40] A possible route for such processes is the association of amidogen NH_2.[21] Since such NH_i-NH_i reactions would be second order in NH_i, their influence will be relatively greater in flames where NH_i concentrations are higher; such an effect would be consistent with the progressively greater overprediction of NH_i accumulation from flames I to IV and also with the unrealistically high values of k_{11} obtained from flames III and IV by partial equilibrium analysis.[18]

The rate of decay of NH_i in flame III, which would occur if the initial rate data of Michel and Wagner[40] were applicable, is 4 ppm/msec, which is considerably less than is required to account for the discrepancy of 30 ppm after 3 msec observed for case A in Fig. 5. This is not surprising, since the overall reactions in a shock tube and in a steady radical-rich flame are unlikely to be the same; the important point is that significant NH_i-NH_i reactions do occur. These reactions may be able to account for the failure of the model based on NH_i-NO processes to predict satisfactorily the behavior of NH_i species, even though such processes [the N-atom reactions (10) and (11)] seem to be adequate to model NO in the absence of hydrocarbons.

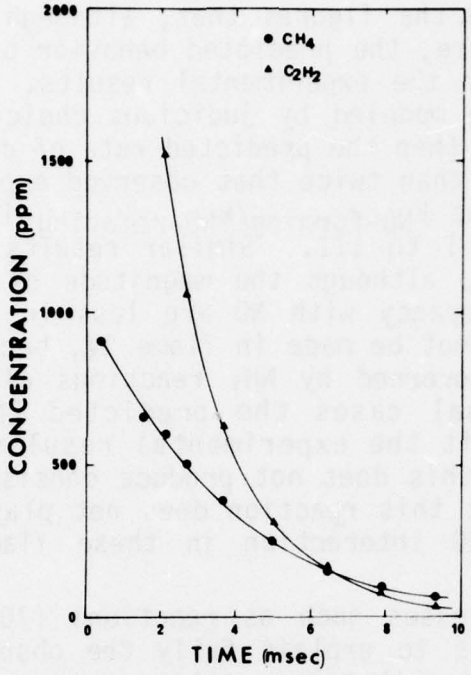


Fig. 7 Measured concentration profiles for CH_4 (●) and C_2H_2 (▲) in the burnt gases of an ethylene-air flame; $\emptyset$ = 1.66, T = 2000 K (flame IV).

C. Influence of Hydrocarbon Species

There is no doubt that hydrocarbon species in the primary reaction zone react with NO and NH_3 to form HCN,[10,17-19] and one would expect such processes to occur also in the burnt gases whenever excess hydrocarbons persist beyond the flame front. Since the reaction of NO in flame IV is found to be too fast to be accounted for by NH_i + NO reactions, we have examined the possibility that some hydrocarbon-NO interaction occurs in the burnt gases of this very rich flame. Sample gases have been analyzed for various individual hydrocarbons using an FID gas chromatograph: the hydrocarbons identified include methane, ethane, ethylene, acetylene, propane, and propylene, but of these only methane and acetylene are present in concentrations greater than 20 ppm. The concentration profiles for methane and acetylene are shown in Fig. 7. By comparison, the maximum hydrocarbon concentrations in flame I are two orders of magnitude less, and these species persist only 1-2 msec beyond the flame zone.

The species analyzed as methane in the quenched sample will be derived predominantly from CH_4 and CH_3 in the hot gases. As has been suggested previously[41] (and verified in the present study by computer kinetic modeling), reaction (19) is balanced rapidly in the burnt gases, thus allowing the concentrations of these flame species to be related to one

another:

$$CH_4 + H \rightleftharpoons CH_3 + H_2 \qquad (19)$$

The concentrations of such species as $[CH_2]$, [CH], and [C] all are expected to be extremely low in the burnt gases. For the acetylene species, C_2H_2 is expected to be the dominant contributor, with perhaps small amounts of C_2H as well.

At this stage, one can only speculate on the nature of the possible processes occurring. Fenimore and Jones[41] used reaction (20) as a means of estimating CH_3 concentrations in the primary reaction zone of methane-oxygen flames. More recently, it has been suggested that reaction (21) could be important in hydrocarbon-NO mixtures at 1200 to 1700 K,[42] but the very low concentrations of CH expected in the present situation would rule this out here:

$$CH_3 + NO \longrightarrow \ldots \xrightarrow{k_\delta} HCN + H_2O \qquad (20)$$

$$CH + NO \longrightarrow ? \qquad (HCN + O) \qquad (21)$$

Reaction (20) was included in the basic N-atom model, as were reaction (19) and the experimental $[CH_4]$ profile, to provide a plausible example of an hydrocarbon-NO interaction. With the addition of this reaction, it now proved possible to choose k_δ to make the computed profile for NO match the experimental results very precisely, as shown in Fig. 8a for the value of $k_\delta = 2.2 \times 10^{11}$ cm^3/mole-sec. When the fuel-nitrogen (as NO) addition to this flame was increased to a total of 2000 ppm, strong decay of NO was observed in the burnt gases, and, as shown in Fig. 8b, the same value of k serves to model this result precisely also. The computed profiles are sufficiently senstitive to k_δ for this value (2.2×10^{11} cm^3/mole-sec) to be considered accurate within 25%; furthermore, the value of k(N + NO) employed in the calculations has very little effect on the k_δ required to model the results because the hydrocarbon interaction dominates.

The value of $k_\delta = 2.2 \times 10^{11}$ cm^3/mole-sec does not agree well with the established rate constant for the primary process of 12×10^{13} cm^3/mole-sec at room temperature.[43] This is not necessarily an inconsistent result, because the formation of HCN can hardly occur directly but perhaps as

$$CH_3 + NO \rightleftharpoons CH_3NO \rightleftharpoons CH_2NOH \longrightarrow HCN + H_2O$$

where the primary association and the oxime rearrangement are reversible.[44] At this juncture, it is interesting to note

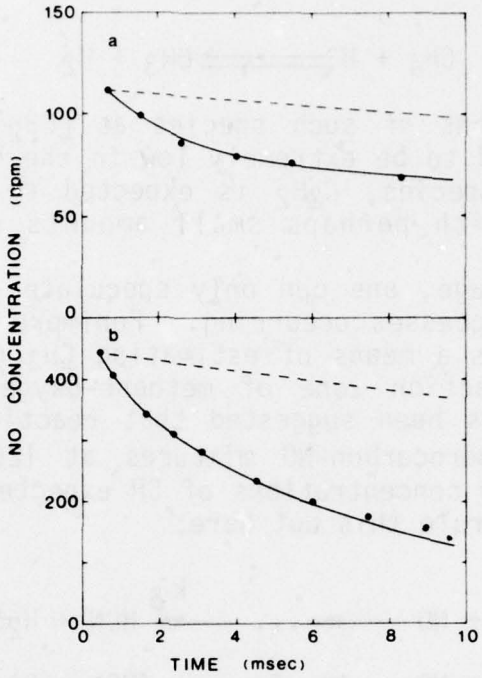


Fig. 8 Measured and predicted profiles of NO concentrations in burnt gases containing hydrocarbons, showing the effect of inclusions of reaction (20). The results pertain to an ethylene-air flame (ϕ = 1.66, T = 2000 K) seeded with a) 500-ppm NO (flame IV) and b) 2000-ppm NO. The predictions are calculated for the following: - - - - the simple N-atom mechanism (case A, Table 5); and ——— the same mechanism, together with reaction (20), $k_{19} = 2.2 \times 10^{11}$ cm^3/mole-sec.

that the isoelectronic reaction (13) well may proceed through a similar pathway, so that it, too, would be expected to show an effective activation energy that is negative, which is consistent with the results of this study.

Thus it is concluded that the anomalous decay of NO in flame IV is explicable in terms of a hydrocarbon-NO reaction such as reaction (20). Reaction scheme I therefore should be modified to include the possibility that such processes occur whenever hydrocarbons are present.

The possibility that NH_i species react with hydrocarbons also should be considered, especially as these species never leave the primary reaction zone as such but appear only in the postflame gases.[19] Such reactions are known to occur at room temperature also, for example, in active nitrogen flames with hydrocarbons.[45] As with the hydrocarbon-NO reaction, the only plausible product for such processes at high tempera-

tures is HCN, and so the effect with NH_i must be slight in the flames studied here, because the same mechanism of HCN decay is found to apply in flames with and without the presence of hydrocarbons.[19] In any case, because the experimentally observed (net) decay of HCN is used as the input to the NH_i system in the computer model, such recycling already is taken into account in this study.

Conclusions and Generalizations

A simple one-parameter reaction model based on reaction scheme I accounts for most features of experimentally observed nitrogen chemistry in the burnt gases of fuel-rich ethylene-air flames at temperatures around 2000 K. The only NH_i-NO reactions needed to model the results are the N-atom reactions 10 and 11, where the ratio k_{10}/k_{11} controls the degree of agreement between prediction and measurement. The value of this ratio is found to be 1.0 ± 0.2. The inclusion of a major route to N_2 via other NH_i+NO reactions, such as 12 and 13, produces inconsistent results, and it is concluded that such processes do not play as important a role in these flames as the extrapolation of room temperature data would imply. Thus, from the variability in the fitted value of k_{10}/k_{11}, we estimate that less than 30% of any N-N bond formation (as N_2 or N_2O) arises through reactions 12 and 13.

The identification of the N-atom as the crucial species in the removal of NH_i and the formation of N_2 is consistent with the observed high sensitivity to temperature and stoichiometry of the overall system. To a first approximation, the N-atom concentration can be equated with the partial equilibrium value derived from equation sets 8 and 9:

$$\frac{[N]}{[NH_3]} = \frac{1}{K_a \cdot K_b \cdot K_c} \left\{ \frac{[OH]}{[H_2O]} \right\}^3 = \frac{\lambda^3}{[H_2]^{3/2}} \exp(-E_a/RT)$$

where λ is the radical overshoot ratio ratio, $[H]/[H]_{eq}$, and where the effective activation energy of E_a = 540 kJ/mole is a measure of the temperature sensitivity. The dependence of [N] on the flame stoichiometry appears to be weak in this expression, mainly due to falling temperature as we go to richer flames. However, there is an implicit dependence which is not obvious from the data presented: under certain conditions, λ is a very strong function of stoichiometry. This arises through the effect of excess hydrocarbons in the burnt gases catalyzing the recombination of radicals.[46,47] The critical stoichiometry at which breakthrough of hydrocarbons

(mainly C_2H_2 and CH_4) occurs is sharply defined and so, therefore, is the catalysis effect: for the series of ethylene air flames used in Fig. 1, measurements[48] show that, for $\phi \lesssim 1.56$, [H] remains a factor of 1.5-2 in excess of $[H]_{eq}$ even after 10 msec have elapsed in the post-flame gases, while already at $\phi = 1.60$, full equilibrium is reached within 2 msec. Thus the average value of λ falls sharply in this range and so does the rate of reaction of NH_i species through N; the net result is an increase in the concentration of these NH_i intermediates and a rapid fall-off in the production of N_2, just as shown in Fig. 1. The fall in radical concentrations slows, as well, the decomposition of HCN which therefore also persists longer in the burnt gases.

The conclusions here with regard to the predominance of the N-atom reactions are strictly valid only for the rather narrow range of conditions examined, and, before accrediting them any generality, it is necessary to consider complications likely to arise under other conditions of temperature, stoichiometry, and flame structure. Qualitatively, the same overall mechanism as used in this work would seem to apply over a wide range of temperatures (1500-2500 K) in fuel-rich post-flame gases.[10,14,17-19] However, the equilibrium distribution of NH_i species at lower temperatures favors NH_2 whereas the supply of N-atoms is kinetically disfavored so that reactions of NH_2 (such as 13) may begin to dominate. (Similar considerations apply to reactions of NH, but the uncertainty in the heat formation of this species makes even the prediction of trends difficult.) Thus, given the relatively high rates of N_2 formation deduced from measurements at temperatures as low as 1500 K,[17] and considering the unlikelihood that the N-atom should be responsible for such observations at these temperatures, it does seem that the full mechanism of N-N bond formation is not yet established. Observations of N_2O in some fuel-N systems (reported in the discussion sections elsewhere in this volume, and long established in the NH_3/O_2 flame zone) emphasize this fact. A further complication may arise in the formation of N-N bonds by NH_i+NH_i processes, as indicated in the present work.

Whenever substantial concentrations of oxidants such as O and O_2 are present (which occurs in lean, stoichiometric, and moderately fuel-rich, $\phi < 1.3$, post-flame gases and in all primary reaction zones), even the qualitative model used in this study cannot be expected to apply. These oxidants may be capable of attacking directly not only most of the known and postulated nitrogenous intermediates such as HCN, OCN, NH_3, NH_2, and NH, but also the parent fuel-N molecule itself.

In some of these reactions, direct formation of an N-O bond is possible, e.g.,:

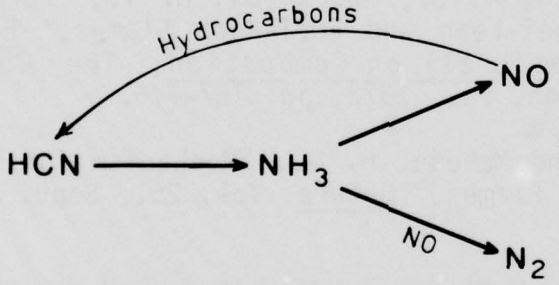
$$OCN + O \longrightarrow CO + NO$$

$$NH_2 + O \longrightarrow H + HNO$$

Although a full mechanism of fuel-N chemistry must take these processes into account, they are probably of little direct importance in overall reducing conditions, where combustion control of fuel-NO is most promising.

At the other extreme, in very fuel-rich conditions where hydrocarbons persist far into the post-flame gases, the disappearance of NO is too fast to be accounted for by any NH_i+NO reactions. This result is explicable in terms of hydrocarbon-NO reactions which we have represented in our analysis by reaction 20; obviously this choice is not definitive, and our understanding of the factors involved remains largely qualitative.

Despite the fact that not all the individual steps are known with certainty, we propose that the overall reaction scheme II is a fairly complete model of nitrogen chemistry in fuel-rich hydrocarbon flames:



(reaction scheme II)

In terms of control techniques for maximizing N_2 production, the optimum can best be described as hot and rich: hot to keep the reaction rate high, and rich to favor N_2 formation. This formula is supported by recent results obtained from laminar diffusion flames in which the conversion of fuel-N to N_2 depends directly on the time spent in, and temperature of, the rich flame zone.[49] Furthermore, under hot, rich conditions, the hydrocarbon-NO reaction will serve to "recycle" NO, thus further increasing the eventual yield of N_2.

Acknowledgments

The experimental and analytical work described here was carried out in the Department of Fuel Technology at the

University of New South Wales and was supported by a grant from the National Coal Research Advisory Committee. The assistance of D. Iverach, N.Y. Kirov, and G.D. Sergeant is gratefully acknowledged.

References

[1]Zeldovich, J., "The Oxidation of Nitrogen in Combustion and Explosions," Acta Physicochimica U.R.S.S., Vol. XXI, No. 4, 1946, pp. 577-628.

[2]Bowman, C. T. and Seery, D. J., "Investigation of Nitric Oxide Formation Kinetics: the CH_4-O_2-N_2 Reaction," Emissions from Continuous Combustion Systems, edited by W. Cornelius and W. G. Agnew, Pleunum Press, London, 1972, pp. 123-129.

[3]Bowman, C. T., "Kinetics of Pollutant Formation and Destruction in Combustion," Progress in Energy and Combustion Science, Vol. 1, No. 1, 1975, pp. 33-45.

[4]Fenimore, C. P., "Formation of Nitric Oxide in Premixed Hydrocarbon Flames," Thirteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, Pa., 1971, pp. 373-380.

[5]Iverach, D., Basden, K. S., and Kirov, N. Y., "Formation of Nitric Oxide in Fuel-Lean and Fuel-Rich Flames," Fourteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, Pa., 1973, pp. 767-775.

[6]Hayhurst, A. N. and McLean, H. G., "Mechanism for Producing NO from Nitrogen in Flames," Nature, Vol. 251, Sept. 27, 1974, pp. 303-305.

[7]Hayhurst, A. N. and Vince, I. M., "Production of 'Prompt' Nitric Oxide and Decomposition of Hydrocarbons in Flames," Nature, Vol. 266, April 7, 1977, pp. 524-525.

[8]Braun, W., McNesby, J. R., and Bass, A. M., "Flash Photolysis of Methane in the Vacuum Ultraviolet. II. Absolute Rate Constants for Reactions of CH with Methane, Hydrogen, and Nitrogen," Journal of Chemical Physics, Vol. 46, March 15, 1967, pp. 2071-2080.

[9]Blauwens, J., Smets, B., and Peeters, J., "Mechanism of 'Prompt' NO formation in Hydrocarbon Flames," Sixteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, Pa., 1977, pp. 1055-1062.

[10]Morley, C., "The Formation and Destruction of Hydrogen Cyanide from Atmospheric and Fuel Nitrogen in Rich Atmospheric Pressure Flames," Combustion and Flame, Vol. 27, Oct. 1976, pp. 189-204.

[11]Bachmaier, F., Eberius, K. H., and Just, T., "The Formation of NO and the Detection of HCN in Premixed Hydrocarbon-Air Flames at One Atmosphere," Combustion Science and Technology, Vol. 7, No. 2, 1973, pp. 77-84.

[12]Haynes, B. S., Iverach, D., and Kirov, N. Y., "The Behavior of Nitrogen Species in Fuel-Rich Hydrocarbon-Air Flames," Fifteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, Pa., 1975, pp. 1103-1112.

[13]Haynes, B. S., "Production of Nitrogen Compounds from Molecular Nitrogen in Fuel-Rich Hydrocarbon-Air Flames," Fuel, Vol. 56, April 1977, pp. 199-203.

[14]Fenimore, C. P., "Formation of Nitric Oxide from Fuel Nitrogen in Ethylene Flames," Combustion and Flame, Vol. 19, Oct. 1972, pp. 289-296.

[15]Axworthy, A. E., Schneider, G. R., and Dayan, V. H., "Chemical Reactions in the Conversion of Fuel Nitrogen to NO_X," United States' Environmental Protection Agency Symposium on Stationary Combustion, Atlanta, Ga., Sept. 24-26, 1975.

[16]Seery, D. J. and Zabielski, M., "Mass Spectrometer Sampling of a $CO-NH_3-O_2$ Flame," Combustion and Flame, Vol. 28, No. 1, 1977, pp. 93-98.

[17]Fenimore, C. P., "Reactions of Fuel Nitrogen in Rich Flame Gases," Combustion and Flame, Vol. 26, Apr. 1976, pp. 249-256.

[18]Haynes, B. S., "Reactions of Ammonia and Nitric Oxide in the Burnt Gases of Fuel-Rich Hydrocarbon-Air Flames," Combustion and Flame, Vol. 28, No. 1, 1977, pp. 81-91.

[19]Haynes, B. S., "The Oxidation of Hydrogen Cyanide in Fuel-Rich Flames," Combustion and Flame, Vol. 28, No. 2, 1977, pp. 113-121.

[20]Hansen, I., Hoinghaus, K., Zetsch, C., and Stuhl, F., "Detection of NH ($X^3\Sigma^-$) by Resonance Fluorescence in the Pulsed Vacuum Ultraviolet Photolysis of NH_3 and Its Application to Reactions of NH Radicals," Chemical Physics Letters, Vol. 42, Sept. 1, 1976, pp. 370-372.

[21]Gordon, S., Mulac, W., and Nangia, P., "Pulse Radiolysis of Ammonia Gas - II: Rate of Disappearance of the NH_2 (X^2B_1) Radical," Journal of Physical Chemistry, Vol. 75, July 8, 1971, pp. 2087-2093.

[22]Gehring, M., Hoyermann, K., Schacke, H., and Wolfrum J., "Direct Studies of Some Elementary Steps for the Formation and Destruction of Nitric Oxide in the H-N-O System," Fourteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, Pa., 1975, pp. 99-105.

[23]Hancock, G., Lange, W., Lenzi, M., and Welge, K. H., "Laser Fluorescence of NH_2 and Rate Constant Measurements of NH_2 + NO," Chemical Physics Letters, Vol. 33, May 15, 1975, pp. 168-172.

[24]Lesclaux, R., Ke. P. V., Dezauzier, P., and Soulignac, J. C., "Flash Photolysis Studies of the Reaction of NH_2 Radicals with NO," Chemical Physics Letters, Vol. 35, Oct. 1, 1975, pp. 493-497.

[25]Schroeter, M. and Schacke, H., private communication, 1976.

[26]Bittker, D. A. and Scullin, V. J., "General Chemical Kinetics Computer Program for Static and Flow Reactions, with Applications to Combustion and Shock-Tube Kinetics," NASA TN D-6586, Jan. 1972.

[27]Baulch, D. L., Drysdale, D. D., Horne, D. G., and Lloyd, A. C., Evaluated Kinetic Data for High Temperature Reactions, Vol. 1, Butterworths, London, 1972.

[28]Baulch, D. L. and Drysdale, D. D., "An Evaluation of the Rate Date for the Reaction CO + OH -> CO_2 + H," Combustion and Flame, Vol. 23, Oct. 1974, pp. 215-225.

[29]Baulch, D. L., Drysdale, D. D., and Horne, D. G., Evaluated Kinetic Data for High Temperature Reactions, Vol. 2, Butterworths, London, 1972.

[30]Mayer, S. W., Schieler, L., and Johnston, R. S., "Computation of High Temperature Rate Constants for Biomolecular Reactions of Combustion Products," Eleventh Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, Pa., 1967, pp. 837-844.

[31]Lange, H. B., "NO Formation in Premixed Combustion," American Institution of Chemical Engineers' Symposium Series, No. 126, Vol. 68, 1972, pp. 17-25.

