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FUTURE SYTHETIC FUELS

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SCIENTIFIC AND TECHNICAL APPLICATION FORECAST

OFFICE OF THE CHIEF OF RESEARCH, DEVELOPMENT AND ACQUISITION
DEPARTMENT OF THE ARMY
WASHINGTON, D.C. 20310

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FUTURE SYNTHETIC FUELS

A Scientific and Technical Applications Forecast

for the

Office of the Chief of Research, Development and Acquisition
Department of the Army
Washington, D.C. 20310

By

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FOREWORD

The documents known as Scientific and Technical Applications Forecasts (STAF) form a series designed to supplement the annual U.S. Army Long Range Technological Forecast. A STAF is intended to provide an insight into one specific field, and is for use by persons in and outside of the Department of the Army who have need for such background information. A STAF is primarily an encyclopedic summary of the current knowledge and a projection of the expected technological environment during the next 20 years. Its purpose is to allow scientifically, technically and operationally oriented individuals to communicate relevant ideas and learn of potentialities in the cited field.

STAF's, while generally comprehensive, are not exhaustive. Hence, the treatment may be properly considered an overall introduction to the current state of the art and an extrapolation to forecast the technological environment of 10-20 years in the future. An extensive bibliography is included in each STAF to document the current knowledge and to provide references for further detailed study.

This particular STAF is an effort to examine alternate sources of fuels for use by the Army in an era of declining resources and increasing costs. Processes which may not appear attractive from an extraction, processing or financial point of view may indeed become so with the passage of time. Some of the recommendations in the report have been implemented by the Army's research community prior to the issuance of this STAF and others will undoubtedly follow.

The conclusions of the authors are subject to modification in the light of new developments and information. Accordingly, readers are urged to submit comments in order to fill in possible gaps, report additional findings or applications, and suggest changes.

U.S. Army RDT&E agencies are encouraged to publish STAF's on specific scientific and technical subjects falling within their area of assigned responsibilities. Additionally, recommendations concerning desired subjects for STAF treatment are solicited and should be addressed to:

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PREFACE

This Scientific and Technical Applications Forecast (STAF) on Future Synthetic Fuels constitutes the final report in accordance with Contract DAAD05-73-C-0559, dated July 1, 1973. Mr. Harold F. Davidson of the Office of the Chief of Research, Development and Acquisition conceived the project and monitored its progress. The project was carried out in the Government Research Laboratory of Exxon Research and Engineering Company in Linden, New Jersey.

The principal investigator was Dr. William F. Taylor, assisted by Dr. H. J. Hall. Contributions were made by the following personnel from Exxon Research and Engineering Company: R. H. Salvesen, F. H. Kant, E. M. Magee, J. K. Appeldoorn, W. A. Herbst, A. L. Schrier, A. H. Popkin, R. C. Green and C. Jahnig. Contributions were made by the following government personnel: H. L. Ammlung, M. E. LePera, C. Schwarz, R.D. Quillian, Jr., R. G. Dodd, K. F. Smith, Capt. T. D. Balliett, Maj. M. Pedersen, R. Furgurson, E. Easterling. R. Burrows, J. A. Krynitsky, R. Lynch, F. Lux, E. March, W. Bryzik and D. Weidhuner. The project was administered by Dr. R. R. Bertrand of Exxon Research and Engineering Company.

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1. EXECUTIVE SUMMARY

This STAF reviews the broad problem of the impact on the U.S. Army of the use of synthetic fuels (defined as a non-petroleum derived fuel) over the time period of 1975 to 2000. The STAF is divided into three basic parts. The first part involves a forecast of which synthetic fuels will have a major impact in the time period under study. This analysis drew heavily on a companion program carried out concurrently by Exxon Research and Engineering Company for the Environmental Protection Agency entitled "Feasibility Study of Alternate Fuels for Automotive Transportation." In the second part of the STAF, those alternate fuels identified as the most feasible synthetic fuels in the future were subjected to detailed analyses. The third part of the STAF consists of the identification of a number of areas which appear to offer promise for fruitful R&D in the synthetic fuel area. This section of the report highlights both the salient features of the complex synthetic fuel question itself and the conclusions relative to it reached in this study.

