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13. ABSTRACT *(Maximum 200 words)*

A research program to study the oxidation and ignition characteristics of hydrocarbon fuels and their mixtures has been conducted at Drexel University. The research focused on three major tasks: examination of the chemistry of autoignition during compression ignition processes by performing parametric studies in a variety of experimental facilities listed below; development of chemical models which can simulate the experimental results; and the development of in situ measurement techniques. Several complementary bench scale experiments, which include a static reactor, an atmospheric pressure flow reactor, and a pressurized flow reactor, were used to examine the preignition chemistry and ignition behavior of progressively larger hydrocarbons over a range of temperatures, pressures, and equivalence ratios. Gas chromatography and GC/MS were used for chemical analysis of the stable reaction intermediates and products. Fourier Transform Infrared (FTIR) spectroscopy and degenerate four-wave mixing (DFWM) spectroscopy were used in efforts to develop in situ species measurement techniques. The overall program has been successfully completed and has added to our understanding of fuel factors and physical effects on the oxidation and ignition processes of hydrocarbon fuels.

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HIGH PRESSURE PREIGNITION CHEMISTRY OF HYDROCARBONS AND HYDROCARBON MIXTURES

FINAL REPORT

N.P. CERNANSKY, D.L. MILLER, AND D.N. KOERT

24 FEBRUARY 1993

U.S. ARMY RESEARCH OFFICE

ARO GRANT NO. DAAL03-90-G-0024
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ABSTRACT

A research program to study the oxidation and ignition characteristics of hydrocarbon fuels and their mixtures has been conducted at Drexel University. The program started in January 1990 with the awarding of a research grant through the Army Research Office (Grant No. DAAL 03-90-G-0024, Project No. 27417-EG) and was completed in December 1992. This project has its origins in a program which began in October 1985 with the initial award of a research grant through the Army Research Office (Grant No. DAAG 29-85-K-0253, Project No. 22437-EG). The research program entailed mechanistic studies examining the oxidation chemistry of single-component hydrocarbons and ignition studies examining the overall ignition behavior of pure single-component fuels and fuel blends. Three complementary bench scale experiments, which include a static reactor, an atmospheric pressure flow reactor, and a pressurized flow reactor, were used to examine the preignition chemistry and ignition behavior of progressively larger hydrocarbons over a range of temperatures, pressures, and equivalence ratios. Gas chromatography and GC/MS were used for chemical analysis of the stable reaction intermediates and products. Fourier Transform Infrared (FTIR) spectroscopy and degenerate four-wave mixing (DFWM) spectroscopy were used in efforts to develop in situ species measurement techniques.

Specifically, the objectives defined for this study were to:

1. Obtain kinetic information in the low and intermediate temperature ranges (600-1000 K) over a range of pressures (up to 20 atm) which will be useful to understand the oxidation of pure hydrocarbons with carbon numbers in the C_6 to C_{12} range;

2. Determine the synergistic and antagonistic effects for binary and ternary mixtures of full boiling range fuel components; and

3. Develop a method for predicting the ignition characteristics of actual fuels based on their composition.

Efforts in this research program have focused on three major tasks: examination of the chemistry of autoignition during compression ignition processes by performing parametric studies in the experimental facilities described above; development of chemical models which can simulate the experimental results; and the development of in situ measurement techniques. The overall program has been successfully completed and has added to our understanding of fuel factors and physical effects on the oxidation and ignition processes of hydrocarbon fuels.

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I. INTRODUCTION

A. Motivation

Federal agencies whose goal is to provide improvements in mobility and transportation face two closely associated combustion related problems over the next decade. The first, deteriorating and variable quality of fuels, was identified in the 80's (AGARD, 1982) and was highlighted during the recent military efforts in the Middle East. The second is the difficulty with balancing increased improvements in engine efficiency with the need for reduced engine emissions. To resolve these problems requires an effort to understand the transport and chemical phenomenon which occur as a fuel reacts in a combustion chamber. Transport phenomena establish the initial reaction environment; while chemical phenomena provides the heat release that initiates and/or sustains the reaction and converts the potential energy of the fuel into thermal energy and the ultimate products (Edwards et al., 1992). The need to understand both has been demonstrated in recent attempts to model in-cylinder combustion processes (Gonzalez et al., 1991; Kong et al., 1992; Henein et al., 1992; Griffiths et al., 1992). A primary facet of both the fuel quality and emissions problems is to determine what conditions are necessary to achieve reliable ignition of the fuel. Difficulties with ignition are responsible for several engine problems, notably: knock in spark ignition engines, and misfire and cold start in diesel engines. Henein (1976, 1992) highlighted the importance of the chemistry by demonstrating that the chemical processes are rate controlling during the delay period in diesel ignition. High emissions are also produced during the initial start-up of a combustion engine (Kamimoto and Kobayashi, 1991).