[32]Zellner, R. and Smith, I. W., "Rate Constants for the Reactions of OH with NH_3 and HNO_3," Chemical Physics Letters, Vol. 26, May 1, 1974, pp. 72-74.

[33]JANAF Thermochemical Tables, 2nd Ed., National Standard Reference Data System, NBS 37, 1971.

[34]Golden, D. M., Solly, R. K., Gac, N. H., and Benson, S. W., "Very low Pressure Pyrolysis. V. Benzylamine, N-Methylbenzylamine, and N,N-Dimethylbenzylamine and the Heat of Formation of the Amino, Methylamino, and Dimethylamino Radicals," Journal of the American Chemical Society, Vol. 94, Jan. 2, 1972, pp. 363-369.

[35]Bohme, D. V., Hemsworth, R. S., and Rundle, H. W., "Chemical Equilibrium of $NH_2^- + H_2 \rightarrow H^- + NH_3$ and the Determination of $D_0^0(NH_2\text{-}H)$," Journal of Chemical Physics, Vol. 59, July 1, 1973, pp. 77-81.

[36]Okabe, H., "Photodissociation of HNCO in the Vacuum Ultraviolet; Production of NCO $A^2\Sigma$ and NH ($A^3\pi, \pi c^1$)," Journal of Chemical Physics, Vol. 53, Nov. 1, 1970, pp. 3507-3515.

[37]Seal, K. F. and Gaydon, A. G., "Shock Tube Measurements of the Dissociation Energy of NH Using Absolute Band Intensities," Proceedings of the Physical Society (London), Vol. 89, Oct. 1966, pp. 459-466.

[38]Kaskan, W. E. and Nadler, M. P., "Enthalpy of Formation of NH," Journal of Chemical Physics, Vol. 56, March 1, 1972, pp. 2220-2224.

[39]Stevens, W. J., "Ab Initio Determination of the Dissociation Energy of the X^3 - State of Imidogen," Journal of Chemical Physics, Vol. 58, Feb. 1, 1973, pp. 1264-1266.

[40]Michel, K. W. and Wagner, H. G., "The Pyrolysis and Oxidation of Hydrazine behind Shock Waves," Tenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, Pa., 1965, pp. 353-363.

[41]Fenimore, C. P. and Jones, G. W., "Formation of Carbon Monoxide in Methane Flames by Reaction of Oxygen Atoms with Methyl Radicals," Journal of Physical Chemistry, Vol. 65, Sept. 27, 1961, pp. 1532-1536.

[42]Myerson, A. L., "The Reduction of Nitric Oxide in Simulated Combustion Effluents by Hydrocarbon-Oxygen Mixtures," Fifteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, Pa., 1975, pp. 1085-1092.

[43]van den Bergh, H. E. and Callear, A. P., "Spectroscopic Measurements of the Rate of the Gas-Phase Combination of Methyl Radicals with Nitric Oxide and Oxygen at 295 K," Transactions of the Faraday Society, Vol. 67, 1971, pp. 2071-2024.

[44]Rees, Y. and Williams G. H., "Reactions of Organic Free Radicals with Nitrogen Oxides," Advances in Free Radical Chemistry, Vol. 3, 1968, pp. 199-230.

[45]Safrany, D. R., "Reactions of Hydrocarbons with Mixtures of Active Nitrogen and Hydrogen Atoms," Progress in Reaction Kinetics, Vol. 6, 1970, pp. 1-43.

[46]Fenimore, C. P. and Jones, G. W., "Determination of Hydrogen Atoms in Rich, Flat, Pre-mixed Flames by Reaction with Heavy Water," Journal of Physical Chemistry, Vol. 62, June 26, 1958, pp. 693-697.

[47]Reid, R. W. and Wheeler, R., "Hydrogen Atom Excesses in Some Propane Flames," Journal of Physical Chemistry, Vol. 65, March 28, 1961, pp. 527-532.

[48]Haynes, B. S., "The Formation and Behaviour of Nitrogen Species in Fuel-Rich Hydrocarbon Flames," Ph.D. Thesis, University of South Wales, 1975.

[49]Fenimore, C. P., "Effects of Diluents and Mixing on Nitric Oxide from Fuel-Nitrogen Species in Diffusion Flames," Sixteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, Pa., 1977, pp. 1065-1071.

DISCUSSION

DR. D. M. GOLDEN (SRI International): We need some controversy. I do not think those reactions can go on in the flame the way you have written them. First of all, NH_2 plus NO might recombine, or CH_3 plus NO might react, at room temperature to give those things. However, in the high temperature of the flame, they are way in the fall-off regime. It is very reversible but also energy-transfer limited. So you cannot extrapolate those numbers at all.

These are simple molecules and we know their structure. It is your blank line in between that is really crucial. How does NH_2NO go to N_2 and water? Those are real things, those atoms that we write. What kind of intermediate do you see? Think about what its entropy will be while you are writing it. I am not saying that it does not go, but if it does, you really need to ask a lot of questions about it.

The same kind of thinking, which I tried to present in my paper by putting things into some rational framework, which we can then criticize, leads me to say that if you look at the reaction of HCN plus OH, and compare it to the reaction of CN plus OH, you should be able to say with a fair amount of certainty that these two reactions ought to have nearly the same pre-exponential factor. In one case, you have two diatonics. In the other case, you have a linear polyatomic and a diatomic. In both cases, you have two rotational degrees of freedom to lose when you make the transition state. You suggested rate constants for them that were more than two powers of ten apart at temperatures over 2000° where small differences in activation energy would not show up. In one case, the number is almost a gas kinetic collision frequency. In another case, it is much lower. It just does not make sense to me in terms of this overall framework. I would like to see rate data evaluated in those terms.

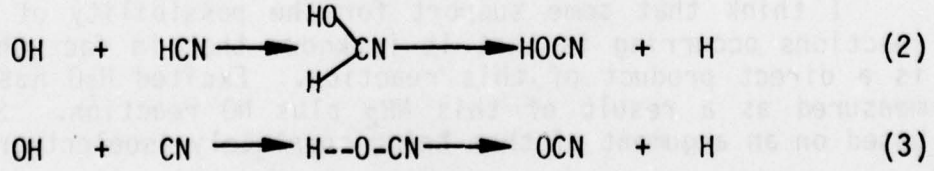
There are other things I could say. NH_2 radicals can both recombine to make hydrazine under certain conditions and disproportionate to make ammonia and NH. If it makes any hydrazine, then hydrazine may react catalytically on probe surfaces to form H_2 and ammonia. There are all kinds of things like that that you have to worry about. I think that it is one thing to model the flames and fit things, but there is a whole framework that we understand well enough to be critical about these rate constants in terms of it.

DR. HAYNES: To take the last point first: I do not think you are really suggesting that there is hydrazine in my sampling system in a flame.

DR. GOLDEN: Not in the flame, but when you sample maybe, or maybe on some surface.

DR. HAYNES: If we look at the concentrations of these species in the flame, there is less than 5% of the total ammonia at partial equilibrium present as NH_2. In terms of the modeling, I do not really mind if all that NH_2 does go to hydrazine on the reaction walls (an unlikely event, given that H, H_2 are much greater than NH_2) because it will not affect my comparisons between prediction and experiment.

[Communicated response to Dr. Golden's comment on the relative rates of reactions (2) and (3): The transition states in these reactions are likely to occur as



Pre-equilibrium of the complex in (2) would lead to a greatly reduced rate for the overall reaction; this would be consistent with the relatively low rate found for this reaction. Dr. Zellner (I.P.C., Göttingen) has pointed out that if the complex in (2) were sufficiently long-lived, reactions such as



also could be expected to contribute to the observed rate of HCN decay. Such processes, like reaction (3), would have a second-order radical concentration dependence so that some of the HCN decay ascribed to reaction (3) actually may occur this way. However, my preliminary analyses indicate that the rate expression obtained for this route, in contrast to that for reaction (3), does not have the correct bulk gas (H_2O, H_2) composition dependence to satisfy both my measurements[18] and those of Morley[10] over the wide range of conditions involved. The (tentative) conclusion is therefore that this process is not kinetically important.]

I would like to go back now to the first part of the question and look at these reactions. Reaction (20) generally is accepted to be occurring at room temperature.

DR. GOLDEN: It may be generally, but I do not know it. The recombination of methyl plus NO can give methyl-NO, but beyond that--I would be willing to say at room temperature--but nothing beyond that. It just does not go through that oxene rearrangement, or whatever you called it, unless it is happening on the surface. There is no way that that hydrogen can move over like that with any kind of a rate constant worth talking about.

DR. HAYNES: I have written these reactions as unimolecular. I do not think that we have to write off the possibility of some bimolecular processes occurring, such as an H attaching to the O in the addition complexes. I am not postulating that as the mechanism. What I am saying is that these (overall) reactions may occur. You are saying they may not. In fact, you are saying they will not. So we have that controversy.

I think that some support for the possibility of these reactions occurring is that it is known that in fact that N_2 is a direct product of this reaction. Excited H_2O has been measured as a result of this NH_2 plus NO reaction. Simply based on an argument of them being completely isoelectronic, I

do not find it totally impossible that reaction (20) should then go to HCN plus H_2O as well.

DR. GOLDEN: Let me just continue the controversy to make my case as strong as I can. If NH_2 reacts to give N_2 and water (and I am aware of some of the data that it does), then it does not do it in the way we are writing it. I am saying that what you say is wrong, and I have no alternative, but I know what NH_2 looks like, and I know what NO looks like. I know that if you put them together at high temperature, first of all, the rate at which they go together is totally energy-transfer controlled. It is not bimolecular; it is termolecular. Second, it will come right back apart. So it just cannot go through NH_2NO. Once you form NH_2NO, the transition state, or whatever you want to call it, that you would need in order to split out water and nitrogen is too convoluted. There have to be faster processes. Now I do not know what they are, and I do not offer an explanation. What I am saying is that, within the framework of a whole body of knowledge, that just does not make sense as a pathway. I really want to insist on it.

We can have a controversy on it. You cannot just take this as an isolated incidence and say, all right, this goes this way, without realizing that what you are saying is that the whole basis on which we judge these rate constants does not make sense. That is the implication.

DR. HAYNES: All right, in the case of NH_2, I back out gracefully. I do not want it to occur in my flames because I have found no evidence for it. In the case of reaction (20), again, as emphasized, all I am saying is that this is a possible reaction. The evidence is that nitric oxide is reacting with a hydrocarbon from the room temperature data, from some old flame data of Fenimore's, and from some data at about 1200 K. There is evidence that in fact this (overall) reaction does go and that HCN is a product. I cannot say any more than that to that comment.

DR. A. E. AXWORTHY (Rocketdyne): Whenever a reaction is written in which you have single nitrogen species forming N_2 or N_2O, you get this type of controversy. Jost Wendt of the University of Arizona wrote a review of fuel nitrogen chemistry for the EPA about five years ago. He tried to list all the possible reactions that form N_2, and there were not many.

We worked at lower equivalence ratios in our studies of flat methane flames at Rocketdyne. Over two years ago, we

proposed the NCO radical as a principal intermediate in the fuel-lean flame (EPA-600/2-76-039). That was also by very indirect reasoning. When adding ammonia to the flame, we found a region where there is essentially no nitrogen species measurable by our probe/converter technique. This means that the nitrogen cannot be in a CN or NH form in that region of the flame. It is also unlikely that the N-atom concentration would be that large. The only explanation that could account for this observation would be the presence of NCO radicals in large concentrations. In our probe, the NCO radicals might disproportionate to N_2 and CO and therefore be unmeasurable. So, in the fuel-lean flame, we proposed without any proof a mechanism in which the NCO radicals react with O atoms just above the flame to give NO and CO. We also proposed the termination reaction NCO + NCO = N_2 + 2 CO. This reaction is in the category of the N_2-forming reactions that appear unlikely but may have to be proposed.

DR. R. M. FRISTROM (Applied Physics Laboratory): I wonder if Dr. Golden has considered the possibility of tunneling during the collision complex. Does that alter it or are your entropy considerations still valid?

DR. GOLDEN: If tunneling is important at all, it is important at low temperatures, not high. What tunneling does is to do away with barriers that have to be crossed. It is important at low temperatures, not at high temperatures.

DR. FRISTROM: I have the impression that there is a great deal of shuffling that goes on at these high temperatures. With hydrocarbon reactions, for example, there are migrations that are somewhat unbelievable.

DR. GOLDEN: They are all hydrogen migrations. I do not know of any scrambling of hydrocarbons that cannot be explained by a series of hydrogen migrations. Now I know that there are places in the literature where the same thing has been explained, perhaps by moving alkyl groups, but it is not necessary to explain them that way. I do not believe they are correct.

DR. FRISTROM: So your impression is that it absolutely must.

DR. GOLDEN: "Absolutely" is very strong, but my feeling is that, if the products are being made, they are not being made through one unimolecular reaction.

DR. FRISTROM: So you are thinking in terms of a chain of reactions?

DR. GOLDEN: A series of reactions.

DR. C. T. BOWMAN (Stanford University): To add to this controversy and perhaps to leave us with the impression that we really do not understand all the details of the decomposition of NO in post flame gases, let me say this. We have become very enamored with the NH_2 + NO reaction. Several investigators have suggested this reaction as a way of removing NO in the post-flame zone. There are other ways in which NO can be removed in post-flame gases. There are very few reactions giving direct formation of N_2 that involve NO. The N plus NO reaction is one. There are others than can go through multiple steps and end up as N_2. One such reaction path is the reaction of NH with NO to give N_2O, with subsequent decomposition of N_2O to give N_2. At Stanford a shock tube study of the rate of decomposition of ammonia in the presence of NO is in progress. One of the principal intermediate products that is observed during the course of this decomposition reaction is N_2O. In fact, Axworthy has speculated that this occurs in flames, and it may in fact be some of the missing nitrogen in your flame.

There is a lot about the decomposition of NO in fuel-rich flames which we simply do not understand. I think it is a mistake to try to bend kinetics around to try to force the issue.

DR. HAYNES: Yes, I endorse all that. I picked this reaction (13) to compare with the N plus NO reaction, through which, in my cases, I am finding enough reaction to explain my results. However, I still think this sort of reaction needs further consideration, particularly if we go to lower temperatures.

The reaction NH plus NO would appear to occur something like this: $NO + NH \longrightarrow N_2O + H$. I hope I do not upset you too much with the way of writing it. The problem with the steady flames which I have been burning is that if one takes the high heat of formation for NH, the partial equilibrium concentration of NH is simply too low for it ever to be important in any reaction. That is strong talk, and I am fairly certain about it.

For example, the ratio of NH to the N atom concentration at partial equilibrium in the flames is usually less than about 0.2. So the concentration of NH is considerably less than that of N at partial equilibrium.

Now there is a lot of uncertainty here. If we go to the low value of the heat of formation of NH, about 81 kcal/mole,

then NH comes up, and there is more of it than there is of N. So I agree that it is possible that this reaction to N_2O may become a handy source of N_2 formation.

As far as the work that I have been doing is concerned, it falls into the same category as reaction (13). It is an unknown reaction, an unknown quantity, at the high temperatures that we are working at. From the modeling work that I have been doing, it is not necessary to invoke these reactions (either (12) or (13)) to explain most of the details we are observing.

The further reaction which I have called upon to account for the increased removal of NO--and this is not the increased removal of total nitrogen, this is just NO--is the recycling mechanism, such as reaction (20). The rate of formation of N_2 is not increased by this sort of reaction. So when you are talking about the removal of NO in fuel-rich gases, I want to re-emphasize that it is not really NO which has been removed. That will go back to NO when we burn out. What we are really interested in is the amount of N_2 that we form.

In this case, one is hard pressed for an alternative. Some investigators have suggested a reaction of CH plus NO. That is totally implausible in the post-flame gases with which I deal. It just simply cannot account for the rate of NO removal that we see.

DR. I. GLASSMAN (Princeton University): To change the tone a little bit, how fast are we approaching the equilibrium value of NO in these flames? Are we still very far away from equilibrium levels of NO?

DR. HAYNES: Yes.

DR. GLASSMAN: So we are still way above the NO. Indeed, this is why I think perhaps we should be studying these reduction reactions in the temperature zone in the after region or the stack.

DR. HAYNES: Yes, there is some evidence for being able to remove these things quite nicely in the stack. I agree that that is an alternative strategy.

EMISSION CONTROL TECHNIQUES FOR ALTERNATIVE FUEL COMBUSTION

G. B. Martin*
U.S. Environmental Protection Agency
Research Triangle Park, N.C.

Abstract

This paper summarizes the available information on the state-of-the-art emission control technology for use of conventional and alternative fuels in stationary combustion sources. The data on alternative fuels are very limited, and therefore experience with conventional fuels is used as the basis for postulating the effectiveness of combustion process modifications on the emissions from alternate fuels. It is concluded that the primary problem will be emissions of nitrogen oxides formed from chemically bound nitrogen in the fuel molecule. There is the potential for a problem with carbon particulate formation if low NO_x combustors are not designed with this in mind. Finally, based on promising results for heavy petroleum fuel oils and coal, it is concluded that burner and combustion process design modifications have a high probability of success for alternative fuels.

Introduction

In the search for energy supplies, the United States is projected to place heavy reliance on coal, which is the most abundant fossil fuel available. Many methods of extracting the energy from coal are being pursued; however, the ultimate decisions on the paths to be followed depend on both economic and environmental considerations. These considerations cover the full range from resource extraction, through processing, to end utilization. On the economic side, it is necessary to include not only capital and operating costs but also the overall energy efficiency of the process. On the environmental side, there are potential impacts in every step, and the overall effect on air, water, and land quality must be assessed. For the purposes of this paper, only the end use processes (i.e., combustion systems) will be considered. The characteristics of the combustion system also influence the route that will be chosen. For mobile sources (i.e., automo-

*Sanitary Engineer, Combustion Research Branch, Industrial Environmental Research Laboratory.

biles and aircraft), light liquid hydrocarbon fuels probably will be required for a significant period in the future. In this instance, the necessity for a specific fuel type may overcome some of the other potential obstacles (e.g., economics). For stationary sources, the fuel used may not be constrained as significantly by the requirement of a fuel of specific characteristics, and the choice of approach may be wider.

The ways in which coal can be used in an environmentally acceptable manner are dependent on the type of combustion source. The pollutants that must be controlled include sulfur oxides, nitrogen oxides, carbon monoxide, unburned hydrocarbons, and total particulate. Perhaps the most options exist for utility generation of electric power. One option currently being used is the direct combustion of coal with stack gas cleaning for sulfur oxides and particulate, and combustion modifications for control of nitrogen oxides, carbon monoxide, and unburned hydrocarbons. Improvement of the existing technology is being pursued by a variety of Environmental Protection Agency (EPA) programs. A second option is the conversion of coal into low-sulfur fuels to be utilized in conventional steam boilers or combined cycle plants. The large energy losses currently associated with fuel-cleaning processes appear to require use of the advanced design combined cycle with integrated gasifier to achieve energy efficiency comparable to the first option. Major unknowns in these designs are the criteria for minimizing nitrogen oxides and other combustion-related pollutants. The third option is the use of fluidized-bed combustion to minimize sulfur oxides and other pollutants. The area of sulfur oxides control was the subject of a recent conference,[1] and many excellent papers were prepared; however, the treatment of other pollutants generated during the combustion process was covered only briefly. One paper by Spaite[2] presented a good summary of cost information for alternate fuel processes. For other stationary source applications, such as residential and commercial heating, low-sulfur high-Btu fuels will be required. Candidates under consideration include synthetic natural gas (SNG), synthetic oils, and alcohol fuels.

This paper will concentrate on combustion and emission characteristics of alternate fuels, an area where information is still very limited. It also will attempt to relate combustion technology developed for conventional fuels to the probable effect on alternate fuel emission characteristics.

Background

A wide range of subject matter relates directly to combustion of alternate fuels. The topics include pollutant

formation mechanisms, applicable emission-control techniques, fuel characteristics, and end use equipment type. Since these areas have been treated in detail for alternate fuels previously,[3] the background presented is a brief general summary. The most recent information on combustion and emission characteristics is summarized.

Pollutant Formation Mechanisms

The mechanisms of formation of nitrogen oxides (NO_x) have been discussed extensively;[4,5] however, a brief summary is in order. [Note: Subsequent discussion will be limited to nitric oxide (NO), which is the primary form of NO_x found in the flue gas of conventional combustion equipment.] The mechanisms for formation of NO are as follows:

1) Thermal NO is formed from fixation of atmospheric nitrogen by Zeldovitch reactions, which have a strong temperature dependence.

2) Fuel NO is formed by oxidation of chemically bound nitrogen in the fuel by reactions with a low-temperature dependence but a strong oxygen availability dependence.

There is also recent experimental evidence[6] to show that nitrogen species (e.g., NH_3 and HCN) can be synthesized in fuel-rich flames as postulated by Fenimore[7] and subsequently oxidized to NO as is fuel nitrogen. The other pollutants of concern are SO_x, CO, hydrocarbons, POM, carbon particulate, and metallic particulate. One of the primary incentives for alternate fuels is sulfur removal, and, therefore, SO_x levels should be low. Since proper system designs for stationary sources can minimize CO and hydrocarbon emissions, no problem is anticipated with alternate fuels. Carbon particulate emissions for heavy liquid fuels are a potential problem that may be complicated further by the higher carbon-to-hydrogen ratios of many synthetic liquid fuels. Metallic particulate is dependent primarily on the mineral content of the fuel and, therefore, on the extent of coal ash removal during fuel processing. Metal form and particle size distribution also may be affected by the combustion process; however, no detailed information is presently available. Use of alternate fuels in combustion systems will require careful design to minimize these emissions.

Fuel Characteristics

The properties of alternate fuels have been summarized previously,[3] and only a brief discussion is presented below.