Present Status

- Both the U.S. and world petroleum reserves at present and projected consumption rates face depletion at a time in the future which can no longer be ignored.
- Current petroleum fuel demand, particularly in the U.S. is so large that finding a substitute for this volume of fuel is an immense task regardless of the alternate fuel chosen.
- The majority of present day mobile power plants have been developed to run on petroleum derived liquids. Thus, a change to a fuel radically different from present petroleum derived liquids would correspondingly require a massive change in power plants.
- Small commercial sized synthetic fuel activities currently are scattered throughout the world (i.e. in the U.S.S.R., China, Canada and South Africa but not in the U.S.). Synthetic liquids are not new materials (some predate the discovery of petroleum). Many synthetic fuel activities have been abandoned in the face of open economic competition with inexpensive and readily available petroleum, and current commercial production appears to exist as a result of government policies rather than economic factors. However, even major past synthetic fuel efforts such as took place in Germany during World War II would be considered small today (when compared to present rather than past consumption levels).

The Change From Petroleum Derived to Synthetic Fuels

- Driving Force

The ultimate driving force for a change from petroleum to other sources for liquid fuels will be the exhaustion of the world's recoverable reserve of petroleum. Thus, the question is not if a change will take place but when the change will take place and what form will the change take.

- Nature of the Change

The change of commercial industry from producing petroleum fuels to synthetic fuels will be evolutionary i.e. synthetic fuels will begin to be used in conjunction with petroleum and that usage will expand as availability increases. The sheer magnitude of the task of substantial replacement of present U.S. liquid petroleum derived fuel production with synthetics, appears to dictate a time frame in the order of magnitude of two decades to accomplish the change, even assuming a strong national commitment.

- Timing

- At present many predict that the U.S. production of petroleum as influenced by recoverable reserves will begin to decline by the turn of the century, and world production slightly thereafter.
- It would appear logical that individual countries for political and/or economic reasons will begin the change prior to being forced into it by a genuine shortage of petroleum.
- Predicting a time-table for the buildup of synthetic crude capacity is difficult at this time. In early 1974 following the shock of the oil embargo, it appeared that the major effort to build a synthetic fuel industry (i.e. to construct commercial sized synthetic plants) would begin within the next few years. At present (Fall-1975), although synthetic fuel R&D activity in the U.S. is intense, the start of the actual construction of a synthetic fuel industry in the U.S. appears to await the establishment and implementation of a national policy to carry out the enormous effort which will be involved.

General Synthetic Fuel Consideration

- Which Ones Are Most Likely

The synthetics most likely to have a major world role in the time frame of 1975 to 2000 in terms of gasoline and distillate (i.e.: diesel and aircraft turbine) type fuels are judged to be:

- Shale rock derived liquids.
- Coal derived liquids.
- Tar Sand derived liquids.
- Methanol as a product from gasified coal.

- Resource Availability

The world's resources of coal, shale rock and tar sands are quite large. The U.S.'s coal and shale rock reserves are also large. However, tar sand reserves are located principally outside the U.S.

- Processes for the Production of Synthetic Crude Oil

- The process technology (without considering economics as a factor) for the production of synthetic liquids from coal, shale rock and tar sands is currently available throughout the world. The existance per se of process technology thus is not a limiting step to the creation of a synthetic fuel industry.

- The investment costs for synthetic crude producing processes are quite large; thus, much effort will be expended to develop more cost effective processes. Because of this process improvement effort it is difficult to predict what specific processes will be used in the future.

- As a result of a major solids handling problem (particularly with shale rock and tar sands) the processing plants when built will probably be located near the resource site. Thus synthetic fuel production is potentially geographically diffuse rather than concentrated because of the world wide distribution of coal, shale rock and tar sands.

- Relative Economics

- At present the cost of building and operating plants to produce synthetic crude oil is much higher than the cost of producing petroleum crude oil, particularly from sources such as located in the Persian Gulf area. Developments will be made to improve the cost effectiveness of processes to produce synthetic crudes, and the cost of finding and producing petroleum will increase as the more assessable petroleum sources are exhausted. Ultimately as the world's supply of petroleum begins to be exhausted the cost of petroleum must reach a level where synthetics will become cheaper. Thus, sometime in the future the relative cost advantage of petroleum versus synthetics will reach a cross-over point.

- However, before this cross-over point is reached, in the absence of some type of government incentives, it is difficult to see how a commercial scale synthetic fuel industry will be built.

Power Plant Considerations

- The nature of mobile power plants used by the Army (which have a 5 year development and 20 year life cycle) is essentially being fixed for the time period 1975 to 2000 by decisions which have been made or are being made in our current time frame.