The compression ignition process is complex and involves preignition reactions which lead up to the point of autoignition. This is the point at which energy is liberated at a sufficient rate to sustain combustion in the absence of an external energy source, and is characterized by rapid rates of pressure and temperature rise. The tendency of a fuel to autoignite is directly related to the manner in which it undergoes oxidation and is determined by its chemical structure. In order to gain insight into the autoignition characteristics of hydrocarbon fuels, it is necessary to understand the chemistry of oxidation, especially the reactions that occur prior to autoignition. The oxidation chemistry determines the heat release rate, the reaction intermediates, and the ultimate products of combustion. The large number of concurrent and competing chemical reactions which involve a correspondingly large number of chemical intermediate species results in a very complex mechanism for the oxidation chemistry. This is the case even for small, single component fuels such as methane, and becomes exponentially more complex as the size of the fuel molecule increases. Consequently, attempting to understand the detailed chemistry of distillate fuels, which are multicomponent blends of a variety of relatively high molecular weight hydrocarbons, from direct studies of the complex fuels has proven to be untractable.

An approach which can be successful for both the prediction of ignition quality and the assessment of ignition chemistry involves testing simple two and three component fuel blends in laboratory scale chemical reactors. With this approach, the physical factors influencing the ignition process can be controlled much more carefully than in an engine, and ignition quality can be evaluated solely in terms of the chemical effects of the fuel components on ignition process. Single fuel components representing the different classes of hydrocarbons within a distillate fuel, such as alkanes, alkenes, and aromatics, can be blended at different ratios and tested in order to develop an understanding of how the different classes of hydrocarbons interact and which control the ignition behavior. Such studies can lead to the development of a method for predicting the ignition behavior of fuels, without extensive engine testing, based on knowledge of their composition. In view of this, a research program to study the oxidation and ignition characteristics of progressively larger hydrocarbon fuels and their mixtures has been conducted at Drexel University. The program started in January 1990 with the awarding of a research grant through the Army Research Office (Grant No. DAAL 03-90-G-0024, Project No. 27417-EG) and has its origins in a prior program which began in October 1985 with the initial award of a research grant through the Army Research Office (Grant No. DAAG 29-85-K-0253, Project No. 22437-EG). This final project report documents our activities on this most recent ARO program which was completed in December 1992.

B. Objectives

The objectives defined for this study were to:

1. obtain kinetic information in the low and intermediate temperature ranges (600-1000 K) over a range of pressures (up to 20 atm) which will be useful to understand the oxidation of pure hydrocarbons with carbon numbers in the C_6 to C_{12} range;

2. determine the synergistic and antagonistic effects for binary and ternary mixtures of full boiling range fuel components; and

3. develop a method for predicting the ignition characteristics of actual fuels based on their composition.

C. Methodology

The methodology of the program was to perform bench scale tests on single component, pure fuels and mixtures of pure fuels. The fuels consisted of branched and straight chain aliphatics and aromatics, which are representative of components in distillate fuels and gasolines. The experiments have been carried out over a range of reaction conditions which are representative of actual engine conditions prior to and during the ignition process. Three separate experimental test facilities have been used to carry out this study: a pressurized flow reactor, an atmospheric pressure flow reactor and a static reactor. Gas chromatographic, mass spectrometric, and Fourier Transform Infrared Spectrometric analyses have been used to determine the stable reaction intermediates and products associated with the oxidation of these fuels. Results from these studies have been used to provide kinetic and mechanistic information, to formulate hypotheses on ignition mechanisms, and to determine the relative effects of the various classes of components within multicomponent fuel mixtures.

In addition, two efforts to develop in situ measurement techniques have been initiated as part of this research effort. The first is a project to develop an in situ laser-based technique for the measurement of $HO_2^\bullet$ radicals using degenerate four wave mixing. The second is a project to develop in situ FTIR spectrometry techniques for the measurement $RO_2^\bullet$ radicals using a newly developed UV-photolysis reactor facility.

II. RESEARCH PROGRAM

As noted, this ARO sponsored program examining the oxidation and ignition characteristics of hydrocarbon fuels was initiated in January 1990 and ran through December 1992 (Grant No. DAAL 03-90-G-0024, Project No. 27417-EG). The overall objectives and methodology were just described in the previous section and, hence, are not repeated here. Following a description of the experimental facilities and procedures in Section A, an overview of the general research activities is given in Section B and a discussion of the specific research accomplishments for this program is provided in Section C. A summary of the personnel supported and their activities is presented in Section D and a list of reports, publications, and presentations currently completed or under preparation appears in Section E.

A. Experimental Facilities and Procedures

The pressurized turbulent flow reactor, shown in Figure 1, has been used in this program for reactivity mapping studies of C_2 - C_4 alkanes and alkenes, and for studies of the detailed chemistry of C_3 and C_4 alkanes at elevated pressures. It is designed for operation up to 1000 K and 20 atm; to date, it has been exercised to 920 K and 15 atm (Koert, 1990; Koert and Cernansky, 1992). The reactor test section is heated and lined with quartz in order to provide an adiabatic reaction zone free from wall effects. The gaseous fuel stream is heated and mixed with the preheated oxidizer in an opposing jet annular mixing nozzle. Samples of the reacting gases are withdrawn from the reactor midway between the reactor center-line and the reactor wall at variable axial locations with a glass-lined, water-cooled gas sampling probe. Control of the probe position is facilitated by the use of a stepper motor driven linear motion positioning table. Extracted gas may be directed to a variety of permanent gas analyzers for CO, CO_2, and O_2 concentration measurements, or stored in a heated storage unit capable of holding 15 - 10 cc gas samples at a typical pressure of 0.2 MPa. The heated sample storage unit has been designed (Euchner, 1980) to prevent chemical changes to the product species contained in the sample. These samples can then be analyzed on a gas chromatograph (GC).