High-Btu Fuels. These fuels are the type that would be potentially economical to transport for use at points remote from the coal conversion sites. Fuels of this type include synthetic natural gas (SNG), alcohol fuels, synthetic coal liquids, and shale oil, for which a number of processes for production are being investigated. These SNG, alcohol fuels, and light synthetic oils can be considered as supplements or replacements for natural gas and light fuel oils and may be used predominantly in combustion equipment currently burning these fuels (e.g., residential, commercial, and small industrial boilers and mobile sources). The heavy synthetic oils may be used as boiler fuels or may be distilled to produce light fuels suitable for turbines or residential furnaces.

Medium-Btu Gas. This is the product of oxygen-blown gasifier systems and currently is projected primarily as a synthesis gas for production of SNG and methanol. Its use as a boiler fuel may depend more on economics than technical considerations.

Low-Btu Gas. Although identified by the single term low-Btu gas (LBG), the actual nature of the fuel is as varied as the airblown gasification systems that can be used to produce it. It is projected primarily as a fuel utiilized in utility boilers or by industrial parks, either of which could be located close to the gasification site, as long-distance transportation is not economical. The actual utilization projected for the LBG depends on the time frame. In the near term, it may be used in conventional utility boilers and gas turbines either as retrofit to existing systems or integrated new designs. However, in the long run, combined cycles based on supercharged boilers or high-temperature gas turbines as the primary combustion device may predominate. To increase the efficiency of advanced-design gasifier systems, there is a strong interest in high-temperature H_2S removal processes to provide a clean fuel gas at 810 to 1090 K. Again, both economics (capital cost and energy efficiency) and technology may come into play in the final decision.

Trace Constituents. The fate of the sulfur is considered fairly well in most studies of medium- and low-Btu gases, and removal of H_2S and COS is well documented. On the other hand, the fate of the nitrogen content of the coal has received less attention. Farnsworth[8] shows the final concentration of bound nitrogen species in the medium-Btu gas after low-temperature cleanup from the Koppers-Totzek process to be less than 1 ppm. On the other hand, there is considerable evidence of the presence of large amounts of NH_3 in the product gases.[9] Robson estimates up to 600 ppm of NH_3 in a low-Btu gas with a low-

temperature H_2S cleanup and 3800 ppm from high-temperature processes under development.[10] It is not clear that these nitrogen compounds could be present in the high-Btu fuels; however, it is quite possible that they are present in the low- and medium-Btu gaseous fuels. Finally, many coal conversion systems producing gaseous fuels also form significant amounts of heavy organic tars, and there is some indication that some of this material may be present in the fuel gas after cleanup. This tar also may contain bound nitrogen compounds.[11]

For the crude synthetic liquid fuels, the bound nitrogen content is generally quite high (<0.5%). In addition to this, the nitrogen is distributed much more evenly over the range of fuel cuts than it is in distillate oil. The most complete information is available on a 2.19% nitrogen Paraho Shale crude, as shown in Fig. 1.[12] The nitrogen content is above 1.2% by weight for all fuel fractions shown here. The sulfur levels are below 1% and decrease in the higher boiling fractions. For comparison, a Wilmington, Calif. crude[13] that contained 0.65% nitrogen yielded only 0.07% in the distillate oil product (corresponding in boiling point to the 33% volume fractions of the shale crude). The nitrogen and sulfur can be removed to low levels by hydrotreating;[14] however, it is an expensive process. Where other considerations are paramount (e.g., fuel stability for aircraft uses), severe hydrotreating may be unavoidable. For other applications, it may be possible to achieve NO_x control by combustion modification on fuels having a minimum of hydrotreating to upgrade the hydrogen-to-carbon ratio for smoke suppression. In addition, this nitrogen distribution in these alternate fuels also may be favorable from the standpoint of NO_x control.

Emission-Control Techniques

The basic combustion modification techniques for NO_x control can be summarized as follows:

1) Diluent addition to reduce flame temperature is accomplished through the use of either water or recycled flue gas added to the combustion air.

2) Staged combustion is based on operation of burners at a fuel-rich condition with delayed secondary air addition to complete heat release, thereby limiting both peak flame temperatures and primary zone oxygen availability.

3) Burner modifications involve changes in fuel and air mixing conditions to promote localized fuel-rich conditions and/or combustion gas recirculation.

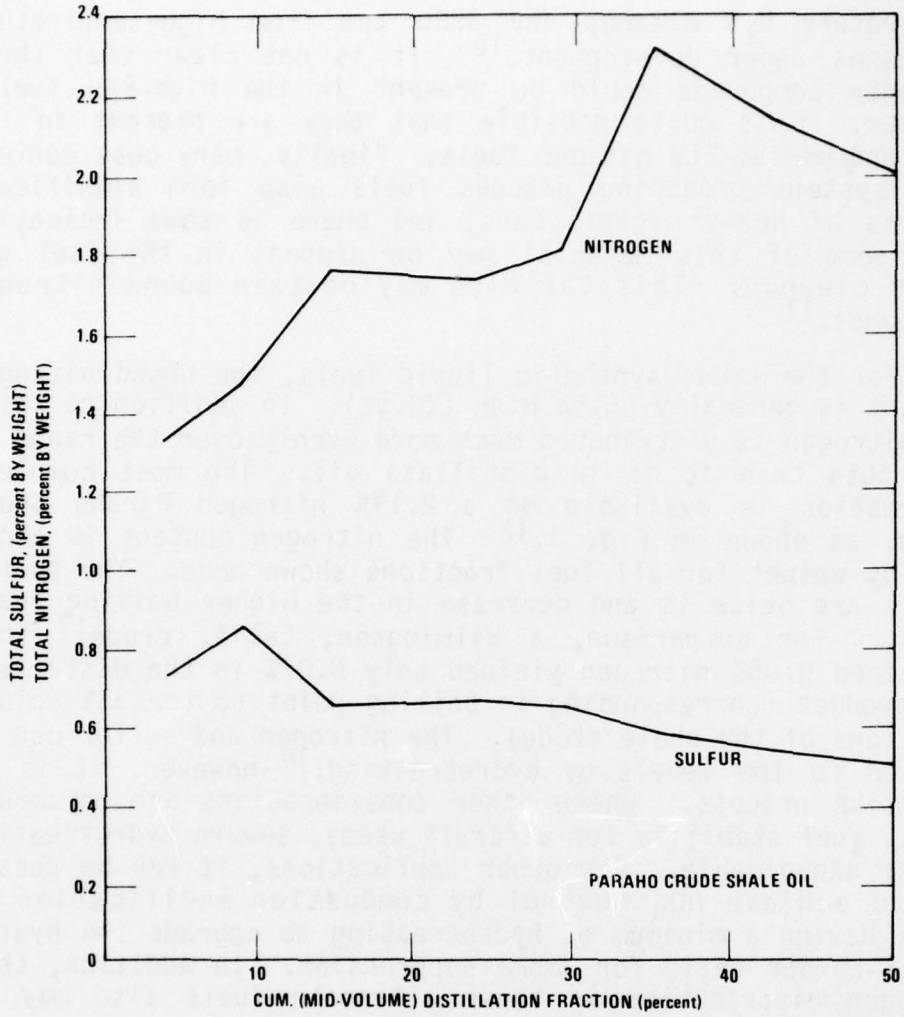


Fig. 1 Total weight of nitrogen and sulfur as a function of the cumulative midvolume distillation fraction.[12]

4) Novel techniques, such as catalytic combustion, may allow NO emissions lower than those achievable for combustion of clean fuels in conventional systems and may be particularly applicable to redesign for maintaining system efficiency.

The first technique controls only thermal NO, whereas the last three also may control fuel NO. The emissions of the products of incomplete combustion (CO, unburned hydrocarbons, and carbon particulate) are subject to being increased as NO_x is decreased past a critical point for fixed system design; however, there is a body of evidence which indicates that these emissions can be controlled if the system is designed or modified with both NO_x and carbonaceous emissions-control requirements in mind.

General System Characteristics

Alternate fuels may be used in a wide variety of stationary and mobile source combustion systems. The emission-control concepts may be different for each of these systems because of unique design features. For automotive and aircraft turbines, weight and size limitations on the combustion system, as well as the range of operating conditions, may limit severely the design changes that can be made. In these systems, the total combustor residence time may be quite short (e.g., less than 10 msec), and the ability to use certain emission-control concepts (e.g., staged combustion) may be limited. These systems also will operate in a nearly adiabatic manner (minimum heat loss), which also removes a degree of flexibility from the emission-control concepts. For these tightly constrained systems, the use of fuels that have been hydrotreated extensively for nitrogen removal and carbon-to-hydrogen ratio upgrading may be more economical and offer greater emission-control potential than extensive combustor redesign.

In the case of stationary heat and steam generation systems, there is more flexibility in the design. Boilers and furnaces operate at atmospheric pressure and have total combustion chamber residence times in the range of 250 to 3000 msec. Weight and size are not dominant features of the design. Approximately 50% of the fuel heating value is removed in the combustion chamber. Because of these features, the system design changes for emission control are constrained rather loosely as long as conventional construction practice is used and the costs associated with the changes are not too great. It seems likely that emission control for alternate fuels burned in these systems can be achieved with combustion technology, and, therefore, significant fuel treatment may not be required. It may be beneficial to do some fuel treatment to decrease the carbon-to-hydrogen ratio, if carbon particulate formation under low-NO_x conditions is related to this fuel property.

The stationary gas turbine represents a case that is intermediate between mobile turbines and stationary boilers. In the past, these stationary machines have been designed using tightly constrained designs; however, since weight and size may be increased if all other system requirements are met, it is probable that new generations of gas turbines can be designed with longer residence time combustors (e.g., 50 msec), which may be required for NO_x control.

Discussion

For all combustion systms (except reciprocating engines, which are not a subject of this paper), the common feature is the use of a burner to provide initial fuel and air mixing. Although the characteristics of specific systems are significantly different, the combustion zone conditions that lead to minimum emissions are quite similar for each of two broad classes of fuels (i.e., nitrogen-free and nitrogen-containing). A large body of information has been built up on burner designs for emission control for conventional fuels, and much of this information should be applicable directly to systems burning alternate fuels.

The primary emission category that is controllable by combustion technology is NO_x. Control of carbonaceous emission (e.g., CO, hydrocarbon, POM, and carbon particulate) also is affected by combustion technology; however, it may be treated as a second-order effect. This is not based on any prioritization of health or environmental effects of the pollutants, but rather on the approaches that must be taken for optimum control of all emissions by combustion technology. There are many conventional design approaches currently in use which offer the potential for low carbonaceous emissions by employing conditions that lead to high levels of NO_x. Therefore, it is necessary to approach the problem from the other direction; that is, to employ the specialized design concepts that give low levels of NO_x and then optimize that technology to achieve minimum carbonaceous emissions. In this way, optimum control of all emissions becomes a primary design criterion and a goal that can be achieved during the development of the combustion process for a specific application.

The discussion that follows will attempt to point out some of the key system features that relate to emission control for these two general classes of fuels. Emphasis will be placed on nitrogen-containing fuels.

Nitrogen-Free Fuels

Fuels that do not contain chemically bound nitrogen produce only thermal and "prompt" NO_x, for which there is a substantial body of control technology already developed. For stationary heat and steam generation systems, the primary techniques are external flue gas recirculation and burner designs that maximize internal recirculation of relatively cool combustion products. The burner techniques can be coupled with combustion chambers designed to achieve early heat removal, thereby further reducing peak temperature and

optimizing the NO_x reduction. These techniques are compatible with low carbonaceous emissions and with low excess air operation for maximum system thermal efficiency. For gas turbines, a number of approaches are being explored. Substantial effort has been devoted to premixed prevaporized primary combustion zones, which produce lower flame temperatures and, therefore, lower thermal NO_x. These concepts also produce low carbon particulate levels, but careful attention must be paid to avoiding excessive CO. This technique is well suited to the gas turbine that normally operates at high excess air levels (i.e., 300 to 400%). A major consideration for this concept is burner stability. These relatively conventional technologies are well documented and do not require further discussion here.

Catalytic combustion is a developing technology that shows substantial promise for combustion of a variety of fuels. One high potential application to gas generators for turbines is for burning clean fuels at high excess air levels with low emissions. Fuel and air are premixed and fed through a catalyzed bed of ceramic monolith, where, dependent on the catalyst and operating conditions, the fuel is oxidized on the catalyst surface and/or in the gas phase.[15] NO_x, CO, and HC levels below 10 ppm are reported, and stable operation to 400% excess air has been observed. Most of the data reported to date have been for temperatures below the kinetic threshold of 1813 K (2800°F) for thermal NO_x formation, and there has been speculation that at higher temperatures the NO_x levels would rise sharply.

Some recent data on high-temperature catalytic combustion which sheds some light on this question have been reported by Kesselring.[16] Figure 2 shows the data for single-stage lean combustion of methane with preheated air. The NO_x emissions are plotted against maximum temperature measured within the catalyst bed for two catalysts. The NO_x emissions are below 50 ppm corrected to 0% excess air for temperatures below 1813 K (2800°F). As the temperature increases, the NO_x emissions increase for both catalysts; however, one catalyst shows a much greater increase. Although the two catalysts are different materials, the difference in performance is attributed to the fact that the catalyst used in the upper curve had partially disintegrated and that the combustion was being completed homogeneously rather than heterogeneously. These data show the potential for very low NO_x emissions for gas turbine combustors at turbine inlet temperatures considerably above those used today. They also point up a significant problem area for catalysts operating at high temperature that is, the thermal stability of the monolith. This and several

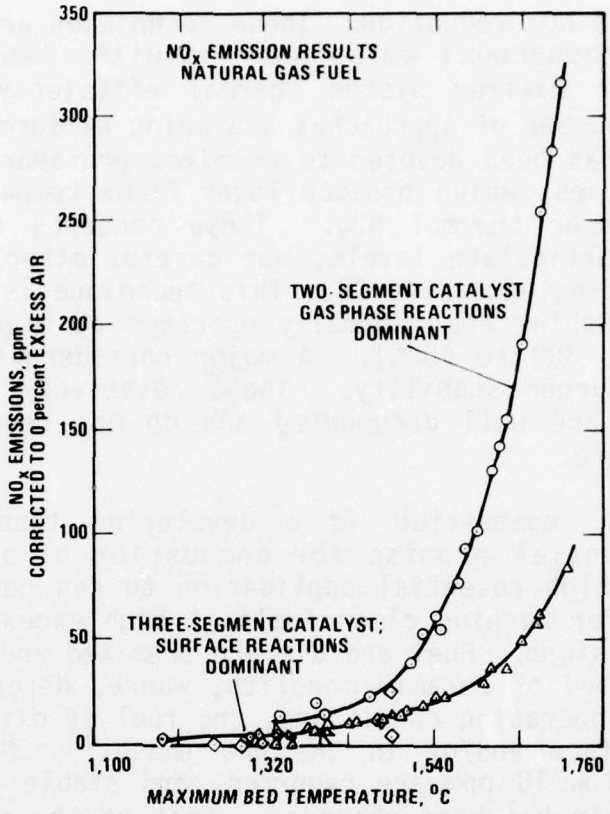


Fig. 2 Graded cell catalyst test results.[16]

other potential practical problems must be overcome before this advanced technology can be applied.

Nitrogen-Containing Fuels

Nitrogen compounds chemically bound in the fuel are oxidized to form what is termed fuel NO_x. This is a significant concern for alternate fuels, since virtually all untreated coal- and shale-derived fuels have large concentrations of bound nitrogen species. Low-Btu gases produced by coal gasification may contain in excess of 4000 ppm of ammonia (NH_3) and lesser amounts of hydrogen cyanide (HCN) prior to treatment for removal of sulfur species (H_2S, COS, etc.). The type of sulfur removal process used also determines the extent of nitrogen removal, with some of the hot removal processes estimated to have very low NH_3 removal.[10] The liquid crudes derived from both coal and shale have in excess of 1% nitrogen prior to any processing, and, since sulfur levels are generally below 1%, minimum hydrotreating is desirable to minimize efficiency and economic penalties. For coal-derived solid fuels (e.g., SRC), the nitrogen compounds

are not removed to a significant degree. For both conventional solid and liquid fuels, the nitrogen is bound within the fuel structure as single or multiple heterocyclic ring compounds, and a similar structure is believed to exist in the alternate fuels.

In addition to the absolute amount of nitrogen contained in the fuel, it appears that the degree of control achievable also may be dependent on how the nitrogen is distributed. The evidence indicates that the nitrogen in the fuel is converted to simple gas-phase species (HCN and NH_3) before it is oxidized to NO or reacts to form N_2. The heterocyclic nitrogen compound in the parent fuel appears to undergo a sequential pyrolysis through a lighter organic form to HCN or NH_3. The extent of this pyrolysis is dependent on temperature, residence time, and ambient conditions (oxidizing or reducing). Although it has been shown that a quantitative conversion of pyridine (C_5H_5N) to HCN can be achieved at 1373 K under inert conditions,[17] comparable conversions have not been shown for any real fuel at residence times achievable in practical combustors, even at considerably higher temperatures. The balance of the nitrogen is contained in a fuel residue that may be char for solid fuels and tar for liquid fuels. The nitrogen evolved into the gas phase is referred to as "volatile nitrogen." The significance of this distribution of nitrogen compounds is discussed in greater detail for specific fuel types below.

The basis of fuel NO_x control techniques is the same regardless of the fuel type. A fuel-rich primary combustion zone is used to maximize the conversion of fuel nitrogen to molecular nitrogen (N_2). A fraction of the nitrogen is evolved as XN species (e.g., HCN and NH_3), which partially oxidize to form NO. The NO then reacts with the residual XN to form N_2. Since any XN species that remain in the rich mixture will undergo high-efficiency conversion to NO in the lean secondary stage and any NO will be retained almost quantitatively, the rich zone conditions must give a minimum value of Σ XN (i.e., HCN + NH_3 + NO). The stoichiometry required to achieve the minimum Σ XN is dependent on several factors, including 1) the rate of evolution of nitrogen species from the fuel; 2) the inevitable distribution of stoichiometries from very rich to lean which exists in an overall fuel-rich zone of a diffusion flame; 3) the overall temperature of the reaction zone; and 4) the overall residence time in the reaction zone. The interaction of these four factors is dependent on the aerodynamic mixing of a turbulent diffusion flame, as well as the nitrogen distribution for a given fuel. It is desirable to extract some energy from the

rich products prior to second-stage air addition to reduce the thermal NO_x formation. In the lean second stage, a significant fraction of the gaseous Σ XN and a smaller fraction of any residual nitrogen in the char or tar will be converted to NO_x. Based on evidence for coal char and petroleum coke, the conversion of this nonvolatile nitrogen to NO occurs at a low fraction efficiency (i.e., <10%). In fact, the NO_x levels from these fuels are insensitive to burner design changes that significantly reduce NO_x from pulverized coal. This char NO_x may impose a minimum level below which NO_x cannot be reduced for a given primary zone condition.

The required conditions can be attained by classical staging, by delayed mixing burners, or by a combination of the two. The available information for gaseous, solid, and liquid fuels is discussed below.

Gaseous Fuels. Low-Btu gas (LBG) that contains residual amounts of NH_3 and HCN is the gaseous fuel most likely to contain bound nitrogen species. It appears that these fuels may be the simplest case for combustion control of fuel NO_x. The fuel nitrogen species are present in simple gaseous form in known quantities. In addition, the air/fuel mixing history should be easier to control if proper attention is given to injector and airflow design. All of the nitrogen species then can be processed through a rich primary zone with conditions chosen to minimize the Σ XN exiting the zone. The question that remains to be answered is the type of mixing which will provide the optimum primary zone condition (e.g., premixed, well stirred, or diffusion flame) for minimum ΣXN. There is some evidence to indicate that the turbulent diffusion flame is the preferred route for achieving low Σ XN at short residence times. This may be related to the natural range of stoichiometries that exist in a diffusion flame from fuel-rich with unreacted XN species to fuel-lean with production of NO_x. The subsequent mixing of rich and lean pockets could give minimum NO_x levels.

It appears that the most likely use for these low-Btu gases is in advanced-design gas turbines for combined cycle plants. Some combustor concepts based on long-residence-time premixed systems have been presented previously.[18,19] The calculations indicate that low NO_x levels can be attained for low-Btu gas containing up to 4000 ppm NH_3.

Liquid Fuels. For liquid petroleum fuels, there is experimental evidence for two distinct types of fuels: 1) light distillate fuels doped with nitrogen compounds; and 2) residual fuel oils containing naturally occurring heterocyclic

nitrogen compounds. In the first case, the nitrogen dopants are low boiling (i.e., 400 to 500 K) and are evolved from the fuel below the 100% distillation temperature of the fuel. In the second case, the nitrogen compounds are the most refractory and highest boiling fractions of the fuel. One might expect that these different nitrogen distributions would give substantially different results on NO_x emissions; however, under single-stage fuel-lean conditions, very similar fractional conversions are noted, and the effect of fuel nitrogen type appears to be a second-order effect. It is only under operating conditions designed to give low NO_x that differences begin to appear. Since the data used have been generated on a variety of experimental systems, care must be taken in making generalizations; however, some implications from the results from each fuel class are discussed below.

Experimental data on small-scale burners have shown that, for a distillate fuel, oil doped with 1% nitrogen as pyridine NO_x emissions can be reduced from 800 ppm to below 150 ppm (an 80% reduction) by two-stage combustion, with a primary zone at 70% of theoretical air. The success with this fuel approaches that expected for gaseous fuel, which might be expected, since all of the nitrogen almost certainly is evaporated and/or pyrolyzed in the primary zone. It may be argued that the nitrogen compounds contained in the light fractions of synthetic crudes will behave in a similar manner. If this postulate is true, the potential for fuel nitrogen conversions below 10% with no carbon particulate is a good possibility. Also any hydrotreating of the synthetic crude should enhance the ability to control NO_x with staged combustion or delayed mixing burner designs.