- In the commercial sector, in order to readily accommodate the long, gradual change from petroleum derived fuels to synthetic derived fuels it is anticipated for the year 1975 to 2000 that highway vehicles will be powered by engines that will not be radically different in terms of compatability with existing petroleum derived fuels.

The Nature of Synthetic Fuels

- The exact composition of synthetic fuels is a function of (1) basic type of resource used i.e. coal, shale rock or tar sands, (2) the type of process used to convert the resource material to a synthetic crude oil (3) the type of secondary processing (i.e. refining) employed to make the finished fuel from the synthetic crude:

    - The chemical composition of synthetic crudes particularly those derived from shale rock and coal is different from that of petroleum crudes.

    - For a given resource type, particularly in the case of coal, the composition of the synthetic crude will vary depending on the process and process conditions used to produce it.

- Although some technology presently exists which may be applicable to the secondary processing (refining) of synthetic crudes to fuels similar to present day petroleum derived fuels, it is not at all clear at this time as to exactly what processing will be employed when a commercial sized synthetic fuel industry is actually created. Although small plants dedicated solely to processing synthetic fuels may be built for special purposes, it is more likely that large quantities of synthetic crudes will be processed in refineries initially handling both petroleum and synthetic crude. In this latter case, the large capital investment requirements will probably dictate a complex optimization of the processing scheme, making it difficult at this time to make predictions. Cost/availability tradeoffs versus fuel specifications will also undoubtedly occur, also adding uncertainty to any prediction of future detailed processing schemes.

- It would appear at this time that although future synthetic fuels will be liquid products grossly similar to present petroleum fuels there will be significant differences between the detailed chemical composition of synthetic fuel and present petroleum fuels. In addition, the differences cannot be predicted with any certitude at this time.

Areas for Fruitful R&D Effort

An examination of the anticipated trend regarding synthetic fuels indicates a number of areas where R&D work would appear potentially fruitful:

- The very uncertainty itself regarding future synthetic fuels suggests a strong need for extensive forecasts, analytical studies and information exchanges relative to synthetic fuels with emphasis on the Army's needs and point of view.
    - Forecasts of the composition of synthetic fuel by analyzing the nature of the processes used to both produce the synthetic crude oil and to refine this crude to a finished fuel.
    - Cost and availability versus specifications tradeoff studies with emphasis on middle distillate fuels.
    - Impact of changes in processing technology on the nature and supply of middle distillate fuels derived from synthetics.

  - Analyses of the foreign synthetic fuel operations. Much of the current emphasis is on U.S. synthetic fuel developments when in reality the only present commercial sized synthetic fuel operations exists outside the U.S. Also, consideration should be given to factors such as the compatability of foreign synthetic fuels with domestic developed engines.

  - Encouragement of maximum interaction between experts in the areas of fuel properties and product quality, power plant design and synthetic fuels process development. This interaction could be effected via joint study efforts or DOD funded workshops.

  - Generation of background and expertise to provide a sound technical basis for an Army input to a national energy policy and to insure maximum integration of the Army's effort with that of other government agencies and private industry.

- Product quality studies carried out to characterize in detail the chemical and physical properties of both pure (i.e. unblended) synthetic fuels and fuels obtained from blends of synthetic and petroleum derived components.

- Storage stability studies should be carried out since the use of even small fractions of synthetic derived materials blended into a stable petroleum derived fuel could result in major stability problems which are not now encountered with pure petroleum derived middle distillate fuels, particularly in view of the Army's long term storage stability needs.

- Studies should be undertaken to assess possible problems in the deterioration, corrosion and materials compatability area.

- The combustion properties of synthetic containing fuels should be studied.

- Toxicity, emission and other problems should be considered from the point of view of the Army's mission.

- Studies to assess potential water reactivity problems should be carried out.

  - Middle distillate fuels might be influenced by the introduction of organic oxygen compounds present in some synthetic fuel materials.

  - Phase separation after contact with water is expected to be a major problem associated with the use of methanol in gasoline blends as motor gasoline fuel.

- A number of other areas for study have potential merit such as the use of synthetic fuel components to produce a high density fuel for volumetrically limited systems.