The atmospheric pressure flow reactor (APFR), shown in Figure 2, has been used in this program to establish reactivities of blended high molecular weight (C > 6) hydrocarbons at 1 atm. This flow system has been used extensively in the past for diesel odor research (e.g., Hsieh et al., 1982), for carbonyl chemistry studies (Koert et al., 1987)

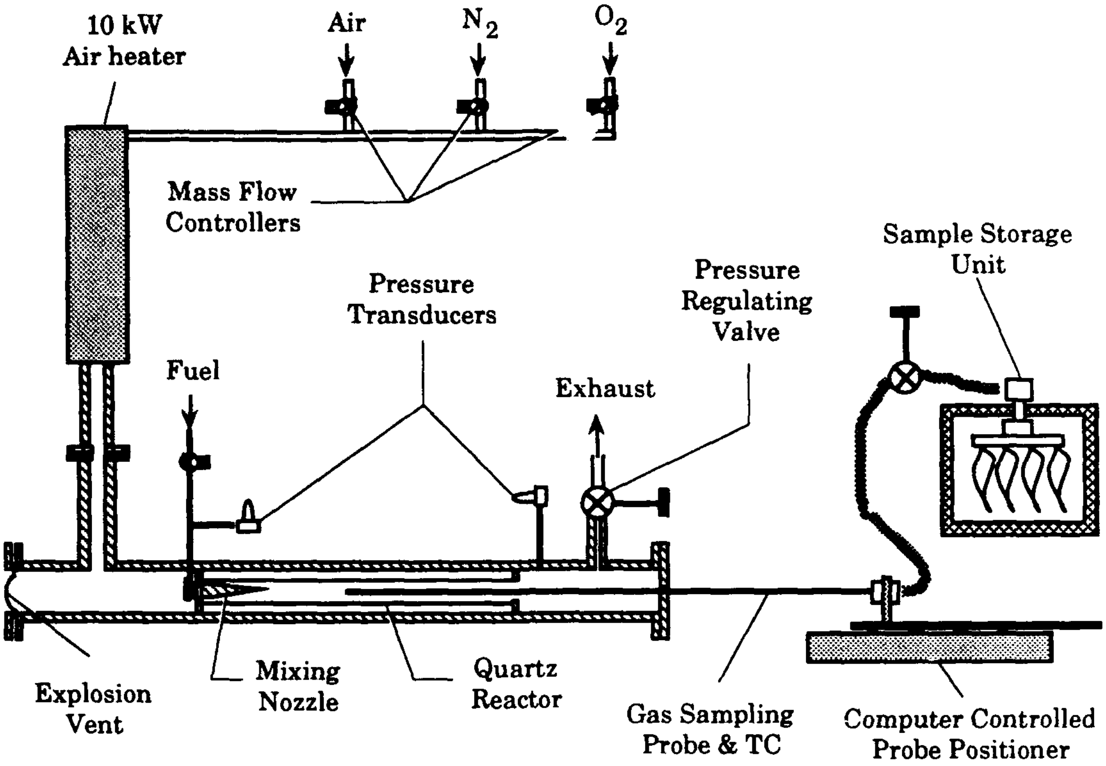

FIGURE 1. Schematic of Pressurized Flow Reactor Test Facility.

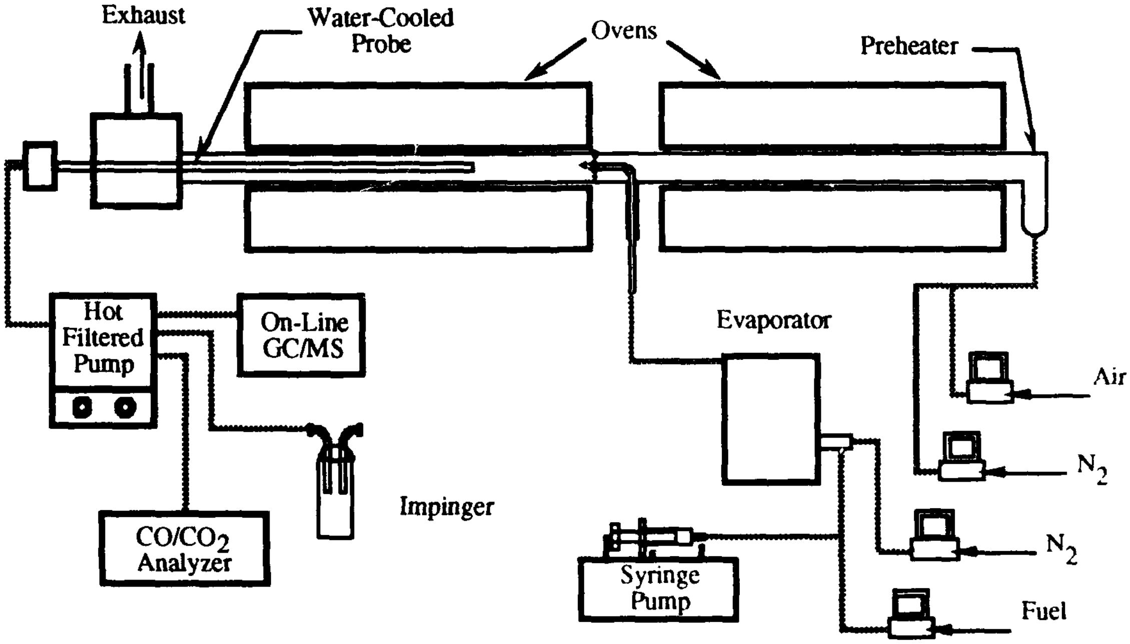

FIGURE 2. Schematic of Atmospheric Pressure Flow Reactor Test Facility.