Experimental and field data for staged combustion of residual fuel oils indicate that control of NO_x is more difficult, and reductions greater than 50% without excessive levels of smoke (carbon particulate) seldom are reported. It appears that this might be attributable to the distribution of nitrogen compounds in the oil. If only part of the nitrogen is evolved in the first stage under conditions that do not produce soot, the nitrogen in the tarry residue will burn out under lean conditions in the second stage and produce NO_x. Extensive work on burner design for control of emissions from heavy liquid fuels has been reported by Cichanowicz.[20] The type of staged burner design which has evolved is shown in Fig. 3. The fuel is atomized into a rich primary zone and partially combusted before secondary air is added via a secondary channel. The emission performance achieved for three residual fuel oils is shown in Fig. 4. For the 0.71% nitrogen oil, the NO_x level can be reduced to about 250 ppm before

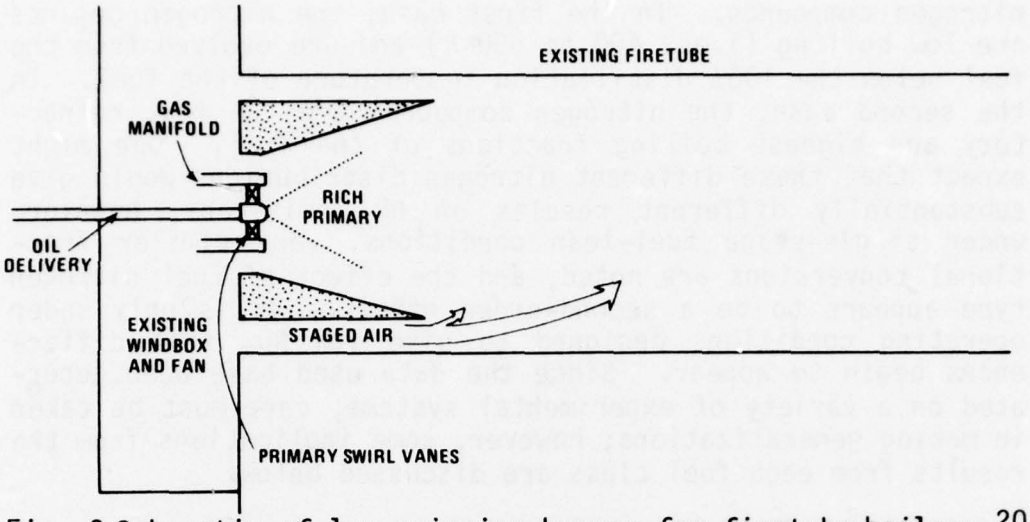


Fig. 3 Schematic of low-emission burner for firetube boilers.[20]

the smoke level becomes excessive (i.e., >4). Although some questions remain to be answered, this technology should be applicable directly to residual fuels derived from synthetic crudes and may be more effective because of nitrogen compound distribution in the fuel.

Solid Fuels. The information on conventional solid fuels also can be divided into two classes: 1) combustion of coal; and 2) combustion of coal char or petroleum coke. In the case of coal, some part of the nitrogen can be driven off in the volatiles, whereas the balance remains in the char. For coal char (from gasification) and petroleum coke, it appears that the nitrogen is associated strongly with the fuel matrix, and only a small percentage can be driven off in the volatiles. This affects the NO_x emissions under both single-stage fuel-lean and two-stage combustion conditions. Each of these cases is discussed in detail below.

The basis for much of the developing control technology for pulverized coal combustion is the small-scale burner work carried out at the International Flame Research Foundation (IFRF) by Heap.[21] He reported that NO_x emissions from pulverized coal flames could be reduced from 800 to 150 ppm by changes in burner design. It was postulated that for the low-NO_x case the bulk of the fuel nitrogen was driven off in the volatiles and converted into N_2 under fuel-rich conditions in the coal/primary airjet. Subsequent fundamental work by Pohl[22] has shown that up to 95% of the nitrogen can be driven into the gas phase at temperatures in the range that might occur in coal combustion. The extent of evolution of

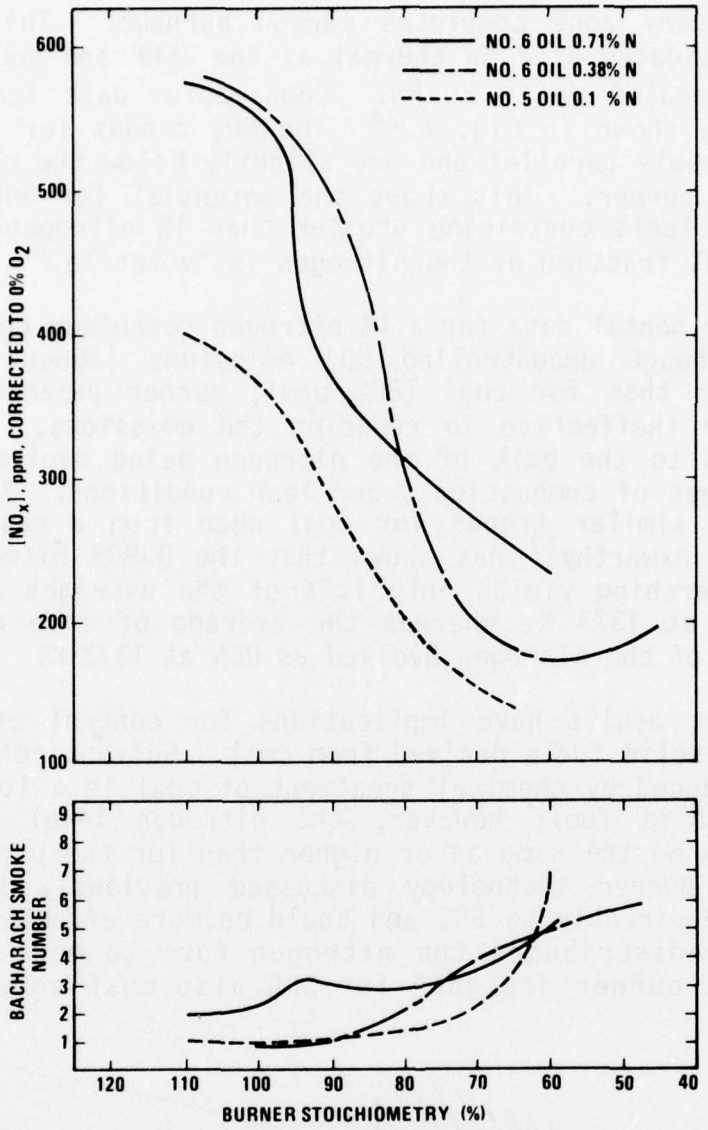


Fig. 4 Performance of optimum residual oil burner.[20]

the nitrogen is dependent not only on the temperature but also on the residence time. Furnace work by Pershing[23] confirmed the postulates that fuel NO_x is the major source from pulverized coal and that the conversion is relatively insensitive to temperature. The IFRF studies resulted in a staged burner design, which is shown schematically in Fig. 5. The coal and primary air are introduced on the axis and are surrounded by secondary air with some tangential momentum. The sum of primary and secondary air is less than 100% of theoretical air, which generates a rich primary zone. The tertiary air is introduced in such a way that mixing with the products of the rich primary is delayed for some time and occurs gradually.

The secondary zone completes carbon burnout. This concept was investigated at 2 MW thermal at the IFRF and subsequently has been scaled up to 20 MW. Comparative data for the two scales are shown in Fig. 6.[24] The NO_x trends for the large burner closely parallel and are slightly below the curves for the small burner. This shows the potential for NO_x control for solid fuels containing greater than 1% nitrogen, where a significant fraction of the nitrogen is "volatile."

Experimental data for a 1% nitrogen petroleum coke showed that, although uncontrolled NO_x emissions (about 300 ppm) were lower than for coal (800 ppm), burner parameters were relatively ineffective in reducing the emissions. This was attributed to the bulk of the nitrogen being evolved in the later stages of combustion under lean conditions. Pershing[23] has shown similar trends for coal char from a gasification process. Axworthy[17] has shown that the 0.99% nitrogen char used by Pershing yields only 1.7% of the nitrogen as HCN on pyrolysis at 1373 K, whereas the average of five coals was about 26% of the nitrogen evolved as HCN at 1373 K.

These results have implications for control of NO_x for alternate solid fuels derived from coal. Solvent refined coal (SRC) produced by chemical treatment of coal is a low-sulfur, low-ash solid fuel; however, the nitrogen level generally appears to be the same as or higher than for the parent coal. The coal burner technology discussed previously should be applicable directly to SRC and could be more effective if the process redistributes the nitrogen form to more volatile forms. A burner designed for SRC also must consider the

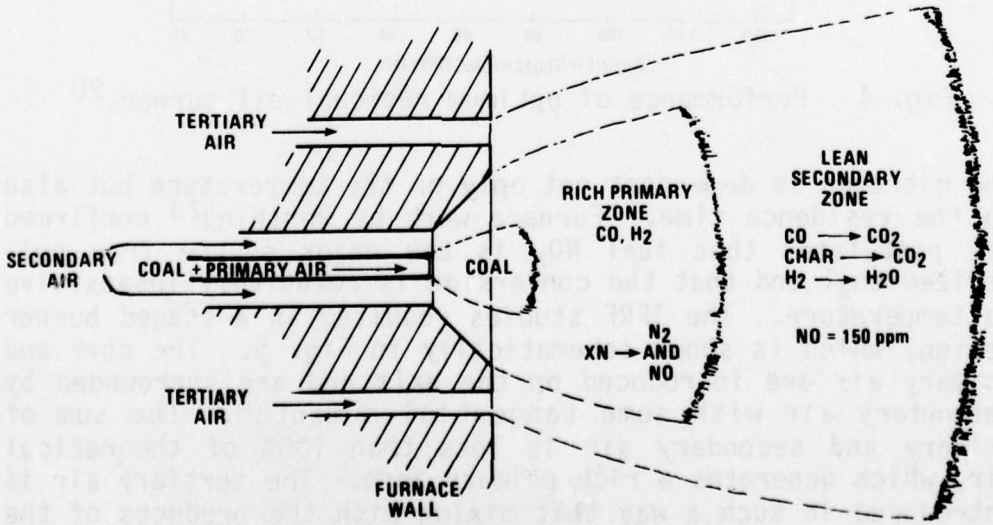


Fig. 5 Low-emission burner concept.

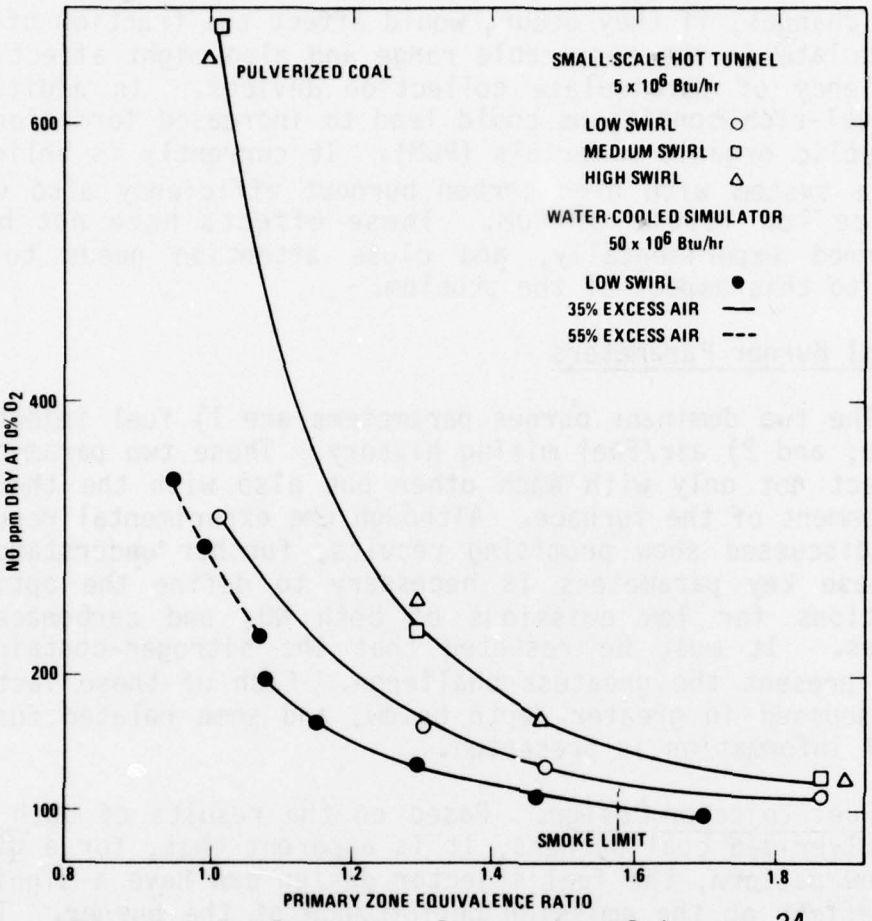


Fig. 6 Performance of staged coal burner.[24]

relatively low melting point of the material and provide for fuel injector cooling. On the other hand, it appears that chars that are a byproduct of coal gasification will give lower baseline emissions of NO_x but will be less subject to control by staged combustion concepts.

In developing low-NO_x technology for solid fuels, particular attention must be given to two other areas: 1) carbon burnout efficiency; and 2) trace species emissions. From an efficiency standpoint, it is important to achieve carbon burnout in the range of 99%, which appears achievable with systems designed for low NO_x. The trace emissions are a more complex problem because many of the species of concern are present in the fuel. For the inorganic species, the effect of NO_x control on both ash particle size and form must be taken into account. There has been some speculation that under fuel-rich conditions some of the inorganic species may form smaller particulate and/or undergo a change of form.

These changes, if they occur, would affect the fraction of the particulate in the respirable range and also might affect the efficiency of particulate collection devices. In addition, the fuel-rich conditions could lead to increased formation of polycyclic organic materials (POM). It currently is believed that a system with high carbon burnout efficiency also will produce low levels of POM. These effects have not been confirmed experimentally, and close attention needs to be given to this aspect of the problem.

General Burner Parameters

The two dominant burner parameters are 1) fuel injection scheme; and 2) air/fuel mixing history. These two parameters interact not only with each other but also with the thermal environment of the furnace. Although the experimental results just discussed show promising results, further understanding of these key parameters is necessary to define the optimum conditions for low emissions of both NO_x and carbonaceous species. It must be restated that the nitrogen-containing fuels present the greatest challenge. Each of these factors is discussed in greater depth below, and some related fundamental information is presented.

Fuel Injector Design. Based on the results of both oil and pulverized coal burners, it is apparent that, for a given airflow pattern, the fuel injector design can have a significant effect on the emission performance of the burner. This is attributable to the influence of the injector design on the early history of the fuel.

For coal, the IFRF results[21] showed that an injector design that rapidly mixed the primary air and coal with the secondary air produced higher NO_x emissions than an axial injector that maintained the primary air and coal in a jet for a period of time. In this latter situation, the primary air was between 10 and 30% of the theoretical air required for combustion which is substoichiometric relative to the ASTM volatile matter in the coal. As the coal volatile reacts with the primary air, the overall stoichiometry in the jet becomes progressively richer, promoting N_2 formation from volatile nitrogen species. This effect is enhanced by the fact that the early volatiles are carbon and hydrogen side chains of the fuel matrix which consume the bulk of the oxygen before nitrogen is released from the ring structure.[22] In the triple concentric burner discussed earlier, this control of stoichiometry is carried even further. Even after the coal and primary air begin to mix with the secondary air, the overall stoichiometry is still rich. The stoichiometry

becomes overall lean only after mixing with the tertiary air. Viewed in this way, the burner results may relate to the progressive staging results reported by Pershing.[25] For coal, the primary control exerted by the injector is on the rate of mixing with the secondary and tertiary airstreams, since the particle size range is fixed by the coal mill.

For oil, the fuel injector (nozzle) determines not only the fuel spatial distribution but also the fuel particle (droplet) size. There is no definitive information on the way in which a heavy oil spray actually burns; however, it is probable that the combustion is either a diffusion flame around a pocket of fuel vapor or a partially premixed air/vapor mixture. In the first instance, the fuel will vaporize and/or pyrolize in a very rich environment. The environment may be air-free for a mechanical atomizer or may have some air or steam present, dependent on the atomizing fluid, for a twin fluid atomizer. It appears likely that any fuel that pyrolizes in this region will produce the precursors for carbon particulate (smoke) formation, as well as nitrogen species. For the partially premixed fuel and air, the stoichiometry may range from rich to lean, dependent on the spatial location in the spray and on the mixing history with the air. The mixture also may be vitiated with combustion products

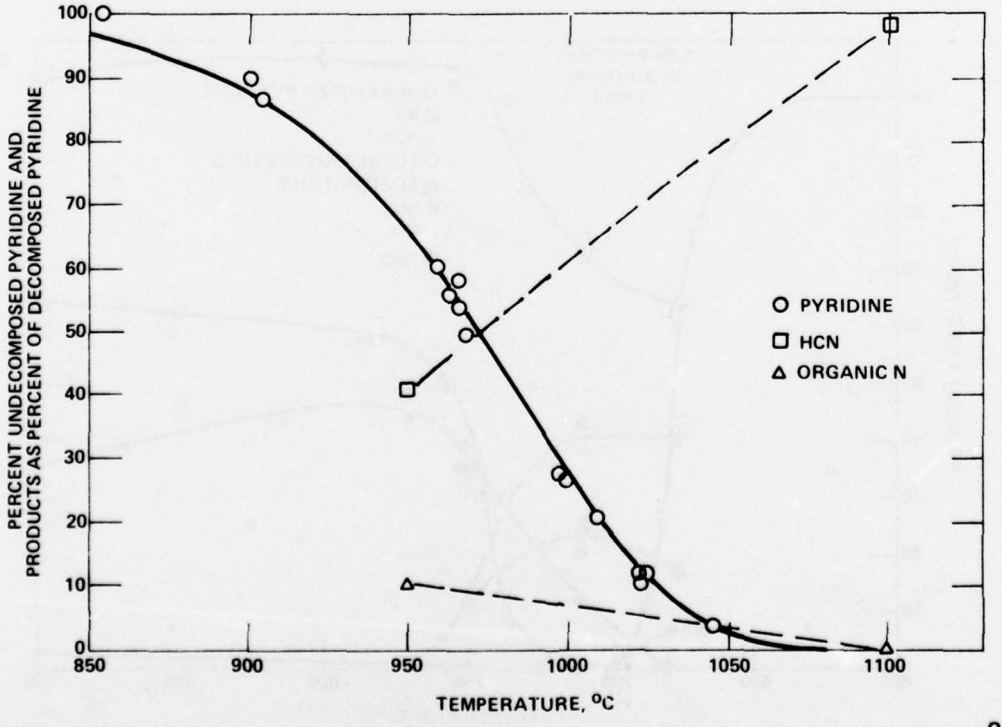


Fig. 7 Pyrolysis products from pyridine under inert conditions.[24]

either in the central recirculation zone or where the combustion air has entrained products from external recirculation zone.

All of these factors may influence the pyrolysis products of a given fuel, as indicated by the results of Axworthy.[17] Although it is difficult to connect simple pyrolysis results to actual combustors, it is interesting to examine the effects of temperature and ambient composition effects on the pyrolysis products of pure compounds.

Figure 7 shows the results of pyrolysis of a model compound (pyridine) under inert conditions (helium carrier) as a function of temperature. Pyrolysis of the pyridine begins below 1123 K and is complete at about 1323 K. At 1223 K, about 50% of the nitrogen from the pyridine appears as HCN or light organic nitrogen compounds, whereas the balance is in the form of a tarry residue. At 1373 K, essentially 100% of the nitrogen appears as HCN. For contrast, under inert conditions at 1373 K, four residual fuel oils yield 35 to 45% HCN, whereas three shale- and coal-derived liquids yielded 51 to 70% HCN. This tends to support the view that the nitrogen in synthetic liquids is more "volatile" at a given temperature. Based on some two-stage inert pyrolysis work with the residual oil (0.71% nitrogen) that yielded 45% HCN, it appears

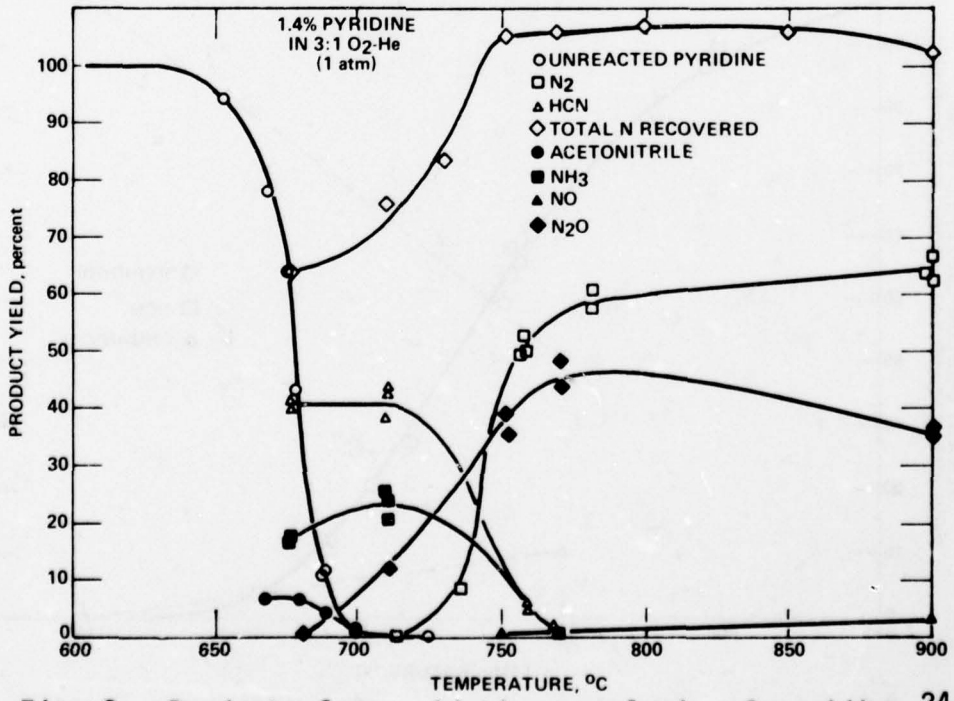


Fig. 8 Products from oxidative pyrolysis of pyridine.[24]

that the nitrogen is evolved as a heavy organic nitrogen at temperatures below 1023 K and that the HCN forms by secondary pyrolysis, reaching a maximum at 1373 K.