2. ALTERNATE FUEL FORECAST

2.1 Prediction of Major Alternate Fuel Types

In this section of the report the major alternate fuels of the future are analyzed so as to identify the non-petroleum crude based fuels which will probably play the greatest role in the future,which then will be subjected to detailed analysis. The time frame of concern is the years 1975 to 2000 with major emphasis on the 1985 to 2000 time frame. This analysis and prediction of alternate fuels is focused on the commercial point of view. Since the Army is committed by policy to use commercially available fuels the development of the commercial sector will also influence the Army's selection of conventional fuel type. This analysis draws heavily on a concurrent program carried out by Exxon Research and Engineering Company for the Environmental Protection Agency entitled "Feasibility Study of Alternate Fuels for Automotive Transportation"(1). The broad outline of the analysis and its conclusions are summarized here. For more detailed information the reader is referred to the final report describing the Alternate Automotive Fuel study (1).

2.1.1 Fuels and Selection Factors Considered

The fuels selected for preliminary analyses (1) were as follows:

1. Coal liquids (gasoline or distillate)
2. Shale liquids (gasoline or distillate)
3. Methanol
4. Ethanol
5. Higher Oxy Compounds
6. Hydrogen
7. Methane
8. Ammonia
9. Hydrazine

The criteria used in evaluation of these fuels were as follows:

Economic Criteria

1. Cost of production and distribution
2. Operating cost (in vehicle)

Technical Criteria

3. Technological status
4. Production efficiency
5. Environmental impact in production

Performance Criteria

6. Compatibility with engines
7. Toxicity
8. Safety
9. Driver acceptability - convenience
10. Environmental impact during use
11. Efficiency of use

Strategic Criteria

12. Fuel shift and entry compatibility
13. Resource availability
14. International considerations

The analysis(1) identified the following synthetic fuels as the most feasible and practical fuels of the future:

- Shale derived gasoline
- Shale derived distillate
- Coal derived gasoline
- Coal derived distillate
- Methanol as a product from gasified coal

The Environmental Protection Agency(1) study was restricted to the United States. It did not consider fuels derived from tar sands, since the U.S. tar sand resources are very small. Tar sand derived liquids are presently being produced outside the U.S. Since the present study is concerned with the worldwide alternate fuel situation the following fuel types were added:

- Tar sand derived gasoline
- Tar sand derived distillate

In addition to the detailed analysis whose results were summarized above, it is useful to consider the restrains inherent in the elemental composition of liquid combustion fuels, which at present represent our major source of energy for portable power plants.

The elements most common in the compounds composing fuels are carbon, hydrogen, nitrogen, sulfur and oxygen. Oxygen has no heating value for combustion, and sulfur and nitrogen pose severe environmental problems because of the formation of sulfur oxides and nitrogen oxides. Thus, the most desirable elements for combustion in fuel molecules are carbon and hydrogen because of the high heat of combustion of these elements and the non-polluting nature of their products of complete combustion (i.e., CO_2 and H_2O).

Also it has been suggested that hydrogen itself be used as the fuel of the future. At present, hydrogen can be produced via the following processes.

- Steam reforming of hydrocarbons
- Partial oxidation of hydrocarbons
- As a by-product during platinum reforming of naphthenes and paraffins in petroleum naphtha to produce aromatics for gasoline
- Pyrolysis of hydrocarbons
- Reaction of coal and water
- Electrolysis of water
- Thermochemical splitting of water
- Steam-iron process

All of these processes for hydrogen production are fossil fuel based with the exception of water electrolysis and thermochemical splitting and the steam-iron process. Indeed, only if non-fossil fuel energy generating sources (e.g., nuclear) are used as the source of energy for water electrolysis, water splitting or to drive the steam-iron process can these hydrogen producing fuel processes become truly carbon independent. Thus, the elements carbon and hydrogen derived from fossil sources and contained in compounds which are liquid at ambient conditions will be the major components of fuels used for combustion powered mobile power plants for the next 25 years.

References Cited in Section 2.1

(1) F. H. Kant et al., "Feasibility Study of Alternate Fuels for Automotive Transportation," U.S. Environmental Protection Agency, Contract 68-01-2112, Final Report, June 1974.

2.2 Anticipated Future Trend Regarding Petroleum and Alternative Fuels

It has been estimated that 75-85% of the original petroleum resource base remains unused(1). In the U.S. the American Petroleum Institute figures indicate an approximate 10 year crude oil proven reserve based on present U.S. production(2). Energy conservation measures dictated by economic and/or political policy, shifts from petroleum to coal and nuclear energy sources for electric power generation, discovery of addition crude reserves in presently unexplored areas, more efficient crude recovery methods, and the use of heavy crude oil reserves not presently economic to produce will all help to extend U.S. petroleum resources. Much larger reserves are present outside the U.S., particularly in the Middle East, upon which the other major users, i.e., Western Europe and Japan, are largely dependent(3). It was noted in June 1973 that quantitative energy forecasts are difficult to make(4). They would appear even more difficult to make in light of the major changes which occurred following the October 1973 Middle East War.