and for preignition studies (Wilk et al., 1989; Gupta et al., 1990). The flow reactor consists of a 2.3 cm diameter, 30 cm long quartz tube located inside a furnace, which allows for the study of reactions up to about 1000 K. Gas sampling is accomplished using an isokinetic sampling probe which can be positioned axially along the reaction tube. Gas samples can be acquired at various points along the spread-out reaction zone, stored in a heated, multi-loop sample valve, and analyzed by gas chromatography.

The static reactor (SR), shown in Figure 3, has been used in this investigation for the examination of low pressure preignition chemistry of n-pentane (Prabhu, 1993). This system has been used in previous studies on ignition behavior of high molecular weight hydrocarbons such as dodecane and tetralin (Wilk et al., 1985b, 1987b). It has also been used to study the detailed chemistry of lighter hydrocarbons such as propane, propene, and normal butane and isobutane (Wilk et al., 1985a, 1986, 1987a; Addagarla et al., 1987). The static reactor system consists of a 1.4 liter cylindrical Pyrex reaction vessel located inside a temperature controlled compartment. The system is equipped with associated instrumentation for monitoring and recording the pressure and temperature as the reaction progresses. For the study of gaseous fuels, the reactants are premixed in a separate mixing vessel after which the homogeneous fuel/oxidizer mixture is admitted into the reaction vessel by way of a solenoid valve. For the study of liquid fuels, a prechamber is used to vaporize the fuel in a nitrogen bath before mixing. Automatic controls have been added so that actuation of solenoid valves for fuel delivery and sample acquisition is carefully timed in order to compensate for the rapid reaction rates of higher molecular weight liquid fuels.

The newly constructed UV-photolysis reactor, shown in Figure 4, has been used in this investigation for the development of in situ FTIR measurement techniques. The UV-photolysis facility consists of an Infrared Analysis, Inc., Model 4-22 long path absorption cell, fitted with UV lamps and placed in the sample compartment of a Biorad Model FTS-60A FTIR spectrometer. The absorption cell is a 4.7 liter, 10 cm inside diameter, heavy-walled fused-silica tube fitted with adjustable mirrors to allow pathlength selection from 2.2 to 31 meters and transfer optics that facilitate its insertion into the optical path in the sample compartment of spectrometer. In this configuration, the absorption cell is itself the reactor. Four Westinghouse Model FS20 Fluorescent Sun Lamps are used to supply UV radiation at 313 nm. Since the fused-silica walls are transparent to UV radiation at this wavelength, the bulbs are placed outside the gas cell around the circumference as shown in Figure 4. The reactor is equipped with pressure regulation and measurement equipment to permit operation over the range of pressure from vacuum to 4 atmospheres absolute. The reactor is operated at room temperature.

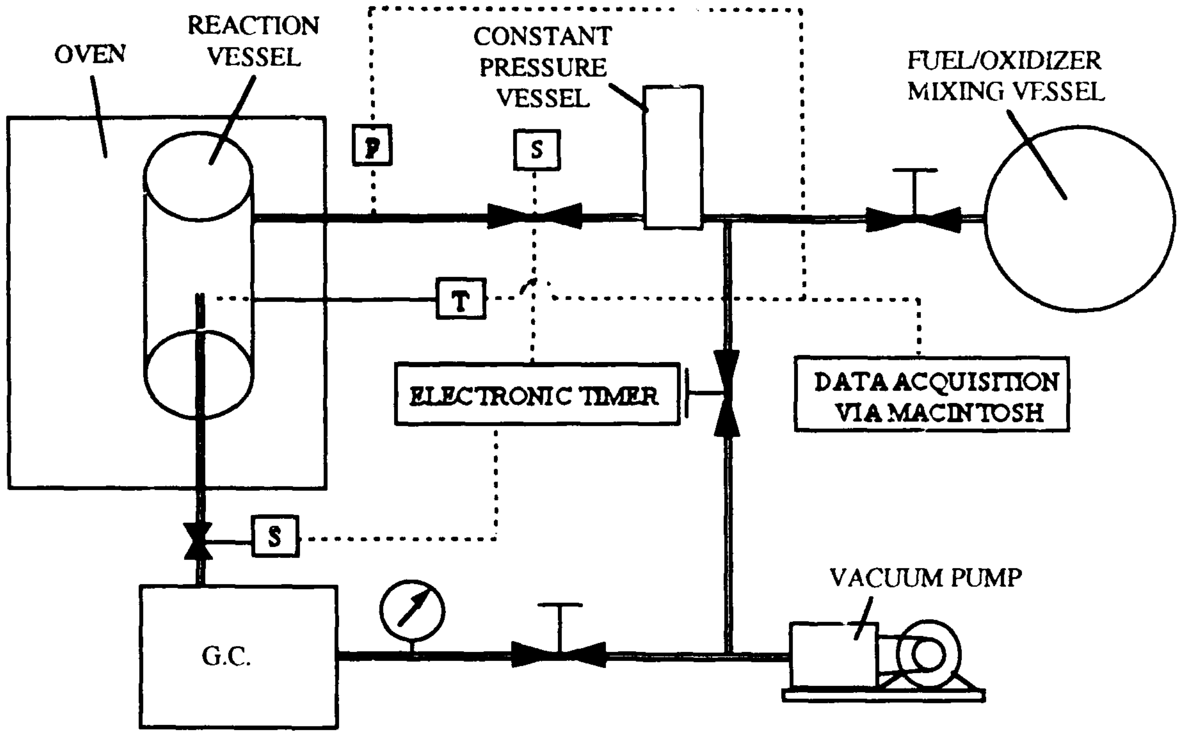

FIGURE 5. Schematic of the Static Reactor Test Facility.