These results must be viewed in light of further oxidative pyrolysis of pyridine, as shown in Fig. 8.[17] Pyrolysis of pyridine begins below 923 K and is complete slightly above 973 K, or 400 K lower than under inert conditions. At lower temperatures (973 K), the product yield is about 5% light organic nitrogen, 40% HCN, 20% NH_3 (a species not observed under inert conditions), and 35% heavy material having the same carbon-to-nitrogen ratio (i.e., 5) as the parent compound. As the temperature increases above 1000 K, these products decrease until the nitrogen appears almost quantitatively as N_2 and N_2O above 1023 K. It appears that the N_2 and N_2O are not formed directly but are products of secondary pyrolysis at the relatively long reactor residence times (i.e., >1 sec). Oxidative pyrolysis of oils is in progress, but results are not yet available. The points to be made are 1) the local conditions under which the fuel vaporizes or pyrolizes will affect the products significantly; and 2) although there is no direct link to flame conditions, fundamental experiments of this type can provide useful insight into possible fuel reaction paths in turbulent diffusion flames.

Another area of fuel property and injector parameter coupling is in the possible SO_x and NO_x interactions reported by Wendt.[26] His results show that the presence of sulfur can either enhance or inhibit the formation of fuel NO_x in sulfur- and/or nitrogen-doped oil diffusion flames and in premixed flat flames. The effect was found to be dependent on the stoichiometry, and the enhancement of fuel N conversion to NO_x was most significant under fuel-rich conditions. It should be noted that for the flat flames only NO_x was measured, and it cannot be demonstrated that the Σ XN was changed significantly (i.e., formation of N_2 decreased). The other factor to be considered is that the sulfur and nitrogen dopants used were quite volatile and were almost certainly in the same concentration ratio in the reactant mixture as in the fuel input mixture. For real fuels, this may not be the case. Recent results from Sarofim[27] indicate that, for pyrolysis of coal in a crucible, the evolution of sulfur as a function of temperature is different from that for nitrogen. This would suggest that the absolute levels of sulfur and nitrogen in the fuel cannot be used a priori to assess probable SO_x and NO_x interactions, but rather some time/temperature evolution history must be considered. For coal, this history also may be a function of the ratio of

pyritic to organic sulfur content. Comparable information is not available for oil; however, distillation data for petroleum and shale crudes tend to suggest that the nitrogen and sulfur evolution may parallel each other more closely. From the standpoint of burner design, the ratio of nitrogen to sulfur in the fuel-rich zone may be the most important factor.

Air/Fuel Mixing History. For any given fuel injector characteristic, the stoichiometric history of the fuel previously discussed will depend on the airflow pattern of the combustor. The goal of the air introduction scheme is to promote the optimum mixing for low emission of all species. In the primary rich zone, the stoichiometry should be tailored to minimize Σ XN while preventing formation of carbonaceous particulate at a level that is difficult to burn out in later stages. Later air addition should accomplish three things: 1) minimize conversion of the residual Σ XN to NO_x; 2) provide burnout for carbonaceous species (CO, HC, POM, and particulate) that may be formed in the first stage; and 3) minimize production of thermal NO_x. This fuel/air mixing may be accomplished by 1) discrete staged air addition; 2) progressively leaning out of the system by burner air distribution; or 3) the two in combination. Classical staged combustion, conventional gas turbine combustor cans, or the experimental concept of progressive air addition investigated by Pershing[25] are all examples of discrete air addition, although in the first two examples a turbulent diffusion flame burner with its inherent range of stoichiometries is used as the primary zone. The axial diffusion flame and the low-NO_x coal burner are examples of the burner-induced distributed air addition concepts.[21] The combination of progressive and discrete air addition for coal could be the triple concentric burner concept running at or slightly below stoichiometric to avoid potential corrosion problems, followed by a discrete air port for final burnout. There is no evidence to indicate the potential of this approach.

These air addition histories will control heat release, which, combined with the thermal environment of the combustion system, will determine local temperatures in the reaction zone. This completes the circle by influencing the fuel heating rate and pyrolysis temperature. There are indications from coal data that a hot rich primary that might maximize nitrogen evolution actually may not yield minimum NO_x levels from the overall system. This indicates that the temperature also affects the kinetics of the reactions that determine the ΣXN exiting a rich primary stage of a given overall stoichiometry.

Summary. From the preceding general discussion, it can be seen that the burner design requirements are known in a general empirical way but that the optimum method of achieving the conditions remains to be defined specifically as a function of fuel characteristics.

Conclusions

1) Technology for control of emissions by combustor design changes is in an advanced state of development for conventional fuels and should be applicable to alternate fuels. The specific application to each type of alternate fuel and the effectiveness of control must be established.

2) There are a number of fundamental and developmental areas that require further work, including a) better definition of the fuel nitrogen evolution and reaction under diffusion flame conditions for conventional and alternate fuels; b) relative evolution of nitrogen and sulfur species and the importance of SO_x/NO_x interactions for fuels containing high molecular weight nitrogen compounds; c) high-temperature inert and oxidative pyrolysis products for liquid fuels; d) the effect of pressure on fuel nitrogen conversion, especially under rich conditions; e) the possibility of suppression of fuel nitrogen under lean conditions by heterogeneous reactions during catalytic combustion; f) the conditions that lead to suppression of carbon particulate formation in fuel-rich zones; g) the extent to which POM forms under fuel-rich conditions and subsequently burns out under fuel-lean conditions as a function of combustor design and fuel characteristics; h) establishment of the experimental techniques to link the results of fundamental research with prototype development studies; and i) development of engineering empirical modeling approaches to be used as short-term design tools in generalizing combustion technology.

References

1 Economic Commission of Europe, Second Seminar on Desulfurization of Fuels and Combustion Gases, Washington, D.C., Nov. 11-20, 1975.

2 Spaite, P. W., "Liquefaction and Gasification of Solid Fuel Prospects for Production of Synthetic Boiler Fuels from Coal," Economic Commission of Europe, Second Seminar on Desulfurization of Fuels and Combustion Gases, Washington, D.C., Nov. 11-20, 1975.

3 Martin, G. B., "Environmental Considerations in the Use of Alternate Fuels in Stationary Combustion Processes," Sym-

posium Proceedings: Environmental Aspects of Fuel Conversion Technology, EPA-650/2-74-118, NTIS PB 238-304/AS, Oct. 1974, pp. 259-276.

4 Brown, R. A., Mason, H. B., and Schreiber, R. J., "Systems Analysis Requirements for Nitrogen Oxide Control of Stationary Sources," Aerotherm-Acurex Corp., EPA-650/2-74-091, NTIS PB 237-367/AS, Sept. 1974.

5 Martin, G. B., "Overview of U.S. Environmental Protection Agency's Activities in NO_x Control for Stationary Sources," Joint U.S.-Japan Symposium on Countermeasures for NO_x, Tokyo, Japan, June 28-29, 1974.

6 Yamagishi, K., Nozawa, M., Yoshie, T., Tokumoto, T., and Kakegawa, Y., "A Study of NO_x Emission Characteristics in Two-Stage Combustion," 15th Symposium (International) on Combustion, Tokyo, Japan, Aug. 1974.

7 Fenimore, C. P., "Formation of Nitric Oxide in Premixed Hydrocarbon Flames," 13th Symposium (International) on Combustion, Salt Lake City, Utah, Aug. 1970.

8 Farnsworth, J. F., Mitsak, D. M., and Kamody, J. F., "Clean Environment with Koppers-Totzek Process," Symposium Proceedings: Environmental Aspects of Fuel Conversion Technology, EPA-650/2-74-118, NTIS PB 238-304/AS, Oct. 1974, pp. 115-130.

9 Forney, A. J., Haynes, W. P., Gasior, S. J., Johnson, C. E., and Starkey, J. P., Jr., "Analyses of Tars, Chars, Gases and Water Found in Effluents from the Synthane Process," Symposium Proceedings: Environmental Aspects of Fuel Conversion Technology, EPA-650/2-74-118, NTIS PB 238-304/AS, Oct. 1974, pp. 107-113.

10 Robson, F. L. and Giramonti, A. J., "The Environmental Impact of Coal-Based Advanced Power Systems," Symposium Proceedings: Environmental Aspects of Fuel Conversion Technology, EPA-650/2-74-118, NTIS PB 238-304/AS, Oct. 1974, pp. 237-257.

11 Lisauskas, A. and Johnson, S. A., "NO_x Formation During the Combustion of Low Btu Gas from Coal," AIChE 80th National Meeting, Boston, Mass., Sept. 7-10, 1975.

12 Bartik, H., Kunchal, K., Switzer, D., Bowen, R., and Edwards, R., "Final Report: The Production and Refining of Crude Shale Oil into Military Fuels," Applied Systems Corp. Final Rept. on Office of Naval Research Contract N00014-75-C-0055, Aug. 1975.

[13] Ball, J. S. and Rall, H. T., "Nonhydrocarbon Components of a California Petroleum," 27th Midyear Meeting of the American Petroleum Institute Division of Refinery, San Francisco, Calif., 1962.

[14] Dzuna, E. R., "Combustion Tests of Shale Oils," Central States Section of the Combustion Institute, Columbus, Ohio, April 5-6, 1976.

[15] Pfefferle, N. C., Carrubba, R. V., Heck, R. M., and Roberts, G. W., "Catathermal Combustion: A New Process for Low-Emissions Fuel Conversion," ASME Winter Meeting, Houston, Texas, Nov. 30-Dec. 4, 1975.

[16] Kesselring, J. P., Krill, W. V., and Kendall, R. M., "Design Criteria for Stationary Source Catalytic Combustors," Western States Section Fall Meeting of the Combustion Institute, Stanford, Calif., Paper 77-32, Oct. 17-18, 1977.

[17] Axworthy, A. E. and Dayan, V. H., "Chemical Reactions in the Conversion of Fuel Nitrogen to NO_x: Fuel Pyrolysis Studies," Proceedings of the Second Stationary Source Combustion Symposium, Vol. IV: Fundamental Combustion Research, EPA-600/7-77-073d, NTIS PB 274-029/AS, July 1977, pp. 39-78.

[18] Martin, G. B., "NO_x Considerations in Alternate Fuel Combustion," Symposium Proceedings: Environmental Aspects of Fuel Converstion Technology, EPA-600/2-76-149, NTIS PB 257-182/AS, June 1976, pp. 373-394.

[19] Heap, M. P., Tyson, T. J., Cichanowicz, J. E., Kau, C. J., Martin, G. B., and Lanier, W. S., "Environmental Aspects of Low Btu Gas Combustion," Proceedings: 16th Symposium (International) on Combustion, Aug. 1976, pp. 535-545.

[20] Cichanowicz, J. E., Lobell, M. H., Heap, M. P., and Pershing, D. W., "NO_x Control Techniques for Package Boilers: Comparison of Burner Design, Fuel Modification and Combustion Modification," Proceedings of the Second Stationary Source Combustion Symposium, Vol. V, Addendum, EPA-600/7-77-073e, NTIS PB 274-897/AS, July 1977, pp. 31-62.

[21] Heap, M. P., Lowes, T. M., Walmsley, R., Bartelds, H., and LaVaguerese, P., "Burner Criteria for NO_x Control, Vol. I. Influence of Burner Variables on NO_x in Pulverized Coal Flames," International Flame Research Foundation, EPA-600/2-76-061a, NTIS PB 259-911/AS, Mar. 1976.

22 Pohl, J. H. and Sarofim, A. F., "Devolatilization and Oxidation of Coal Nitrogen," Proceedings: 16th Symposium (International) on Combustion, Aug. 1976, pp. 491-502.

23 Pershing, D. W. and Wendt, J. O. L., "Pulverized Coal Combustion: The Influence of Flame Temperature and Coal Composition on Thermal and Fuel NO_x," Proceedings: 16th Symposium (International) on Combustion, Aug. 1976, pp. 389-400.

24 Gershman, R., Heap, M. P., and Tyson, T. J., "Design and Scale-up of Low Emission Burners for Industrial and Utility Boilers," Proceedings of the Second Stationary Source Combustion Symposium, Vol. V, Addendum, EPA-600/7-77-073e, NTIS PB 274-897/AS, July 1977, pp. 65-78.

25 Pershing, D. W., Wendt, J. O. L., and Lee, J., "Fate of Coal Nitrogen Under Fuel Rich and Staged Conditions," 70th Annual Meeting of the AIChE, New York, Nov. 13-17, 1977.

26 Wendt, J. O. L., Corley, T. L., and Morcomb, J. T., "Interactions Between Sulfur Oxides and Nitrogen Oxides in Combustion Processes," Proceedings of the Second Stationary Source Combustion Symposium, Vol. IV: Fundamental Combustion Research, EPA-600/7-77-073d, NTIS PB 274-029/AS, July 1977, pp. 101-137.

27 Sarofim, A. F., personal communication, unpublished results of EPA Grant R805552 with Massachusetts Inst. of Technology, Cambridge, Mass., Dec. 1977.

DISCUSSION

DR. A. H. LEFEBVRE (Purdue University): I cannot accept the view that with staged combustion you would have a rich first zone. If you did use this system for aircraft, it would almost certainly be a two-staged system. At low power conditions, such as idle, one would employ all the fuel in the first stage. It would burn at a fairly high equivalence ratio because high temperatures are needed to minimize CO and unburned hydrocarbons. I would suggest an equivalence ratio of 0.8. I would not go higher because then one might run into problems of equilibrium CO.

Under maximum power conditions, although combustion would be maintained in the primary zone, or the first stage, most of the fuel would be injected downstream into the second stage. It would be injected in a premixed form with an equivalence

ratio of about 0.6 or a little below. At that time, the equivalence ratio in the primary zone would be lowered to about 0.5 or 0.6. Thus, a two-stage system for aircraft application would have an equivalence ratio of about 0.8 maximum in the first stage and about 0.6 maximum in the second stage. At no time, unless it happened during a transient condition, would the equivalence ratio be allowed to exceed unity anywhere.

My second comment concerns the recirculation of exhaust gases. At the Allison Division of General Motors they have demonstrated very substantial reductions in both NO and CO on gas turbine combustors featuring exhaust gas recirculation.

At the end of your paper, you showed a fuel injector for boiler applications. You stressed that both atomization and air/fuel ratio were important. You commented that you were trying to decide on the relative effects of these two different parameters. The point I would like to make is that many people have tested the effect of atomization quality on soot formation and smoke. In particular, they have used swirl atomizers where, by reducing the flow number of the atomizer, they have been able to reduce the mean drop size. However, this has not always been beneficial in terms of reduced smoke. The reason is that, when the droplets are made smaller, the total surface area of the spray is increased. Consequently, the aerodynamic drag of the spray goes up, and the fuel does not penetrate as far. This means that the fuel becomes involved with less air and therefore burns richer. Also, because the drop sizes are smaller, the evaporation rate is higher, and more fuel vapor is liberated. So, what happens under these conditions is that the beneficial effect of improved atomization is more than outweighed by the detrimental effect of the increase in effective fuel/air ratio in the soot-forming region.

Where tests have been carried out on the effect of reducing drop size without changing fuel/air ratio, then a lower drop size always gives reduced smoke. The best practical example is the airblast atomizer, where reduced drop size always reduces smoke. Of course, if one looks further ahead to premixing and prevaporizing, then droplets can be taken out of the picture altogether.

MR. MARTIN: If I understand your first comment, you are essentially saying that you would always be lean in your combustor. If that is the case and you are burning a nitrogen-containing fuel, you will have a fuel NO_x problem. Fuel-rich staging is required to control fuel nitrogen conversion.

If we look at these fuels and believe that there is going to be significant nitrogen in them, then a rich staged system will be required if we are to control NO_x emissions.

As far as your second comment is concerned, yes, exhaust gas recirculation does significantly reduce NO_x. It does for stationary systems, but it is a mechanical complexity. If you can avoid it, you should. I think you can avoid it by structuring the combustor to achieve that recirculation internally. It is generally less effective for a gas turbine than it is for a stationary source because the gas turbine has a higher percentage of air in the exhaust gases that are recirculated. The diluent effect is not as significant.

The third comment is well taken. It does happen that those flow patterns that concentrate the fuel are in fact the ones that suppress NO formation but increase the smoke potential. I do not necessarily say that you would go with small droplet sizes alone. I think the point of that last comment was that the combination of atomization and air flow needs to be optimized to achieve both NO_x control and particulate control. That is the goal of that type of R&D for emission control development for all fuels.

Chapter V - Summary and Conclusions

PANEL DISCUSSION

ALTERNATIVE FUELS POLICY

Moderator: Dr. Jerry Grey, Administrator
Public Policy
American Institute of Aeronautics and Astronautics

Panelists: Mr. E. Eugene Ecklund, Program Manager
Division of Transportation Energy Conservation
Energy Research and Development Administration

Mr. A. Lee Wallace, Counsel
House Committee on Science and Technology

Mr. Charles Weisel, Manager
Division for Aviation Sales
Exxon International

Dr. Grey: The purpose of this panel is to discuss alternative fuel policy. If we are not sure what "policy" means, we can assume that it is most of those subjects relating to alternative fuel implementation and utilization which have not been discussed in technical sessions of this workshop.

We have here a qualified group representing three sectors concerned with alternate fuel policy: Eugene Ecklund who basically will represent the Administration's viewpoint, Lee Wallace, who represents the Congressional viewpoint, and Charles Weisel, who represents the viewpoint of industry. I have asked each of the panelists to prepare a brief discussion, stating the issues as he sees them from his sector. I will then ask several questions directed specifically to certain panelists who are most appropriate to answer them. Following that, we will have questions from the floor. Mr. Ecklund will make the opening remarks.

Mr. Ecklund: As a program manager on alternative fuels for highway vehicle applications, it is not fundamentally the function of my particular office to establish policy. Indeed, along with many of us, I must look to other people for that. I will speak to the situation from the point of view of an administrator in the government and try to assess what is happening and what it means to those here.



First of all, I would like to remind you that it has been four years since the oil embargo. The predecessor activity to that in which I am now involved started activities on alternative fuels prior to that, and so my comments are based on experience in two agencies. My view is from the civilian sector, but, since we try to build on experience, and part of that experience emanates from DOD, I shall reach back into that. As far as alternative fuels are concerned, both the military and the civilian sectors can be lumped together.

The existing policy is made up of segments which are either stated, the result of action, or of a combination thereof. The stated aspects deal with conservation, improved efficiency, and a shift in the resource base. Only the latter, more specifically a shift from petroleum, has any lasting effect. All of the other measures are temporary. From an action point of view, the government effort has been aimed primarily at conservation and the direct combustion of coal. I believe that you know enough about all of those factors to appreciate their ramifications. One significant factor is the law mandating automotive fuel economy. In transportation, there are only two ways that we can get away from using petroleum. One is to shift to electricity from nonpetroleum resources. The other is to use alternative fuels directly.

There is major action in the government to develop processing to make fuels from coal, oil, shale, biomass, and municipal solid wastes. These are all aimed, as they should be as a first-level proposition, at making known fuels—fuels like those of today. However, such an approach does not take into account the overall system or even the fuel/combustor couple. I mention this because I think it gets to the heart of the policy situation. The policy of the fossil energy people, who are responsible for the production side, is to test the fuels that come from their processes. They would like users to take what comes out and do whatever good things are possible to the combustor. If we follow that approach, we are never going to marry the fuel/engine couple on any kind of an intelligent tradeoff basis.

There is no reason to talk about the same kinds of fuels as we use today. Indeed, as we look downstream, they probably should not be, and probably will not be, identical. The driving force in the long run is economics. It is not economical to make gasoline from coal that looks like gasoline from petroleum. They are just two widely different resources. Therefore, I submit that approaching alternatives strictly from a process viewpoint is not viable.

Now, I want to reference three actions that are taking place that I think are or could be significant. Two of these have taken place in ERDA in the form of planning exercises. One of them was the Market Oriented Program Planning Study (MOPPS). It looked at finite fuels to the year 2000. The outcome of that exercise indicated that supply is going to meet demand. I was not involved in the fuel supply end of MOPPS but was involved in the demand end. Although the results may indeed be true, I think the basis on which they were put together was invalid. Therefore, I find it very difficult to look at these results and draw any conclusions.

There is another exercise that is going on covering the longer term situation and inexhaustible resources—fundamentally nuclear and solar. In general there seems to be a feeling at this stage that there is plenty of supply technology being pursued. It may get reduced a little bit, but emphasis appears generally well balanced. However, this effort is basically aimed at electricity. Essentially nothing is being done on liquid fuels, so the entire transportation area is left up in the air.