In response to economic and/or political factors, and ultimately to the overwhelming pressure of reduced petroleum production as the world approaches the exhaustion of petroleum reserves, a major synthetic fuel industry will be born and grow. Present production of synthetic fuels is non-existent in the U.S. and worldwide is extremely small compared to petroleum production throughout the world. (Total production from tar sands in Canada, from shale in the U.S.S.R. and China and from coal in South Africa is estimated to be equivalent to less than 1/2 of 1% of world petroleum production.)

Predictions of where and at what pace a transition from crude oil derived fuels to synthetic derived fuels will occur are difficult to make. In June of 1974, the Alternate Fuel Study(5) concluded that initial production of shale and/or coal derived fuels would occur in the U.S. within five to seven years, would approach 800,000 bbl/day total shale and coal derived liquids in 1985, and 6,000,000 bbl/day of shale and coal derived liquids in the year 2000. The National Petroleum Council(6) forecast predicted in 1980 a 100,000 bbl/day of synthetic liquid production in the U.S. (plus 400,000 bbl/day in Canada and 300,000 bbl/day in Latin America), and predicted for 1985 a 500,000 bbl/day synthetic liquid production in the U.S. (plus 1,000,000 bbl/day in Canada and 800,000 bbl/day in Latin America). In early 1974 U.S. automotive fuel consumption approximated 6,000,000 bbl/day. Thus, under these predictions synthetic fuels could make only a minor contribution to total automotive fuel supplies in 1985, but would have the potential to become a major factor in subsequent years. Cost analyses also made by the Alternate Fuel Study(5) for June 1974, building upon previous National Petroleum Council study economics, predicted for the time period 1982 to 1985 a $5 to 7 per barrel cost for shale syncrude and $8 to $11 per barrle costs for coal syncrudes (in 1973 dollars). Based on the sudden dramatic increase in foreign crude oil prices to well over $10 per barrel, following the oil embargo, a synthetic fuel oil industry appeared economically feasible, and its rate of development limited by other factors such as environmental constraints, water availability and rate of government leasing of shale and coal lands. Indeed, at the time major investments were made in oil shale leases by private industry which leased a number of shale rock containing tracks from the government whereas a previous leasing attempt had failed(7). Hanging over this apparent economic advantage for synthetic liquids was the ever present possibility of a sharp drop in crude oil prices, whose actual production costs have been stated to vary from $0.10 to 3.00 per barrel(8). Long lead times for the development of a synthetic fuel industry and the large capital requirements for its construction further intensified the uncertainty regarding the economic viability of synthetic fuels relative to petroleum derived fuels.

In October 1974 it was announced by the Colony Department Operation, a joint venture of Atlantic Richfield Company, Shell Oil Company, Ashland Oil Company and the Oil Shale Corporation, that its plans for the U.S. first commercial oil shale plant (50,000 bbl/day) has been suspended indefinitely(9). The following reasons were cited:

- Inflation increased costs- e.g., product costs increasing from $7 per barrel to $11 per barrel and higher with plant investment costs increasing from $450 million to 800 million in one year.
- Government energy policy uncertainties, i.e., the failure to get government protection against the possibility of a drop in crude oil prices.
- Stronger than expected environmental opposition to shale oil development.
- Tight money.

Similarly, plans for synthetic crude production from tar sands in Canada experienced difficulties(11,12,13). Shell Oil withdrew from a planned 100,000 bbl/day plant in Alberta (11). Syncrude Canada Ltd.(11,12,13) experienced a halt in construction following withdrawal by Atlantic Richfield Canada Ltd. Construction was resumed after their replacement by the Canadian federal and provincial governments in the consortium (other members are Imperial Oil Ltd., Canada City Services and Gulf Canada, Ltd.)

In November 1974, it was reported from the American Petroleum Institute's annual meeting(10) that in general, petroleum industry interest in commercial synthetic fuel plants was decreasing because of inflation increased costs and the lack of government guarantees against the possibility of lower crude oil costs.