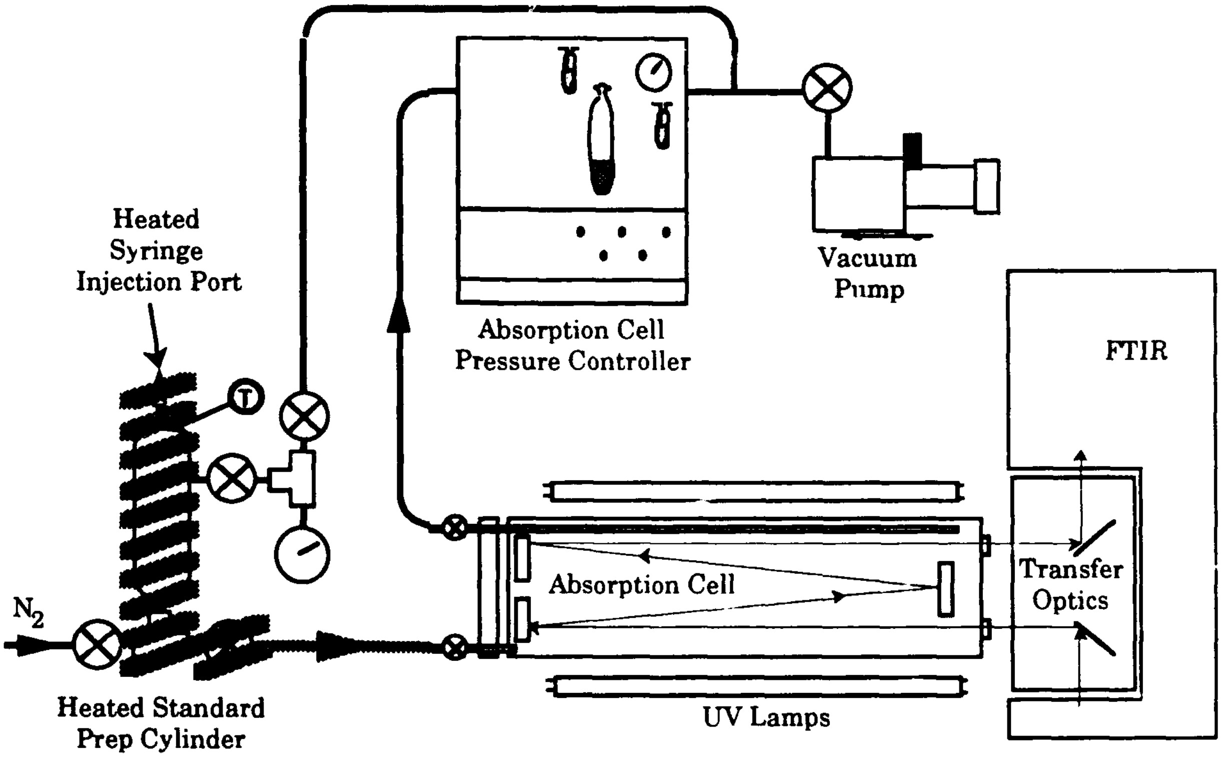

FIGURE 4. Schematic of UV-Photolysis Reactor Test Facility.

The facility has been used to study the room temperature photolysis reactions of azomethane/oxygen mixtures at 340 torr. Infrared absorption spectra of the reacting mixture were obtained during a 40 minute experiment at a resolution of 0.25 cm^{-1}. The reaction rate is slow, allowing the acquisition of detailed spectra with high signal-to-noise ratio by the averaging of several spectra obtained sequentially. Studies such as these are useful because the total number of species in the reaction are low allowing relatively simple resolution of the individual species from complex absorption spectra of the mixture. Of particular interest in these studies is the potential for isolating the absorption spectrum of methylperoxy radical.

Analysis of stable species from any of these facilities is possible by GC, GC/MS and GC/FTIR. For our more recent work with larger hydrocarbons, capillary column and multi-dimensional separation techniques have been implemented. The MS and FTIR techniques provide the ability to identify species by their mass or by their infrared signature. This latter technique is particularly valuable since certain groups of stable compounds called structural isomers are difficult to independently quantify using standard gas chromatography. Examples of groups of these compounds are 1-butene, cis-2-butene, and trans-2-butene, all of which have the same chemical formula C_4H_8; and ethylene oxide and acetaldehyde both of which have the chemical formula C_2H_4O. The FTIR is especially important in differentiating the possible isomeric structures formed during the oxidation processes.