The third thing I would like to do is to quote the only portion of the National Energy Plant that I know of that deals with alternative fuels. It says, "Some very important questions currently remain unanswered. It is not yet clear what energy source will replace petroleum for transportation. Coal can be converted to petroleum products as Germany demonstrated during World War II, but current synthetics are extraordinarily expensive—more than double the world price of oil. Perhaps electric cars, buses, and trains will be part of a long-term solution for reducing oil consumption. Methanol and alcohol, even now sometimes used for fuel, also could make a major contribution as a substitute or additive to gasoline. New opportunities no one can foresee may appear during the next two decades. The United States will need to pursue research and development on all promising options to determine whether any of them fill the petroleum gap."

I now want to add a couple of things parenthetically. During the four years that the alternative fuels utilization program for highway vehicles has been in existence in our transportation program, we have spent about $2,500,000. Our budget for 1978 is about $2,000,000. DOD and NASA have been doing some selective work on aircraft fuels. Beyond that no one elsewhere is working the problem in the utilization sector. As a matter of fact, if you grant me the liberty of putting Karl Bastress and Jørgen Birkeland in the field of research, then, in the development of end-use application of

alternative fuels technology, the only active participant in all of Washington is addressing you.

With that, I will summarize by saying that, from a utilization viewpoint, there is no significant alternative fuels policy.

Dr. Grey: That is a provocative way to start off this panel. Thank you, Mr. Ecklund. I will now ask Mr. Wallace to present the Congressional viewpoint on the subject.

Mr. Wallace: First of all, I would like to mention that the section of the ERDA authorization bill which would provide loan guarantees for synthetic fuels has just been sent to the House floor for consideration.

In my opening remarks, I will recall some of the history behind the development of synthetic fuels or alternative fuels policy. The starting point seems to be President Ford's energy message of 1975. At that time, the administration determined that there would be a shortfall of natural fuels and that some kind of synthetic fuel production would be needed in the United States well before the year 2000. The administration also commissioned a Synfuels Task Force. The deadline for that task force report was around December 1975, but, as politics would have it, the Democrats put in another "synfuel policy" with Section 103 of the ERDA authorization bill for FY 1976.

The first amendment, originally authored by Senator Randolph, was put in by Senator Jackson. President Ford, who had his own policy, came out in support of the amendment. However, he backed it up with all of the draft documents that he had ready for the synfuel commercialization program. They seemed to coincide almost exactly as far as the scope and depth of the programs was concerned. Both called for approximately $6 billion in United States government aid to industry. The Randolph Bill or the Jackson amendment only called for loan guarantees, whereas the President's program called for a combination of loan guarantees, grants, price supports, and, in some cases, direct loans. The House, however, was reluctant to accept the Senate's version of a synfuels policy. Our Committee held hearings on it during the months of September and October, but there was no actual vote. Since the Senate had voted to send this amendment to the House, the parliamentary situation was that it was only in a conference, and therefore only the conferees representing the House of Representatives could vote on it.

In conference, many changes were made to Section 103 and, when it finally went to a floor vote, it lost two to one. In analyzing the vote, the opposition seems to have come from several sources. First of all, there was confusion about what the synfuels policy was. There was no doubt that the President's program had been hurried along, with the original deadline pushed back to September, and the Randolph Bill was put in without a full set of hearings, although there had been sufficient hearings in prior Congresses. Opposing the bill was a mixture of conservatives and liberals. Liberals tended to oppose it on the basis of environmental reasons. They did not like the idea of large central station complexes or facilities, mainly because of the need either to strip-mine large sections of the countryside, or else because it put a great deal of emphasis on coal and fossil fuels and diverted capital expenses from solar, geothermal, and other smaller energy sources.

After that vote, President Ford still wanted to support some type of synfuel policy. Congressman Teague, the Chairman, introduced Bill H. R. 12112, which was a modified version in that it went to only $2 billion in February 1976. We followed that bill throughout the entire Congress. It eventually went up to a $4 billion program.

Again, the main forces opposing it were a combination of conservatives and liberals. The conservatives were mainly opposed to it on the basis of a free-market philosophy. Their argument was that, if you really want to see coal gasification plants built, what you should do is deregulate natural gas prices and let the market bring these plants on line in time. The Committee voted against that argument and against the environmentalist argument by about two to one. The argument of the Committee and the basis for the voting was that, although the free market might actually bring these on in time to match supply, the problems that surround these large facilities will not necessarily be studied in depth prior to the plants being built. In this bill, we were attempting to build a small number of plants, a maximum of 24, using all sorts of nonnuclear energy technology—coal, solar, oil shale, biomass, geothermal, and some conservation. The object was to assess what the environmental, regulatory, and socioeconomic impacts would be.

In visiting a small town like Rifle, Colo., our Committee found that a town of 500 or 1000 people would be host to a work force, at peak, of 5000 people. Obviously, this would put a severe strain on such towns where oil shale was developing. We built into the bill safeguards or programs to

deal with the impacts and provide money for these communities when the need would be there to handle these large plants. An economical plant for oil shale has to process approximately 50,000 barrels per day and represents a cash flow of $1.5 billion which causes a severe impact in any community, let alone one of a 1000 people. Furthermore, the Committee thought that this information needed to be generated in the early 1980's, because these plants would have to begin to face the regulatory hurdles soon to meet the demand that is foreseen in the early 1990's.

When H. R. 12112 came to the floor in the waning days of this past conference, the vote was on the rule. The opponents had put in well over 100 amendments and had recorded 16 hours of reserved time for debate on amendments. The leadership just did not want to take that up so they brought it to the floor for a vote on the rule. The rule lost by one vote, 193 to 192. Now the Committee has voted again to put a loan guarantee provision into the ERDA authorization bill. However, this contains no money. It is just a simple authorization with statutory language. The Senate has already approved it, and we do not expect as much opposition this time, but the Congress still has to vote on it.

Dr. Grey: Thank you, Mr. Wallace. Mr. Weisel will now discuss the industry viewpoint.

Mr. Weisel: Perhaps a number of you saw the Wall Street Journal's statement of the first law of forecasting—namely, that forecasting is very difficult, particularly when forced to deal with the future. We have some comments about the future.

Dr. Longwell mentioned that conventional crude production will peak about 1995. The scenario says that there will be substantial but not adequate quantities of conventional crude oil through that period. However, he also pointed out that there would be competition from other end uses for the distillates going into jet fuel. The inference was plain. In the face of tightening supplies, steps should be taken to extend the jet fuel supplies by dipping further into the conventional barrel, into the gas oil fraction, or by using suitably processed alternative fuels either directly or by blending. The work reported at this workshop to utilize jet fuels of poorer combustion quality is timely and necessary if we are to have any degree of freedom in meeting the needs of aviation in the future. This is particularly true in view of the long lead times needed for the hardware systems development.

Dr. Longwell also mentioned that by 1990 the production of synthetic crudes from shale, coal, and tar sands in the United States might reach 500,000 barrels a day. Our own somewhat optimistic projections are that by 1990 synthetic crude production possibly could reach 1% of the world's total energy needs. Now 1% does not sound all that great, but it amounts to almost 2,000,000 barrels a day. It means that between now and 1990 we will have to build the equivalent of 30 or 40 plants, each having a capacity of 50,000 barrels a day. The capital required for this is staggering, being on the order of $35 billion to $45 billion in 1976 dollars. Although much of the basic technology is available, large pilot plants are needed to scale up to commercial size and show technical and economical viability. The lead time for completion of these first commercial-sized pioneer plants is on the order of seven to ten years, so time is short. I believe that, if timely development of alternative fuels production is to be obtained, the United States will need an energy policy which provides private industry with appropriate incentives for obtaining practical, cost-effective production of alternative fuels. First and most important, existing regulatory and legislative barriers or disincentives, together with unnecessary environmental constraints, should be removed. A specific and important step would be the exemption of pioneer plant products from price controls. In addition, incentives such as accelerated depreciation and investment tax credits that have maximum effect in the early stages of production should be provided. If these initial steps prove to be insufficient, partial grants in support of construction which would be convertible to loans upon demonstration of operating and economic viability should be offered for the initial pioneer plants only. In exchange, an operator who accepts government incentives for a plant should be required to make the test results available both to the government and to the public. This of course is different from the loan guarantees that were mentioned, because the loan guarantees in general protect only the lender. They do not really give the incentive for pushing ahead to fruition of actual production.

To demonstrate that incentives can work in encouraging industry to develop an energy resource, we can look at the syncrude project involving the Athabasca tar sands. This $2.6 billion project is designed to produce a 125-thousand-barrel-a-day plant. The first train is expected to start up in the middle of 1977. The Canadians have established that this synthetic crude will be priced at parity with world crude. They have provided significant and early tax incentives. They have set clear, definite, and stable environmental requirements. What they have really done is create a favor-

able business climate for this resource development. They have provided a basis for planning, so that they can calculate in advance the fact that the project may have some economic viability.

Clearly, the development of synthetic fuels to a level which produced only 1% of the world's energy is only part of the overall energy requirement. Meeting this requirement is dependent on developing a business climate in which private industry is encouraged to go after all forms of energy production; conventional crude, gas, coal production, nuclear power, and the development of the other forms of energy.

Dr. Grey: Thank you, Mr. Weisel. I would like to touch on some things that the panelists have mentioned. Mr. Weisel has actually stated what he thinks industry would like to see in the form of an energy policy. If I can restate it, he asks, first of all, for the removal or proper adjustment of regulatory barriers such as price controls and certain environmental constraints, and accelerated depreciation in tax credits; in other words, financial incentives of some kind. He also implies that in some cases direct subsidies rather than simple loan guarantees might be necessary. I would like to ask Mr. Ecklund for his viewpoint on those policy matters. Do they identify the policy that he feels does not exist?

Mr. Ecklund: I do not want to get into the specifics of a policy, but I think it is certainly inherent in anything that we do. We, as a nation, constantly have said that energy and all other business is the province of industry. We want to let the market place function. The reason that government is in energy is that people do not believe there is time available for the market place to function in a normal fashion. The government's role is to try to help make things happen in a timely way. I can see this being discussed one way or another as to whether we are going to have price supports, or whether we are going to have incentives, or whether we are going to have loan guarantees and how long they are going to go on. We can get into the proposition once in a great while of whether we ought to have a government owned or operated facility. I think that generally people do not want that sort of thing. As a taxpayer, I do not either.

Certainly we have to provide the incentives for industry. The first thing that is going to happen will happen in natural gas. Substitute gas projects are going to be the bellwether of whether we are ever going to move or not. There are a half dozen projects all ready to go, but the people do not have the money. They know we are going to wind up short of fuel, and

they would like to provide it. In one particular case, a large pipeline company in Texas had a plan for a coal gasification plant. The cost of that gasification plant was as much as their total invested capital. We are taking huge sums of money.

Dr. Grey: That same pattern was encountered in the aviation industry when it was decided that, if the aviation industry were to build a supersonic transport, the total investment should come from the industry. It turned out that the capital required was about triple the Boeing net worth at that time.

I would like to return, though, to this whole question of whether or not the loan guarantee provisions that are in the bill today are the first step in producing what Mr. Weisel would think would be a satisfactory policy. For example, a major factor in the defeat of the previous loan guarantee provision was a GAO report which made statements that many people thought were absolutely wrong. The GAO study said that these things should be handled totally by industry, that government should not take any steps, that the plants that were being built were much too large, that conservation would satisfy their requirements, and so on. Have they been changed enough so that you think the loan guarantee provision and subsequent follow-on policies are possible at this time? I would like Mr. Wallace to answer that, because he has the bill on the floor and knows more about it right now.

Mr. Wallace: The GAO report, of course, did contribute quite a bit to the defeat of the bill. We held follow-up hearings and proved that quite a bit of the report was just completely wrong, and they admitted on the record that a lot of their facts were wrong.

The main difference between the bill presently on the floor and the one that was defeated in September 1976 is money. There is no dollar figure in the present bill. The Administration has asked us to put into being the authority to make loan guarantees. I think that ought to be appreciated here. Loan guarantees are the only financial assistance that DOE lacks to assist corporations in building large plants. They want to have that authority in place, so that when they come up with a program they can make loan guarantees part of it.

It is really on the record that the first plants will be natural gas plants. What the companies want in the form of assistance is loan guarantees. They do not want a loan. They

do not want a grant. They figure loan guarantees would be the best way to handle it. This is partially due to the regulatory climate, but it is also due to the banking community. The banking community is really just not ready to go ahead with it.

Dr. Grey: Mr. Weisel, what is your view on that?

Mr. Weisel: As long as gas price is controlled so that the cost of Btu's of gas is cheaper than the cost of Btu's from world market crude, there is an incentive for more and more use of that gas. If that gas price is low, then the builders of these plants cannot really earn a return that makes the plant construction an economically viable project. The fact that there is a loan guarantee when companies go broke protects the bankers, but it does not do very much in terms of making the company project into a viable project. Yes, they can get loans to build and can hope that things change in the future, but they are rolling for some pretty high stakes and, when the deck is more or less against them and things may or may not change, they are not in a very sound position.

Dr. Grey: That brings up the whole question of future pricing of synthetic fuels as compared to both imported and domestic natural fuels. Should market price be the only factor to govern the implementation of production facilities—in other words, removal of all price controls, no matter what? I do not think that is realistic. It might be nice from an industry point of view, but I do not think it will ever happen. What kind of price control changes do you think might be effective in the real world in allowing a company to go ahead and build a synthetic fuel plant with or without a loan guarantee? I want to ask for Mr. Weisel's viewpoint on that also.

Mr. Weisel: First of all, when we hear projections that crude production will peak in the 1995 period and that we will be living largely on conventional crude production in the foreseeable future, there is a basic premise that the shortfall in the United States will be made up with imports. Now these imports may or may not continue. We do not know, because at any time, for whatever reason, there could be a moratorium, and we would be shy about 50% of the requirements in the United States. That says that we should be getting on with the development of alternate sources. There is a recoverable reserve in shale of something on the order to 50 to 100 billion barrels. (Just for comparison, the Prudho oil field has on the order of a 10-billion-barrel reserve as

people now understand it.) The tar sands have another 50 to 100 billion barrels, but to get it out will involve tremendous investments. If we are going to plan for this, perhaps the way to do it is to say that the products from these plants will be guaranteed at an equivalent world crude price. We also must depend on increased production in other areas, and there should be some incentives there, too.

Dr. Grey: Do you think the world crude price will be satisfactory? Right now the typical price is roughly $13 a barrel for imported oil. The estimates that I have seen for syncrudes and others run well over $20 a barrel in most cases. Is that consistent? Can it be done economically?

Mr. Weisel: That is the reason for some of the tax incentives and early write-offs.

Dr. Grey: So you are saying it is not just price controls. Some other things also are needed.

Mr. Weisel: We are talking about something that is ten years in the future. We are thinking in terms of the current world price being held constant, except for inflation. That is a big exception.

Mr. Ecklund: I tend to believe that price controls will never really be given up because people want to be sure that prices do not get totally out of hand. The question I would like to raise concerns both upper and lower level price controls. One of the dangers in pegging things to world oil prices is that that price can be dropped at the appropriate time. Even if it does not happen, it at least scares the investment community. The implication here is that, even with regulatory controls which allow prices to rise to levels at which there are incentives, there has to be some lower level that protects the industry insofar as any investment is concerned. I would like Mr. Weisel's view on that aspect of it.

Dr. Grey: Before we get to that, I would like to ask Mr. Wallace to comment on the whole question of how Congress views the price control situation. I think that is what will determine what price controls get set.

Mr. Wallace: I think you are right that Congress will continue price controls, as least for the foreseeable future. I believe, though, that we will see the iceberg breaking up around 1990, because economists to whom I have talked (including Exxon economists) say that the world supply at that time

actually crosses the demand curve at the level of pricing that we are experiencing now, in today's dollars, and will begin to move up. At that point, I think we will start seeing some significant rethinking on price controls.

Getting back to alternative fuels, I think shale oil will never be economical at a lower tier price or at any type of control price. It will have to be decontrolled. I think that was the intent of the programs in the two bills that we presented in the 94th Congress. Coal gas also will have to be priced at a high level. I just note that naphtha-based SNG is now priced at the higher level by the FPC. It is rolled in, and that of course presents another issue.

Part of the program from President Ford was that there would be some type of price support for products such as the product gas from biomass plants. This type of support could be forthcoming. However, the product is not one on the current market. It is a low Btu gas of the type we had in the 1920's and 1930's, and earlier. It would be hard to try to correlate what we would be paying for that except on a Btu basis, but it would require its own distribution network.

Dr. Grey: You have raised another point which I think we ought to bring out. Up to now, we have been talking about coal, shale, and synthetic fuels derived from tar sands. Is there a real role for some of the other organics or for some of the biomass and waste-derived alcohols? Mr. Ecklund, I believe you have studied this as much as anyone else. Do you see this making any impact at all on the overall policy setting of synthetic fuel plants?

Mr. Ecklund: I suspect that there is going to be some action in this particular area in the near future. The support for alcohol actually comes from the Congressional representatives of the grain producing states. There is something fundamental involved here. We are interested in alcohols in transportation, and the reason we are interested in alcohols is pretty basic. The only domestic resources that are large enough to support transportation are oil shale and coal. Although we can make synfuels from these, we also can make methanol from coal. If we make methanol from coal and if we use it, then we open up the door for alcohols from other resources. In making alcohol from coal, and possibly from wood products, we can make methanol for around 50 cents a gallon, which on a Btu basis is equivalent to about $1.00 a gallon in today's market. That would compare to a price of about 80 cents a gallon for imported oil, so we still have a 20% premium on it. If we go to ethanol from agricultural

products, we are talking about $1.20 a gallon or $2.00 a gallon on an equivalent Btu basis. Even if we blend that in at 10% blend with gasoline, we are talking about a significant increase in the price.

The interesting part about this is that all the pressure is coming from the agricultural states. There is no pressure coming from the wood-producing states or from the coal people. Nevertheless, there has been a big uproar over this. Certainly, the use of alcohol as a blending agent is potentially viable if we choose to go that particular route. The principal driving force is that we know how to do it, whereas we just do not know how to overcome the problems of getting any other kind of fuel on the market.

Dr. Grey: What percentage of our alternative fuel production do you see as being ethanol or methanol? Just give me a guess to put it in the right framework.

Mr. Ecklund: The total methanol manufactured today represents 1% of the volume of petroleum we use and 0.5% of the energy that we use. We would have to build an industry that is ten times as large as the industry that exists today, which in its own right is an enormous proposition. The question is: do we put our money into alcohol plants or do we put it into something else? That gets into our perception of the problem. Do we have an immediate problem or do we just go along with business as usual for another ten or twenty years and live with the situation? I do not really know the answer. I do perceive using alcohol as a blending agent, not directly, perhaps, the way we normally talk of taking a pot of alcohol and dropping it in the gas tank, but looking at it as a refiner would look at it—i.e., as another hydrocarbon ingredient in the total composition. Use would vary with region and with time of the year. It probably would not be used at all in hot climates, if it could be avoided, because of vapor lock.

Dr. Grey: What you are saying is that it is subject to economics like everything else. Right now, the economics do not look too great. As a result, you do not really foresee a major influx of alcohols into the system. I am putting words in your mouth.

Mr. Ecklund: That is right, but I am not sure that we do everything on a totally nonemotional basis.

Dr. Grey: That brings up the next subject. So far, we have discussed what probably is the main policy problem in

synthetic fuels—i.e., economics. What is the price? How do we set the price? How do we get incentives going, and so on? Mr. Weisel mentioned one other very important factor: making the environmental control requirements consistent. In many cases this becomes an emotional rather than a factual issue. In eastern Long Island, for example, environmental concerns dominate energy matters over and above everything else, including cost. I would like to ask Mr. Weisel first to define just what kind of environmental control changes he would like to see in order to make it possible for industry to invest in synthetic fuel plants in a major way.

Mr. Weisel: I think the first thing we need is a stable situation to provide a basis for planning. There are a number of environmental regulations that I wonder about. For example, coal scrubbers are being required on all new electric power plants designed to use coal whether they use low sulfur coal or not. In our opinion, this is an unnecessary requirement when high-quality coal is used. Strip-mining, for example, has been held up by the Sierra Club. That has just been settled, but it caused a delay. Delays in development of a project that has been started represent real costs. Perhaps these costs are not directly environmentally related, but the bill that is being considered could cause delays.

Dr. Grey: What do you think should be done? What are you recommending? We are not going to wipe out environmental controls, but we do need stabilization. How do we go about getting it?

Mr. Weisel: That is a good question, but it is a difficult one to answer because there are so many different aspects to the problem. What I am pointing out is that we must set controls and then maintain them. Those controls should be set on the basis of balancing energy needs with environmental protection.

Dr. Grey: Mr. Wallace, how do you see Congress viewing this particular question, which I think is one of the most critical ones?

Mr. Wallace: Once again, it is very difficult, mainly because of the large number of committees involved. In the House of Representatives, there are six different committees trying to outdo each other on environmental laws, regulations, and impact. Maybe the problem really centers around a lack of understanding of how fossil fuel combustion and other activities impact on the environment and what it is we actually have

to be protected from. Unfortunately, this is not going to be an easy question to answer. Until we have an answer, the Congress is going to propose more and more regulations. I am really not optimistic about it.

Dr. Grey: I think we all agree that some consistency in these regulations would be a good idea, but the sense I get here is that it is going to be very hard to get that consistency.

Mr. Ecklund: As I understand it, one of the reasons for ERDA's synfuel commercialization program is to have the first plants go ahead and prove out what people think is going to happen. In other words, we have some fairly good ideas of what we think the environmental impact will be, but there will be some difference in practice from what we anticipate. I would like to raise the question as to whether or not it might be helpful to have site-specific environmental requirements for the first plants.

Dr. Grey: That really would be difficult. In fact, I think that the general direction has been the other way. I know the Carter administration is looking as much as possible for standardization of nuclear components and even complete plants. It seems to me that we are going the wrong way when we look for site-specific requirements. It might be a good idea, but I see endless litigation going on for every site that is selected.