A Nd:YAG pumped dye laser optical system (purchased with partial funding by ARO) has been configured to utilize the degenerate four wave mixing (DFWM) technique Recently we successfully measured the DFWM signal of OH radical in a propane flame. A complementary system has also been developed to simultaneously measure OH via Laser Induced Fluorescence (LIF).

B. Program Summary

Efforts in this research program have focused on three major tasks: examination of the chemistry of autoignition during compression ignition processes by performing parametric studies in the experimental facilities described above; development of chemical models which can simulate the experimental results; and the development of in situ measurement techniques. Testing and modeling of fuels with carbon number < 6 is still an important part of our research efforts investigating preignition behavior of higher molecular weight fuels. This is because complete and accurate kinetic descriptions of fuels with carbon number < 6 are essential to the mechanisms of the higher molecular weight hydrocarbons, and significant features of the preignition kinetics of the lighter species are not presently understood. The parametric studies conducted during this research project involved detailed low and intermediate temperature testing of C_3 and C_4 alkanes in the PFR, examination of the effects of fuel structure and blending on autoignition using fuels with carbon number ≥ 6 in the APFR, and detailed low and intermediate temperature testing of n-pentane in the SR. Development of chemical models involved numerical modeling of PFR results on propane oxidation at pressures of 10 and 15 atm, using and modifying the kinetic mechanism developed by Pitz and Westbrook at LLNL. Development of in situ measurement techniques involved the use of FTIR spectroscopy and degenerate four-wave mixing spectroscopy.

C. Specific Research Accomplishments

A number of specific research accomplishments for the current program are identifiable. The major accomplishments are listed below along with a brief discussion of their significance.

a. The turbulent flow structure of the PFR mixing nozzle was measured with hot-wire anemometry using a scale model at room temperature. These measurements showed turbulence levels that produce mixing within the first 1% of typical reactor flow times and showed that gas residence times at the centerline are within 3% of bulk flow residence times.

b. PFR nozzle flows were simulated using the FIDAP fluid dynamics analysis package.

c. A novel experimental procedure designed to map the reactivity of hydrocarbon/air mixtures in the low to intermediate temperature regimes using carbon monoxide measurements as an indicator of the degree of oxidation was developed and validated by comparison with gas chromatographic measurements of fuel and oxidation products.

d. The negative temperature coefficient regions in the oxidation of ethylene, ethane, propene, propane, and n-butane over a range of temperatures (600 to 900 K) and pressures (2 to 20 atm) were measured. The mapping results for propane indicated a narrow temperature range extending from 640 to 770 K in which the rate of hydrocarbon oxidation reaches a peak and then diminishes. No significant reactivity in the low temperature regime corresponding to that observed with the propane/air mixtures was found for the ethylene, ethane and propylene at these conditions.

e. The temperature range over which NTC behavior occurs was observed to shift to higher temperatures and to broaden as pressure is increased. NTC region broadening was indicated by a shift of the starting temperature to lower temperatures, and a shift of the ending temperature to higher temperatures as the pressure is increased.

f. Analysis of Benson's (1981) turnover temperature for the $\dot{R} + O_2$ mechanism was found to predict the NTC region temperature shift best if the fuel concentration changes proportionally with pressure.

g. A unique experimental procedure was developed whereby gas sampling was done at fixed residence time isobaric operation while the temperature of the flow reactor was varied. This procedures allows one experiment to traverse the boundary between low and intermediate temperature oxidation regimes.

h An experimental study of the detailed product distribution from propane oxidation at 10 and 15 atm, $600 \text{ K} < T < 900 \text{ K}$ and equivalence ratio of 0.4 was conducted. All of the species concentration profiles show the low temperature hydrocarbon oxidation regime extending from approximately 680 to 770 K. They indicate peak species yields, corresponding to the maximum rate of reaction, occurring at approximately 720-732 K. They also show that the NTC region extends from approximately 730 K to approximately 780 K, as indicated by the rapidly decreasing species concentrations. Lastly, at temperatures above approximately 780 K, those species that show increasing species concentrations indicate the onset of intermediate temperature chemistry.

i. Numerical modeling of previously reported experimental results was conducted. Propane oxidation at pressures of 10 and 15 atm, temperatures covering the range $600 \text{ K} < T < 900 \text{ K}$, and an equivalence ratio of 0.4 was modeled using a modified chemical kinetic mechanism developed by Pitz and Westbrook at LLNL. The modeling effort involved using both Drexel's Mac IIfx version of the H.C.T. code and LLNL's computational resources. The mechanism models alkylperoxy radical reactions using only uncoupled, parallel reaction paths. Specifically, the mechanism incorporates the Benson (1981) model of the $\dot{R} + O_2$ reactions. The calculated species concentration versus temperature profiles reproduced the NTC behavior indicated by the experimental species data. An attempt was also made to model the experimental data using a coupled, multichannel unimolecular scheme to model alkylperoxy radical reactions. This channel was unable to reproduce the NTC behavior. It was concluded that the use of a direct path for $\dot{R} + O_2 \rightarrow$ olefin + HO_2 is required until such time as RRKM or QRRK calculations for the alkyperoxy radical reaction are incorporated into detailed kinetic mechanisms.

j. A series of PFR experiments studying propane oxidation at constant inlet temperatures were performed in which detailed species measurements were made as a function of residence time at pressures of 10 and 15 atm. Experiments of this type trace the development of the reaction mechanism in time so that clues as to the source of products can be obtained by observing the order in which species appear. These experiments have provided data necessary for the proper interpretation of the effect of heat release in constant residence time studies and will be useful in refining the detailed chemical kinetic mechanism.