Mr. Ecklund: I am not talking about the long run but about the first plants. I have talked to consultants to the industry, and their general comment is that it is impossible to build a plant of any type in the Rocky Mountain area without violating the existing laws. How do you handle that problem? That is really the reason I raise the question. Is it possible to go about it by limiting certain emissions on a one-time-only basis for the first plants in order to get the information that we really need?

Dr. Grey: There is one final question that I would like to ask the Panel before we ask for questions from the floor. We have been talking research and research activities for two days. From a policy viewpoint, what are the research areas that are most important to accelerate the utilization of alternative fuels?

Mr. Ecklund: Our policy is that we are going to produce fuels from new resources and that this is going to be a magic answer. I think that is wrong. We have to get the other half

of the program into our policy. What are we going to do with those products, once they come from a processing plant, to get them into a combustor? Until we get some sort of a program and a balanced policy that takes into account all aspects of the problem the rest of it, in a sense, is academic. Our management people do not understand what the problem is. This understanding may be a long time in coming so, as researchers, we need to continue to do the things that we think are essential. The technological community must move ahead rapidly with its work in the R&D area because the longer we lack a policy, the more important it is that the technological community move ahead at a faster speed. We are being robbed of the time that we need to do things in a systematic manner and will have to make up for that with a lot of extra effort.

Dr. Grey: Mr. Wallace, can you suggest any specific things that the research community might be doing that would be helpful?

Dr. Wallace: I agree with Mr. Ecklund. I think that there are still many questions, at least in the minds of the Committee members, as to exactly what fuels will be used, and whether or not they actually will be useful. In regard to alcohol fuels, there are still some problems with transportation, mixing, and storage. As I said earlier, one thing that I think really needs to be done, from a legislative and policy making standpoint, is to look at fossil fuel combustion and its impact on the environment, determine what the impact is, and what it is that we need to protect ourselves from. There has been a lot of controversy in our own Committee in trying to delineate that.

Dr. Grey: There is another area that no one has mentioned yet. There is going to be competition for various cuts of some of the fuels. For example, jet and diesel fuel come from the same general cut. If we implement increased utilization of diesels, we may have a conflict with the demand for jet fuel. The question of logistics is also important. If we go to nontraditional fuels, the question of transmission capability, pumping stations, distribution, and so on, becomes an area that we have only barely touched on. Everyone knows distributing liquid hydrogen is a problem, but there may be problems distributing even different cuts of synthetic fuels that we do not know about yet. Mr. Weisel, is there anything that you would like to bring up on that subject?

Mr. Weisel: Our whole system is oriented toward liquid fuel technology. The existing economics are premised on a cost buildup, the cost of production of the conventional

fossil fuels. We are moving in a direction in which, instead of being cost-oriented on existing easy-to-get-at fuels, we will have to think more in terms of replacement costs. This will drive us toward some of these alternative fuels if we are to have the energy that keeps our economy going.

Other problems related to some of these fuels are handling problems. What are the properties of some of the polynuclear aromatics. I think this area will require additional research. I do think the work reported in this workshop is directed toward some of the real needs for learning how to use these less-than-good combustion quality materials.

Dr. Grey: Basically, the Panel speakers have covered three main areas: the question of price stability and price controls; environmental policies and what is needed; and finally, a brief rundown on some research topics that are important. You have heard our views. Now I would like to ask for questions or comments from the floor.

Dr. Glassman: I think that the question we face in regard to synfuels is really part of the broader question of what we are going to do with large technologies. I would like to challenge Mr. Weisel to say that, if fuel prices and all energy prices were completely deregulated and that if there were a stable price for energy on a Btu cost value, then the big oil companies would take the investment risk to develop the synfuels. If I owned their stock and they did, I would certainly sell it.

I think what is happening with regard to industry in the development of large technologies is that the technological risks have risen to a point where it is no longer prudent for sensible management investment. This is evident not only in synfuels; it is evident in the development of large gas turbines for power generation. When we consider the cost of development, the risk that the developed turbines may not be attractive to the customer, and the general competition, we can take that money and either develop video cassettes, as one of the companies chose to do, or buy an elevator company, and be much surer of a profit. I am not critical of Mobil Oil, but I think this is exactly the philosophy which motivated them to try to buy the Irvine farm. I really believe we are heading toward a sort of socialized technological development. It distresses me. What will happen is what happened in South Africa. The government had to step in and develop the synfuel plant, because it just was not prudent for private industry in South Africa to develop it. I do not know what the answer is, but I really do not believe that, if we

completely deregulate and completely guarantee a stable price, industry would develop the plants.

Mr. Weisel: You clearly have a point. One of the areas of cooperation between industry and government right now is in the pilot work that is anticipated for the production of coal liquids. This is an area in which no single company wanted to go alone on building a pilot plant. Not too long ago, it was announced that the pilot plant that will run 250 tons of coal per day is a $240 million investment. It is hoped that it will give data that will decide whether the proposition can be economically and environmentally viable. This is a joint project, however, half supported by the government and half by members of private industry. Even the Athabasca tar sands synfuel project, a $2.6 billion investment, is supported to a large degree by the Canadian government. The national government and two provinces have money in it as well. So your point is well taken.

Dr. Glassman: Then why are we asking for deregulation?

Dr. Weisel: We are asking for deregulation because syncrudes are not the only thing involved in getting energy. We have to develop the other areas as well, and these other areas also demand a lot of capital.

Dr. Ecklund: I would like to comment from an observer's point of view. ERDA has a philosophy that as we get closer to commercialization we get more cost-sharing by industry. We have a lot of cost-sharing projects going on, mostly pilot or demonstration plants. The way most of these projects are structured is that all the government money is up front and all the industry money is at the back. So far, we have not gotten any project beyond the government money.

Dr. Fristrom: To reinforce Dr. Glassman's point, I would make the point that historically this has always been the case. Now the economy is one or two orders of magnitude larger than it was when the real innovations were brought in. The real innovations were always brought in on a shoestring and not by the large establishment. Anything that is established is in the hands of a management that is conservative. This is by definition, because if management was not conservative, the system would be destroyed. If we want innovation, we cannot expect it from an industry that is so ponderous that it outweighs most nations. I am not sure that the government does such a good job either. If you look at the Soviet Union, which has been trying to do this with complete government control, they are not doing so well either. I think what we

need is a third gadfly. We have a real role to play in that we have two behemoths on either side, both of whom are terribly conservative and do not understand science. Unless we as scientists and citizens do something, I do not think things will get done.

Dr. Kendall: There is one group that is really not too well represented on the Panel. That is the military, which has a very substantial interest, as the Germans demonstrated in World War II, in the availability of alternative fuels. There has been a suggestion, at least from one part of the Navy, that perhaps it could provide an incentive in terms of an established market price at which it would purchase fuels generated during some period in the future. Is there anyone from DFSC, for example, who could speak to the issue?

Dr. Grey: I think this was a part of the GAO report. In fact, GAO recommended this as a major policy, not just for the Navy. It is a method for generating a stable price. In effect, this method would finance synthetic fuel plants by having the Federal government go out and obtain bids from the various companies on their future requirements for the whole Federal establishment. That would help to stabilize the price. Mr. Wallace, whatever happened to that? Do you think that is a viable price support mechanism?

Mr. Wallace: I think the main impetus in the Congress has been thrown behind the approach of loan guarantees, but you bring up a very interesting point. We have examined those possibilities, not only for the Navy, but for fertilizer manufacturers who are running out of natural gas. National security has always been a good justification for practically anything. In South Africa, the plant was built partly for national security reasons. In Germany, those plants were built almost entirely for national security reasons. Our laser fusion research at present is justified almost entirely for national security reasons.

As far as we are concerned, it is now up to the Administration as to how it wants to proceed in the development of alternative fuels. This is very viable. There are many attractive options with this, because not only the fertilizers and the manufacturers in the Navy are interested, but also chemical manufacturers are running out of feed stocks. They might be very interested in utilizing coal liquids. They can run the high cost into the product price and not see a dramatic effect.

Dr. Grey: I would like to raise just two more points that we really have not covered yet. We can leave at least one of these as a charge to Dr. Bowman's Panel.

The first question is whether or not the allocation of our remaining petroleum resources should be assigned preferentially to those sectors of the economy which need it most. Who is to decide how that fuel gets allocated? For example, the aviation industry has often said that its very expensive machinery requires a certain narrow cut of petroleum fuels. Aircraft engines run at variable speeds, variable thrusts, and variable conditions, whereas stationary power plants,which run at 3600 or 1800 RPM all the time, can use slightly wider cuts without difficulty after only a single modification. Now, who is to determine how these policies are set? Obviously the aircraft industry has views. So does the stationary powerplant industry, the automotive industry, and so on. The same dichotomy appears within the Congressional and the Administration structures. This is a point that we do not have time to discuss.

The second point is very important for this group in particular to look at. How do we get from the fundamental or basic research studies that are done to those who must implement a system? How do we get from those who do heat transfer research to those who build air conditioners? There is a gap which I feel has not really been satisfied. I am talking about applied research. How do you get from the basic research into the development process in a consistent way? The project manager will do only the applied research he needs to manufacture his project or to build his piece of hardware. He has to brush aside anything he finds along the way, because he did not budget for it. Who is the one who groups together 6 or 10, or 15 or 30, similar projects and who has an applied research program going to feed basic research of the same kind to all of them? I think it is really the kind of a thing that the Technical Summary Panel ought to discuss.

With that, I would like to thank the Panel. I did not give you a chance for a closing statement because I made it myself.

PANEL DISCUSSION

ALTERNATIVE FUELS TECHNOLOGY

Moderator: Dr. Craig T. Bowman, Associate Professor
Mechanical Engineering Department
Stanford University

Panelists: Dr. Hartwell F. Calcote, President
AeroChem Research Laboratories

Dr. Raymond B. Edelman, Manager
Science Applications, Inc.

Dr. Irvin Glassman, Professor
Department of Aerospace and Mechanical Sciences
Princeton University

Mr. Stanley A. Mosier, Program Manager
Technology and Research Department
Pratt and Whitney Aircraft

Dr. Bowman: This Panel will discuss research needs in the areas of combustion and chemical kinetics of alternative fuels. There will be brief presentations by each of the Panel members, followed by comments from workshop participants. The objective of this discussion is to obtain recommendations for specific research needs.

Combustion and chemical kinetics, when related to alternative fuels, are largely those same processes that occur when burning regular fuels. We do not want to redefine a general overall combustion research program. It is necessary to limit the scope of our considerations insofar as possible. We want to deal with those combustion and chemical kinetics problems which are the consequence of the special physical and chemical characteristics of alternative fuels, as we now understand them, with perhaps a certain emphasis on the use of these fuels in the transportation sector.

A comment was made earlier that we may be premature in holding a workshop on combustion of alternative fuels, since

we do not really know the fuel properties, but I think that now is an appropriate time to start to lay out a coherent and comprehensive research program in the area of combustion of alternative fuels. At the very least, consideration of the combustion and chemical kinetic problems associated with burning these fuels might help in the specification of the physical properties of these fuels.

Dr. Glassman: First of all, I believe there is a gap in the conceptual thinking of what research really contributes to the development of practical devices. I think, in general, the developer brings up a conceptual idea and then goes and develops it. He never expects to get a complete analytical model from which to build a plant and have it work efficiently.

When I occasionally taught the rocket course at Princeton, I would tell students never to try to design a rocket after they finished the course because it probably would not work. However, I would expect them to have the basic fundamental insight to be one of the most astute persons to tackle and solve a development problem, should one arise.

I think that it is in this basic context that the particular fraternity that I see here will contribute. What we must seek to achieve, and be astute at, is picking the research problems that will assist in the development of the actual device in solving particular problems when they occur.

I agree with the earlier statement that we can burn any fuel efficiently. The problems with alternative fuels really revolve around the emissions, and the chemical kineticist must play a very strong role there. Even when dealing with military aircraft, emissions are the problem, simply because it is more than likely that one of the emission characteristics will be high sooting. Thus, combustor cans can burn out, and plume visibility may be a problem. So it is not just an environmental question, but an emission problem introduces actual operating problems. Indeed, saying that we can burn fuel efficiently means that we can have a beautiful alternative fuel in the crude itself. We could save an automatic 12% if the economics of our oil distribution system would permit it.

That is enough philosophy. Let me get down to what I think are the specific problems that we should undertake as a research community contributing in the vein that I have just expounded. I still insist that one of the major conclusions of the Princeton workshop holds. There is simply a lack of

fundamental data in many different areas, e.g., kinetics and flame speed. Recently, the combustion community has been emphasizing research on applied problems and has forgotten that it is not building a firm data base. That lack eventually will be felt.

To be specific on another point, it is obvious that there will be high aromatic content fuels. Indeed, the absolute importance of the pyrolysis and oxidation of aromatics and how these contribute to soot formation is obvious. At first, we simply have to know the mechanisms. We are not ready to try to measure actual rates. We simply have to do the experiments which will tell us explicitly what the mechanisms are. There are some very interesting things that happen. When we burn an aromatic hydrocarbon very rich, then the CO_2-to-CO ratio is much more than we expect — we get more CO_2 than expected. Maybe this fact also contributes to the sooting problem because we rob the oxygen for the oxidation of the other elements which are present. This mechanistic analysis is just to give an idea of how a fundamental concept can lead to an overall mechanism. I think we have overlooked sulfur oxidation mechanisms. In a recent review of the sulfur oxidation literature, I was surprised to find that the fraternity switched so strongly to nitrogen-oxygen kinetics and completely left some of the early beautiful work that was beginning to originate in sulfur oxidation.

Another area that has been overlooked at this particular meeting is heterogeneous catalysis. The whole area of surface chemistry just must be exploited. We do not know what we can do with regard to reducing emissions. We also do not know very much about the reduction processes of nitrogen or sulfur oxides or how we can handle them. If we did understand more about surface chemistry and how catalysis really works, instead of thinking of it as a magic art, we would make a significant contribution.

We would like to have more kinetic data for hydroperoxyl reactions and specific rates on hydroperoxyl attacks so that we can supply kinetic data to the people who are doing the modeling. We have overlooked the basic phenomenon of quenching kinetics, that is, the heterogeneous/homogeneous processes that occur in a boundary layer close to the wall. Again, I think this can be evolved as a pure chemical homogeneous rate, but it is very obvious that certain heterogeneous processes must again play a role. Again, this idea of surface chemistry arises.

I believe that we are spending too much effort in finding out how fuel nitrogen goes to NO. I believe that staging

combustion processes and the stratified combustion process will never reduce the fuel nitrogen produced to the NO levels that we want. We tend to forget that we are still way above the equilibrium value, which is too high as far as emissions regulations are concerned. If I were going to work in this field, I would study the NO reduction process. I think that the rate data and the mechanisms of the NO reduction process are more important than how the NO forms. We saw from Haynes' work that we have a pretty good idea of how NO forms. We know the rates are fast. That is all we really need to know if we are going to attack a specific problem. It would be well to place most of the emphasis on a study of the destruction of NO or reduction of NO.

Dr. Calcote: Before I identify the three major research areas that should be pursued because of the new fuels that we are going to have to use, I have a couple of general comments. The first is that at all of these workshops the kineticists spend a lot of time apologizing for studying chemical kinetics. It seems to me that we should stop apologizing and take the offensive. Let us get down to the business of defining what kinetics needs to be studied.

The second thing that I would like to point out arises from the number of workshops that we have had. There is a real need for a U.S. combustion program—a real program in combustion with mileposts and with practical objectives at given times. One reason we need such a program is to obtain adequate funding. One reason there is so little funding in the combustion community is that no such program exists. The lack of support for combustion research has been commented on several times during this workshop. Now this is simply a criticism, and one should not make a criticism without a suggestion. So I have a suggested mechanism by which I think we could develop a realistic program. It would be as follows. We would get together six or ten people, not more than ten, representing the development, research, and user communities. We would ask them to meet for a week or two and develop a long-range program with mileposts and objectives — something that Congress and the public can understand. They would then present this program to a workshop or a group such as we have here and thus obtain the important input of the combustion community. Armed with such a program, the various government agencies involved with combustion should be able to persuade Congress to provide adequate funding for combustion research.

So much for politics. I am going to make two assumptions when I make my recommendations. The first assumption is that there will be a continuous development and application of

theoretical models of both the global type and the detailed type. By this means we will apply the new data that should be developed in chemical kinetics to new real practical systems as they become available. This is important.

The second assumption is that there will be a continual feedback from the engine community to the research community not only on what the engine needs are today, but what the engine manufacturers think their needs will be five and ten years hence. It is too late to do research when you know what the research needs are. You have to know what the research needs are five and ten years hence. So the engine community will have to let us know what they are thinking about and what the possible engines will be five or ten years hence so that we can have the data available when they need them.

Now for my recommendations for three specific areas of research. The theme of several presentations and comments was the mechanism of soot formation. I think we include in that the mechanism of formation of polycyclic aromatic hydrocarbons. These mechanisms should be studied under the real temperature and real pressure conditions that are going to exist in engines. The mechanisms should be studied not only in the gas phase but in the liquid phase as well — e.g., in liquid droplets.

I make the point that it is not important in what system one studies the chemistry of carbon formation or soot formation. We can study this in a laminar flame, in a turbulent flame, in a stirred reactor, or in a flow system. The important thing is that the mechanism be studied under the conditions that will occur in an engine. All that chemistry knows is the local temperature, pressure, and composition. This assumes, of course, that someone will be working on the very important interaction of turbulent combustion and chemistry. If we understood that interaction, and we understand the chemistry, then we would know what happens in a real system.

I would stress that one ought to study carbon formation in three steps: nucleation, growth, and agglomeration. We need more emphasis now on nucleation. It has been a difficult problem to study. New tools are available, and we should be putting emphasis there, but we should not stop studying growth and agglomeration. I include in the mechanism of soot formation the mechanism of oxidation of soot, because the amount of soot we get out of an engine is a balance between production and oxidation.

The second area where I would argue for chemical kinetics studies would be in the oxidation and pyrolysis of aromatics,

particularly aromatics including nitrogen and sulfur in the molecule. This should include chemistry in the liquid phase as well as in the gas phase, but again it should be done at temperatures and pressures that are realistic for storage of the new fuels, injection of the new fuels, and combustion. Particular attention should be paid to NO_x and SO_x formation mechanisms.

The third area was not mentioned at all in this workshop; that is, we need basic information on the combustion of lean mixtures. In some of the previous symposia and workshops, this area came out very strongly. We need such simple information as minimum ignition energies, auto-ignition temperatures, laminar burning velocities, and flammability limits at engine conditions. I would point out that in the past people who studied flammability limits generally studied them at 1 atm and below. There are a few studies above 1 atm which indicate that some strange things happen at the flammability limit when 1 atm is exceeded — e.g., in an engine.

Dr. Edelman: I want to start by emphasizing the importance of mechanisms other than chemical kinetics. For example, to maintain a balanced perspective in the approach and resolution to questions related to the impact of burning alternative fuels in current and future combustion systems, aerodynamic effects and the processes of spray formation and disposition also need to be addressed.

During this workshop we have seen and heard evidence supporting the contention that broadening of fuel specifications will be necessary for energy and cost-effective production of fuels from sources including coal and shale. These fuels will have significantly different chemical and physical properties compared with the more conventional hydrocarbons with which we are accustomed to dealing. For example, significantly higher viscosities, higher surface tensions, lower hydrogen/carbon ratios, and the higher content of aromatics are known to affect the physical and chemical aspects of the combustion process. Since the current state-of-the-art in combustion system design has evolved mainly from empirical methods, fuel properties effects, per se, cannot be clearly distinguished from the geometric and aerodynamic features of the combustion chamber.

To develop an adequate understanding of fuels effects on combustion, coupling of the chemical and physical mechanisms must be taken into account. Flow patterns and fuel distributions depend on the heat release distribution as does the converse. Turbulence represents a dominant mechanism in this

cross coupling between the flow and chemical processes. The importance of turbulence is associated with the sensitivity of the fuel consumption processes to fluctuations in velocity, temperature, and species concentrations. The degree of completeness of combustion and the formation of soot, which is an area of considerable concern with alternative fuels, constitute problems complicated by the coupling of turbulence and chemical kinetics. It seems evident to me that meaningful research programs must involve more closely integrated elements of fluid dynamics and chemistry. Many research-oriented studies ostensibly designed to isolate chemical effects have turned out to be influenced by aerodynamic effects. This accounts, at least in part, for the lack of agreement between the results developed by different investigators.

The complexity of the problem with alternative fuels becomes even more acute with liquid injection. Spray formation and the control of the liquid fuel distribution has been an integral part of overall empirical design methodologies. The higher viscosities and surface tensions and lower volativity of alternative fuels will change the relative importance of the ballistic and turbulent transport of the droplets in the spray through their effect upon droplet size distributions. This requires a better quantitative understanding than we now have of primary atomization and secondary shattering of droplets in a turbulent flow. The multiphase flow problem is further compounded by the potential increase in soot formation. Particle growth through collisions and agglomeration may be a significant mechanism to include in understanding the fate of soot particles formed with the use of alternative fuels. These processes require a more precise definition of the intensity and scale of the turbulence.

In general, I would summarize our requirements for research by emphasizing the need for integrated programs within which studies are made in environments which are controlled and yet representative of those encountered in current and future combustors. Specific research efforts should include the investigation of turbulent flames in configurations which allow a systematic progression in complexity starting with premixed/prevaporized systems through diffusion flames with direct liquid injection. Stirred reactor technology should be exploited for the characterization of the behavior of recirculation zones with intense backmixing. Plug flow reactors and shock tubes should be used for aspects of the problem for which isolation of specific mechanisms can best be achieved through their use.