k. PFR experiments studying n-butane oxidation using the reactivity mapping, controlled cool-down and constant inlet temperature techniques described above were performed. These data are newly obtained and will be the subject of continued study. Interpretation of these results and the results of continued investigation will yield the information of the same type as the propane results discussed above.

l. The APFR work examined the effects of fuel structure and blending on autoignition. The APFR was used to oxidize several fuels and binary fuel blends consisting of straight chain and branched alkanes, alkenes and aromatics. The effects on autoignition tendency were investigated at temperatures in the range 570-920 K which encompassed the low and intermediate temperature reaction regimes. CO concentration was measured at the exit of the reactor as the temperature was varied. The degree of CO production was used as a measure of reactivity or autoignition tendency. A maximum in the CO concentration was observed for nearly all fuels and occurred at approximately 675 K. The decrease in the CO production above 675 K indicated a decrease in the overall oxidation rate which was attributed to the negative temperature coefficient behavior. n-Heptane was used as a baseline fuel and blended in binary mixtures with aromatics, alkenes, isooctane, and MTBE. The aromatic components, isooctane, and MTBE all inhibited the oxidation of n-heptane. The alkenes inhibited the low temperature oxidation but promoted the intermediate temperature reaction. For the n-alkanes, a good correlation was obtained between the maximum low temperature CO production and cetane number.

m. A correlation between low temperature reactivity, as measured by carbon monoxide concentration, and octane number was determined using controlled cool-down experiments of octane reference fuel blends in the APFR.

n. Experiments have been conducted in the static reactor to study n-pentane oxidation at equivalence ratios of 0.36 and 0.8, initial pressures of 200-400 torr, and initial temperatures in the range 548 K to 744 K. The experimental results showed a region of cool flame behavior from 565 -648 K and a negative temperature coefficient region at temperatures above 673 K. Results from detailed chromatographic analysis indicate a transition in the reaction mechanism during the NTC region, evidenced by a change in the major products from oxygenated hydrocarbons to olefins as the temperature is increased.

o. Preliminary analysis of product distributions measured during the n-pentane oxidation studies indicate that homogenous gas phase dihydroperoxide decomposition reactions best explain the formation of acetone. There has been a long-standing point of disagreement among researchers who argue either that surface reactions or homogeneous gas phase reactions are responsible for acetone formation.

p. Two new FTIR spectrometer systems were installed. The first system was a gas chromatograph (GC) with an FTIR spectrometer acting as a detector. This system has been installed in the lab in order to add new capabilities for stable product species identification. The second system was a 0.25 wave number FTIR spectrometer that has been installed for use in the development of in situ species analysis, i.e. online optical access to a reactor to analyze the chemical composition (both stable and radical species) of an ongoing reaction.

q. A 10 cm gas cell and a variable path length gas cell (2.2 - 22 m) have been used to develop a library of FTIR spectra for single component standards prepared in the laboratory. A computational technique has been developed to allow the use of the spectrum library in quantifying species concentration when optical path length and pressure are varied.

r. A UV-photolysis reactor with optical access to the FTIR spectrometer has been built that allows in situ species measurements during low pressure, room temperature hydrocarbon oxidation experiments.

s. Studies of the photolysis of azomethane/air mixtures at 760 torr, 298 K have been performed. The photolysis of azomethane with UV radiation in the 290-430 nm range results in the formation of methyl radicals which react to form methylperoxy radicals. The main absorption bands of the major products of reaction have been identified in the absorption spectra. No absorption band for methylperoxy radical has yet been identified. Differences in the azomethane decomposition rates between experiments with and without oxygen may indicate significant rates of hydrogen abstraction by methylperoxy and hydroperoxy radicals at these conditions.

t. A Nd:YAG-dye laser system (purchased with partial funding by ARO) has been installed and is operational. We have made qualitative measurements of OH radical in a premixed flame using both laser induced fluorescence and degenerate four-wave mixing (DFWM) techniques.

D. Reports, Publications, and Presentations

Work accomplished as part of this research program has contributed to and resulted in the following publications, reports and presentations:

Gupta, A.V., D.N. Koert, and D.L. Miller, "Investigation of the Relationship Between Octane Number and Low Temperature Reactivity for Primary Reference Fuel Blends," Paper No. CSSCI 90-34, presented at the 1990 Central States Section Combustion Institute Meeting, Cincinnati, OH, May 1990.

Koert, D.N., R.D. Wilk, D.L. Miller, and N.P. Cernansky, "A Pressurized Flow Reactor Study of Low and Intermediate Temperature Ethane and Propane Oxidation," Poster No. P266. presented at the Twenty-Third Symposium (Int'l.) on Combustion, Orléans, France, July 1990.

Koert, D.N., D.L. Miller, and N.P. Cernansky, "Propane Oxidation Through the NTC Region: A Comparison of Results at 10 and 15 Atmospheres," Paper No. ESSCI 90-8, presented at the 1990 Eastern States Section Combustion Institute Meeting, Orlando, 'FL, December 1990.

Koert, D.N., "The Effect of Pressure on Hydrocarbon Oxidation Chemistry," Ph.D. Thesis, Department of Mechanical Engineering, Drexel University, Philadelphia, PA, December 1990.