Diagnostics should be directed toward time-resolved measurements whereas the conventional methods should be more

fully exploited. Obviously, measurements should include all properties, but techniques involving measurements and analysis of residence time distributions should be developed as a means of inferring the degree of completeness of mixing, particularly in multiphase systems.

Modeling should proceed as an integral part of the research, and the use of the models should include inverting techniques to allow direct computation of rates, etc., from measurements of the primitive variables.

Finally, although I have suggested that existing technology is lacking, there is nevertheless a substantial body of knowledge which can be brought to bear on the current questions related to alternative fuels combustion.

Mr. Mosier: After listening to the comments of the preceding speakers, all that I should really say is "me too." However, I do have a few thoughts that I would like to share with you.

First, inasmuch as I am more of a developer than a kineticist, I would like to see a strong interaction emphasized between developers and researchers. Often, each charges off in his own direction with preconceived notions about the functions and responsibilities of the other. Each even speaks his own language. Progress will be made in developing alternative fuel technology when each begins to realize that he needs the other. Research or development for its own sake is far less fruitful than a judicious interaction of the two.

Second, I would like to suggest that a unified plan be developed by a joint Government-industry team to address alternative fuel technology needs. I think that currently we have disjointed, underfunded alternative fuel programs throughout the United States. These programs are being sponsored by the Navy, Army, Air Force, NASA, DOE, and others without benefit of a central theme or of unified priorities. These types of activities often end up being technology races rather than activities to maximize technology output for minimum funding. These diffuse efforts need to be unified and priorities established. I do not know who is going to do this; I have no specific plan to recommend. Perhaps a committee such as the one that Dr. Calcote suggested, a national combustion committee, might be the guiding force. I would recommend, however, that the Government and industry be equally represented in the membership of the committee. All-government groups lack the understanding of industrial driving forces and needs; all-industry groups lack the Govern-

ment's capacity to acquire risk capital. Both groups are needed.

Finally, I would like to suggest that the members of the policy panel talk to the engineering and scientific talent at these important technical meetings. Perhaps their approach to many of our problems might be tempered with more realism than I heard from their prepared statements.

Now, to more specific comments. When we try to identify the technology that might be needed in order to accommodate alternative fuels and engines, we must first consider fuel specifications. Specifications are simply compromises between suppliers and users that are normalized by economic factors relating to supply and demand. This does not mean that I would go along with regulation. A question that came up earlier was: What are the priorities regarding fuel allocation? I think we should let the marketplace handle the allocation problem through cost. This approach will work out well if regulators will simply let it happen.

Under ideal circumstances, the user can impose rigorous requirements on a supplier to provide a high-quality product at a reasonable price in nonrestricted quantities. This has been the situation in the past. However, circumstances are changing rapidly. Fuel vendors are currently supplying fuels at the outer limits of the specifications. Some vendors have refused to supply fuel to well-established military specifications. They simply refuse to bid on fuel solicitations. We are beginning to observe subtle differences in the operating characteristics of gas turbine engines. Why? Because we design these devices to operate on Utopian fluids. When specifications were allowed to float a little, the hardware responded accordingly.

However, as we enter the alternative fuel era, we must prepare to accommodate continually changing fuel specifications. I do not believe that the civilian and military sectors will be able to continue obtaining the high-quality fuels of today. Fuel vendors will not be amenable to pulling out the best part of a barrel of petroleum for JP5 or JP8 when they could convert this crude to a more profitable, higher yield of wide-specification fuel. We must now develop the technology to be incorporated into our design systems so that we can provide nonrestrictive engines.

One area of investigation that needs to be embarked upon immediately is the determination of short-term and long-term thermal and oxidative stability characteristics of candidate

alternative fuels. I think we know enough about what we might expect as far as the aromatic, olefinic, and paraffinic content of the fuels might be. I think we must synthesize some ersatz-type mixtures now and begin looking at the thermal stability characteristics of these fluids. By properly designing the thermal stability experiments, we should be able to acquire both fundamental and applied data that can be used to develop design systems. The practicing kineticists should work on this problem.

In conclusion, we need to commence on a serious, domestic alternative fuel technology program ... now. We must determine how to design to use the "fuels of the future." A concerted effort among kineticists and practitioners guided by a Government-industry plan that is adequately funded is certainly a candidate approach to acquire the needed technology.

Dr. Bowman: I would like to thank the panel members for their comments, and I would now like to solicit comments from the floor.

Dr. Wolfson: An interesting point was brought up that we really did not cover sufficiently. That pertains to the fuel characteristics as they are involved with the actual engine system—in other words, liner degradation, carburization, and metallurgical effects. I think we should consider that we need researchers in addition to fluid dynamicists and combustion dynamicists. We need specialists in metallurgy and materials.

What I think we should do is to look at the entire system. Now I am not talking about coupling between turbulence and kinetics. I am talking about overall system utilization of practical systems. It is very important when looking at fuel characteristics to look not only at stability but also at corrosion effects and the interaction of these various trace elements within the shale oil fuels or the newer types of fuels. These trace elements can cause tremendous damage by their own influences. Arsenic and ammonia types of compounds can just tear apart a copper system and other systems.

Mr. Gallopoulos: First of all, I must say that this is a very comprehensive and very realistic list of research topics. Some of the same things appear in my paper. I say this because I think it answers the request for the engine designer to tell the kineticist what should be done in the future.

To reinforce another comment that was made, I want to add that many of these research projects should be done under realistic conditions for the engines in which these fuels will be utilized — realistic in terms of pressures, temperatures, and so on.

I have just a few more specific things that pertain to the research topics discussed. In the case of nitrogen compounds in alternative fuels, one of the areas of heterogeneous catalysis involves the refining of these fuels. This is another area in which work should be done because the catalysts that are used in refineries are not resistant to nitrogen compounds, and they must be removed prior to some of the refining steps.

Another item discussed is the interaction of nitrogen compounds with materials in engines, and the stability of the fuels containing these nitrogen compounds or sulfur compounds for that matter. One of the areas that can be investigated is the utilization of additives to improve the stability of the fuels and reduce the reactivity of the nitrogen compounds or sulfur compounds towards various materials in engines and fuel systems.

Finally, also in the area of additives, when investigating mechanisms of soot formation, the possibility of devising additives to eliminate or reduce the formation of soot should not be overlooked. In the area of soot formation, there is one more thing. We must change not only the size distribution of soot particles, but we must reduce the total mass of soot. Also, if we change the size distribution of soot particles, let us make sure we do not make it worse than it is because health effects are related to the size of particles present.

Dr. Glassman: I agree that one should carry out experiments under realistic conditions, but let us realize that when we know fundamentally that something is not a function of pressure, we should not go to 40 atm. If it is argued that maybe there will be another effect found that will not even be thought of, let the developer find it, not the researcher.

In regard to the soot question, I feel that, if we are going to be successful in controlling particulates in power plants, then the approach is not going to be to burn off the soot, but to prevent its formation. That is why I said I am more interested in what happens and what we can do about the precursor formation and the nucleation formation than I am about the agglomeration.

Dr. Gevantman: I would like to reinforce the comment made by Dr. Glassman for a firm data base. I do not want to be in the position of lecturing this group, because I am sure they all realize it, but lots of times when we say that we need more information on this,that,and the other thing, and we consider that to be firm data, it does not appear ultimately in one common source that everybody can use and use with reliance.

Dr. Howard: I would like to respond to Dr. Glassman's comment about soot burnout vs soot formation. I believe both of these topics to be important and would like to encourage work on burnout as well as formation. Until we know how completely to prevent formation, the burnout problem of course will be with us. We will have soot being formed as long as we use diffusion flames, but this does not mean that soot emission is unavoidable in these cases, thanks to burnout.

Another point pertains to the comment that has come up often here, namely, that we can burn any fuel. The statement is true, but it implies going to a substantial effort in some cases. We also can make any fuel, starting with coal or oil shale, but again the effort and expense are large in some cases. The combustion community would like the coal conversion people to project what kind of fuels are going to be made so that the combustion problems to be faced can be better defined. At the same time, the fuel conversion people are wishing that the combustion community would specify what kind of fuels can be burned so that boundary conditions can be established for the conversion processes. There is clearly an opportunity for cross fertilization between these two communities, especially at the research and development level. For example, as Dr. Longwell has pointed out, improved knowledge of how to burn cleanly the highly aromatic fuels which are easily made from coal would relax substantially the constraints imposed on the conversion process. A similar statement can be made about improved knowledge on the conversion side. Since the molecules being produced in conversion are the ones to be burned later, there is obviously common ground between the two communities that should be explored for optimization opportunities.

Dr. Golden: I agree with what has been said about measuring things under "realistic conditions." I want to reiterate that there are certain areas in which we understand why extrapolation works, and it does not make sense to conduct experiments under "realistic conditions."

Of the topics discussed, I see two different kinds of research. I do not want to use terms that are pejorative and

call one fundamental and one applied, but there is a different level. When we talk about looking at reactions involving HO_2 radicals, we are talking about one kind of research. When we talk about thermal oxidative stability of a specific fuel, we are talking about something else. I think it might be helpful to find the right words and break these down. I am not arguing that there is not a need for both of them, but I think we really are talking about two different levels here.

Dr. Lefebvre: Chemistry is not all that important in practical combustion systems. For example, we have all heard hundreds of papers on the chemistry of nitric oxide formation. Yet, for all practical purposes, all we have to do to minimize NO_x is to operate the combustor at a low and uniform flame temperature.

We have problems of carbon monoxide and hydrocarbon emissions. To avoid these, we need to keep the flame temperature high. So from a practical viewpoint, the solutions to these various problems are known. Soot formation has had a lot of attention in this discussion. Again, the engine designer knows how to control problems of soot. Certainly, there are many engines flying today that produce a lot of soot in their exhaust, but that is not because the combustor designer does not know how to get rid of it. The trouble is that, if he does, he finds he has other problems, e.g., altitude relighting.

The key point I am trying to make is that the real fuel problems we face are mainly physical ones. If I may repeat what I said earlier, if we can get the fuel inside the combustor, then I believe we can burn it without undue difficulty. However, I am concerned about thermal stability and freezing point. On a more positive note, if studies of chemistry and reaction kinetics could lead to worthwhile fuel additives, then I think a very significant contribution would have been made. A really major contribution could come from a study of these chemical aspects.

I would certainly like to know more about the physical properties of the fuels that we are likely to encounter because this could have a radical effect on the fuel preparation process. I have heard more than one respected engine designer say that he would contemplate putting an extra-small compressor on the engine in order to provide air to assist atomization. With some of the alternative fuels, we may need to consider "air assist" in order to get them properly atomized and properly distributed.

I fully support the points that Mr. Mosier made. I was interested to learn about the rich primary zone in a staged combustor giving low NO_x. I knew this was technically feasible, but it is interesting to learn that it has been achieved. I certainly agree that more knowledge of jet mixing and jet interaction would be valuable.

Dr. Calcote touched on inflammability limits in a way that I could not understand. He said they have received extensive study at pressures below 1 atm but have not been investigated at higher pressures. Surely, the reason is that inflammability limits broaden so much at high pressures that they no longer pose any problem.

Dr. Calcote: To respond to the last comment on inflammability limits, there have been enough studies at high pressures to see that strange things do happen. For example, the percent of fuel reacted in some cases decreases as the pressure increases. The lean flammability limit actually becomes less lean on occasion when we go to higher pressures.

Dr. Bowman: I would like to respond to Professor Lefebvre's first comment regarding the importance of chemistry and reaction kinetics in gas turbines. In particular, I would like to ask him how he decided that he wanted to have low temperatures and not particularly lean zones in a gas turbine combustor to reduce NO formation. Was it because he knew the reaction mechanism and the temperature dependence of the rates of those reactions? In fact, the NO_x control technology which exists for gas turbine engines, both for atmospheric nitrogen and for fuel nitrogen, is derived almost exclusively from qualitative and quantitative information provided by kineticists.

Dr. Edelman: I would like to make a further comment regarding the utility of modeling. There are many values of modeling, and one very important application is that of scaling. Furthermore, modeling represents an unambiguous way of documenting what we have learned so that others can use it in the future.

Dr. Longwell: I have one specific and one rather general comment. I would like to see studies of the atomization process included on the list of research needs. Professor Lefebvre has mentioned the virtues of air-blast atomization a number of times. We might wonder why everybody does not use it. Actually, it is very wasteful of energy. It requires extra equipment, and people generally are very reluctant to install it. Its virtue is that it gives good atomization,

regardless of flow rate, and is more or less independent of fuel properties, if one is willing to supply compressed air over the total operating range. There must be a better way. I think it is a real research challenge. The normal pressure atomizers worked well over a limited range, but they can cause trouble for start-up and relight. Also, they put limits on fuel viscosity. So there is room for improvement, both on the theoretical and on the practical side.

My more general comment is that some of us have been working hard on reoptimizing the aviation fuel specification vs the equipment. It is an extremely complex optimization. We ask what it is that we really need to do in an optimization program. We need to have a good understanding of what the trade-offs are on fuel manufacture, costs, etc., and what the various trade-offs are in the engine design and operations. To do that in any kind of a compact way, I think we need the sort of models that can be practically used on both to solve an optimization problem.

Now this is not necessarily what is called modeling by someone who has the world's biggest computer and wants to see if he can solve the Navier-Stokes equations. What it means is setting up models to serve a number of purposes. One purpose is to give a mechanism for introducing basic information into this optimization procedure. The Zeldovich chemistry is probably the best example of that.

From the chemistry side, I believe that we could carry the quasi-global approach a lot further. We can make use of fundamental elementary reactions as far as possible, which will not be very far in some cases, such as soot formation, and then do a really good job on the quasi-global side. I think this whole activity perhaps could be formalized a little more. It is hard to compare one approach with the other.

Dr. Lavoie: I would like to speak about the reciprocating engine, which has not received as much attention as gas turbines. Perhaps that is because the reciprocating engine works so well. Nevertheless there are some fundamental chemistry problems. In particular, there is the quench layer problem, and there are problems with regard to both the quantity of hydrocarbons that end up in the quench layer and also the type of hydrocarbon. As a practical example, methane is not considered to be a reactive hydrocarbon in the atmosphere, yet it is measured as a pollutant for the purposes of E.P.A. standards. If this legislation is changed, it could have a significant effect on automotive control strategies. The introduction of alternate fuels could further complicate

the issue. For this reason the quench layer and the associated low-temperature oxidation processes are important areas of research for the conventional automotive engine.

Dr. Kesten: I have one general comment and then a specific one. We do tend to get a little sophomoric in justifying chemical kinetics or mathematical modeling. I think it is obvious to most of us, if not all of us, that there is virtue in both of those things. I do not think we really need to spend time justifying either.

There was a comment by Dr. Golden on the difference in the nature of the programs that we have discussed. Some of the programs are fundamental chemical kinetic type programs. Others involve many coupled phenomena. I wonder if we might explore this coupling just a bit more. If we can get phenomenological insight out of coupled phenomena, it may well be wise to study the phenomena as coupled. For example, if we find that soot formation around clouds of burning droplets which contain bound nitrogen is a strong function of the interaction between nitrogen chemistry and particulate formation, we really should study the coupled phenomena. We should do these types of experiments although they are often complicated ones to define and to perform. If we always have to simplify in order to get phenomenological insight, and if we have to simplify to the point where we define the fundamental chemistry program or the fundamental physics program, we often lose the coupling. Sometimes we suffer by that loss; that is, by not doing the coupled program, we may well not gain the results or the insight we are looking for.

So we often have the question of whether to go to realistic conditions and then produce such a complicated experiment that we do not know what we are studying or to go to the fundamental experiment where we get clear information which may not be useful. The middle ground is a gray area that is often the critical regime to be studying and the one that is difficult to define.

Dr. Sarofim: I would like to reinforce what Dr. Kesten and Dr. Longwell have said. We have heard about the necessity for system integration and the need for tying fuels with combustion. If we are going to control NO_x and soot formation, there are interactions; the SO_2 and NO_x chemistry interact. In soot formation and oxidation, the type of soot that is formed determines the oxidation kinetics, and shock-tube studies sometimes are not pertinent. I would like to see some recognition of the fact that, if the practical design is going

to use fundamental information, then there has to be a model framework which will accept the fundamental data.

Dr. Lefebvre: I was pleased to hear Dr. Longwell speak in support of research on atomization because I believe this is a key area in the problem we are discussing. I would add to atomization the processes of vaporization and of fuel preparation generally.

I would like to clarify one point of terminology. An airblast atomizer does not require additional energy because it uses high-velocity air that is available anyway. If a hole is drilled anywhere in a liner, the air will rush through that hole at about 100 m/s. This will give very good atomization.

What I had been talking about earlier was the "air assist" atomizer. If better atomization is needed than is obtainable with air flowing at 100 m/s, then there is a demand for an external supply of air, which imposes a penalty on performance, as Dr. Longwell indicated.

Dr. Wolfson: One thing that we have missed is the instrumentation diagnostics necessary to look at these phenomena. That is one area that must be pushed with great speed, not only for this particular one but for other areas. What I am talking about is sophisticated instrumentation with which spatial and time resolution of these very fast phenomena in both practical systems, as well as in the laboratory situation, can be obtained.

Dr. Glassman: I would like to express great caution in that area. As I said at the Project SQUID Workshop on Combustion Diagnostics, I think we need advanced instrumentation. One of the biggest contributions that can be made is to be able to make an in situ steady-state temmperature measurement. However, I wish to express the concern that trying to solve the problem of turbulent reacting flows with the diagnostics is a problem that will not be solved until we probably have all solar energy in the United States. I just think the problem is too complex. I do not think we will be able to measure $\overline{\rho' u' T'}$. It is very difficult to make that measurement in simple heated flow, much less in a chemical reacting flow. Indeed, let us push laser diagnostics. I am using it in my own laboratory to measure velocities.

By all means, let us develop a method of measuring temperature. By all means, let us use these methods even to try to measure a time-dependent element. I think we should.

However, I am afraid of the time and money this problem will consume. Indeed, I must admit that one of the major conclusions of the Princeton workshop was to go in this direction, but my personal opinion is very different. I have seen some of the brightest minds get caught up in the turbulence problem, and they are still working on it. When we start considering a chemical reacting flow, I worry whether or not this might be a big drain on funding. I think we are jumping much too far ahead. I think it is a process that has to be built up very slowly because we still find it difficult to measure a steady-state temperature in a real system with laser diagnostics. Let us do that first, and then I will be willing to change my statements as to what we will be able to do in a time-dependent flow.

Index to Contributors to Volume 62

Bittner, James D., *Massachusetts Institute of Technology* **335**
Blazowski, William S., *Exxon Research and Engineering Company* **21**
Bracco, F.V., *Princeton University* **160**
Calcote, Hartwell F. (panelist), *Aero-Chem Research Laboratories* **445**
Dryer, Frederick L., *Princeton University* **255**
Ecklund, E. Eugene (panelist), *Energy Research and Development Administration* **425**
Edelman, Raymond B. (panelist), *Science Applications, Inc.* **445**
Gallopoulos, Nicholas E., *General Motors Research Laboratories* **74**
Glassman, Irvin, *Princeton University* **255, 445**
Golden, David M., *SRI International* **233**
Haynes, B.S., *University of New South Wales, Australia* **359**
Heap, M.P., *Energy and Environmental Research Corporation* **116**
Howard, Jack B., *Massachusetts Institute of Technology* **335**
Jordan, J.B., *The University of Leeds, England* **180**
Lefebvre, Arthur H., *Purdue University* **137**
Longwell, John P., *Massachusetts Institute of Technology* **3**
Maggitti, Lawrence, *Naval Air Propulsion Test Center* **21**
Martin, G.B., *U.S. Environmental Protection Agency* **395**
Mellor, Arthur M., *Purdue University* **137**
Mosier, Stanley (panelist), *Pratt and Whitney Aircraft* **445**
Peters, James E., *Purdue University* **137**
Sarofim, Adel F., *Massachusetts Institute of Technology* **199**
Vranos, Alexander, *United Technologies Research Center* **307**
Wallace, A. Lee (panelist), *House Committee on Science and Technology* **425**
Weisel, Charles (panelist), *Exxon International* **425**
Williams, Alan, *The University of Leeds, England* **180**

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER PU-R2-78	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Alternative Hydrocarbon Fuels: Combustion and Chemical Kinetics		5. TYPE OF REPORT & PERIOD COVERED Workshop Proceedings
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Craig T. Bowman Jorgen Birkeland		8. CONTRACT OR GRANT NUMBER(s) N00014-75-C-1143
9. PERFORMING ORGANIZATION NAME AND ADDRESS		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR-098-038
11. CONTROLLING OFFICE NAME AND ADDRESS Project SQUID Chaffee Hall, Purdue University West Lafayette, Indiana 47907		12. REPORT DATE 13. NUMBER OF PAGES 463
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) Office of Naval Research, Power Program, Code 473 Department of the Navy 800 No. Quincy St. Arlington, VA 22217		15. SECURITY CLASS. (of this report) Unclassified 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

This document has been approved for public release and sale; its distribution is unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Engine Fuels
Alternative Fuels
Hydrocarbon Fuels
Chemical Kinetics
Combustion
SQUID Workshop

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Alternate Fuels and Combustion Problems; Future Fuels in Gas Turbine Engines; Alternative Fuels for Reciprocating Internal Combustion--A Literature Review; The Use of Alternate Fuels in Stationery Combustion Sources; Ignition/Stabilization/Atomization - Alternate Fuels in Gas Turbine Combustors; Combustion & Chemical Kinetics Problems in Internal Combustion Engines; The Combustion of Droplets and Sprays of Some Alternate Fuels; Flame Emissivity - Alternate Fuels; Pyrolysis & Oxidation of Aromatic Compounds; Combustion Chemistry of Chain Hydrocarbons; Liquid Phase Reactions of Vaporizing n-Hexadecane; Soot Formation;

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-LF-014-6601

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)