Wilk, R.D., W.J. Pitz, C.K. Westbrook, and N.P. Cernansky, "Chemical Kinetic Modeling of Ethene Oxidation at Low and Intermediate Temperatures," Twenty-Third Symposium (Int'l.) on Combustion, Combustion Institute, Pittsburgh, PA, 1991, pp. 203-210.

Wilk, R.D., W.J. Pitz, C.K. Westbrook, S. Addagarla, D.L. Miller, N.P. Cernansky, and R.M. Green, "Combustion of n-Butane and Isobutane in an Internal Combustion Engine: A Comparison of Experimental and Modeling Results," Twenty-Third Symposium (Int'l) on Combustion, The Combustion Institute, Pittsburgh, PA, 1991, pp. 1047-1053.

Koert, D.N. and Cernansky, N.P., "A Flow Reactor for the Study of Homogeneous Gas-Phase Oxidation of Hydrocarbons at Pressures Up To 20 Atmospheres (2 MPa)," Meas. Sci. Tech, 3, 1992, pp. 607-613.

Koert, D.N., Miller, D.L. and Cernansky, N.P., "Results of Reactivity Mapping Studies Through the Negative Temperature Coefficient Region for Propane at Pressures from 5 to 15 Atmospheres," Energy & Fuels, 6, 1992, pp. 485-493.

Koert, D.N., Jauoabi, K., Miller, D.L., Cernansky, N.P., Pitz, W.J. and Westbrook, C.K., "Propane Oxidation through the Negative Temperature Coefficient Region at 10 and 15 Atmospheres: Results of Experimental and Modeling Studies," Poster No. 187, at the Twenty-Fourth Symp. (Int'l) Combust., Sydney, Australia, July 5 - 10, 1992.

Ramotowski, M.J., "Pressure Effects on the Low to Intermediate Temperature Oxidation of Propane and N-Butane," M.S. Thesis, Drexel Unversity, Philadelphia, PA October 1992.

Wilk, R.D., R.S. Cohen, and N.P. Cernansky, "The Oxidation of n-Butane: Transition in the Chemistry Across the Region of Negative Temperature Coefficient," submitted for publication in Industrial & Engineering Chemistry Research.

Koert, D.N., Y.I. Cho, and N.P. Cernansky, "Comparison of Velocity Measurements to Numerical Flow Calculations for a New High Pressure Flow Reactor Test Facility," submitted for publication in Experimental Thermal and Fluid Science.

Koert, D.N., Miller, D.L. and Cernansky, N.P., "Experimental Studies of Propane Oxidation through the Negative Temperature Coefficient Region at 10 and 15 Atmospheres," submitted for publication in Combustion & Flame.

Koert, D.N., Jauoabi, K., Miller, D.L., Cernansky, N.P., Pitz, W.J. and Westbrook, C.K., "A Note on Modeling Negative Temperature Coefficient Behavior," submitted for publication as a Brief Communication in Combustion & Flame.

Prabhu, S.K., "N-Pentane Oxidation Studies in the Low and the Negative Temperature Coefficient Regime," M.S. Thesis, Drexel University, Philadelphia, PA (expected March 1993).

McCormick, T.W., Koert, D.N., Miller, D.L. and Cernansky, N.P., "Methylperoxy Radical Identification and Quantification using FTIR Spectroscopy," Paper No. WSSCI 93-012, to be presented at the Spring Meeting of the Western States Section of the Combustion Institute, Salt Lake City, UT, March 22-23, 1993.

E. Research Personnel and Activities

This research project was coordinated under the supervision of Dr. Nicholas P. Cernansky (Hess Chair Professor of Combustion) and Dr. David L. Miller (Associate Professor) as Co-Principal Investigators. They shared overall responsibility for conducting, directing, and reporting the various phases of the research program. However, the primary responsibility for carrying out and implementing the details of the experimental and analytical aspects of the program fell on the other technical personnel supported by the project. Dr. David N. Koert (Ph.D.-1990; Research Assistant Professor) earned his degree with support from this program and continued his involvement as a Post Doctoral Fellow with special responsibility for the pressurized flow reactor, the UV-photolysis reactor and operation of the FTIR spectrometers. Mr. Shang Jih Tsay (Ph.D. candidate [expected June 1994]) has worked on the installation of the laser facility and the development of in situ species measurement techniques using DFWM and LIF. Ms. Patricia A. Partridge (Ph.D. candiate) and Mr. Srinivasa K. Prabhu (M.S. candidate [expected March 1993]) were primarily responsible for static reactor operation, gas chromatographic method development, sample collection and analysis, and data interpretation. Mr. Alok V. Gupta (M.S.-1991) earned his degree with support from this program while conducting experiments on the atmospheric pressure flow reactor. Mr. Michael J. Ramotowski (M.S.-1992) earned his degree with support from this program while conducting experiments on the pressurized flow reactor. Mr. Ajay Anand (M.S. candidate [expected June 1993]) has also been conducting experiments on the pressurized flow reactor. Mr. Thomas W. McCormick (M.S. candidate [expected June 1993]) has been conducting UV-photolysis experiments and developing in situ species measurement techniques using FTIR spectroscopy. In addition, several undergraduate students have participated in the research program through Independent Study and Research activities or as Laboratory Aides.

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