Thus, the details of the timetable for the development of a synthetic fuels industry is clouded at the time of the writing of this report, and would appear to be largely dependent on the initiation of a government policy designed to create such an industry, at least until such time as a substantial depletion of world petroleum reserves creates a clear economic incentive for synthetic fuels. Indeed, in such areas where a shale rock and coal derived synthetic fuel industry exist at present, i.e., U.S.S.R., China and South Africa, it would appear to be a product of government policy rather than world economic conditions.

References Cited in Section 2.2

(1) F. A. L. Holloway, "Synthetic Fuels...Why, Which Ones and When," Oil Daily Forum, May 2, 1973.

(2) J. C. Davis, Chemical Engineering, 81, No. 7, p. 30, April 1, 1974.

(3) Oil and Gas Journal, 71, No. 46, p. 119, November 12, 1973.

(4) M. H. Farmer, "Energy Scenarios - Supply Considerations," submitted to Environmental Protection Agency, Energy Analysis Branch, June 12, 1973.

(5) F. H. Kant et al., "Feasibility Study of Alternate Fuels for Automotive Transportation," U.S. Environmental Protection Agency, Contract 68-01-2112, Final Report, June 1974.

(6) M. W. Nichols, "Balancing Requirements for World Oil and Energy," Chemical Engineering Progress, 70, No. 10, p. 39 (1974).

(7) H. A. Meshlein, World Oil, 179, No. 1, p. 27 (1974).

(8) Forbes, November 1, 1974, p. 74.

(9) Wall Street Journal, October 7, 1974, p. 7.

(10) Wall Street Journal, November 14, 1974, p. 1.

(11) Oil and Gas Journal, April 14, 1975, p. 39.

(12) Oilweek, 26, #5, pages 26,27 & 32 (March 17, 1975).

(13) Forbes, May 1, 1975, pages 18 & 19.

2.3 Anticipated Trend Regarding General Army Fuel Requirements

In order to identify missing technology which will necessitate R&D effort resulting from future alternate fuels, it is necessary to assess the impact of the introduction of synthetic fuels in the coming years upon U.S. Army operations.

To accomplish this objective,for the purposes of the STAF only, a simplified analysis of U.S. Army fuel situation was formulated for the years 1975 to 2000. This prediction was developed principally from discussions with various experts, but also drew from material in a number of reports(1-4). Some major points are as follows:

(1) Army power plants require approximately 5 years to develop and then are employed in service for 20 years. Thus, the power plants to be used over the next 25 years are essentially fixed by decisions that have already been made or will be made in our current time frame.

(2) Army policy requires conventional combat fuels to be procured from commercial sources.

(3) Both the nature of commercial vehicle fuel types expected to be available and the nature of mobile Army power plants in use and in development lead to the conclusion that liquid hydrocarbon fuels will be dominant over the period 1975 to 2000.

(4) The major fuels of Army interest in their order of importance are and will be:

   (a) middle distillates

   (b) motor gasoline

   (c) aviation turbine fuel (JP-4 or JP-8 if the Air Force changes fuel).

(5) DOD policy is to procure fuels locally as much as possible. Thus, both U.S. and foreign produced fuels impact on Army requirements.

(6) The need for good storage stability is more important to the Army than to civilian users as combat fuels must be designed for a storage life of 3 to 5 years. Moreover, the policy of prepositioning fuels by storage at terminals suggests an advantage for fuels capable of even longer storage life.

(7) War-time demand levels (general, maximum, non-nuclear war) for conventional fuels could range up to a volume equivalent to 12% of maximum U.S. refinery output (approximately 5 times military peacetime demand).

(8) Emergency fuels need only provide a short life time operation since it is expected that the combat life of the equipment will be short.

References Cited in Section 2.3

(1) "Executive Summary of Twenty Year Plan for Propulsion Systems for Ground Combat Vehicles," U.S. Army Tank-Automotive Command, Warren Michigan, 13 September 1973.

(2) "Executive Summary on the AMC Long Range Fuels R&D Program," The Army Fuels and Lubricants Research Laboratory (AFLRL), revised. Draft, 22 August 1973.

(3) R. A. Block, "Impact of the National Energy Crisis on the Defense Department," Advanced Research Projects Agency, October 12, 1972.

(4) R. D. Quillian, Jr., "A Report on the Energy Crisis," USAMC Laboratory Directors Conference, Charlottesville, Virginia, 22 March 1973.

3. ANALYSIS OF FUEL TECHNOLOGY

In this part of the STAF, those alternate fuels identified as the most feasible synthetic fuels in the future were subjected to detailed analyses. The analyses included factors such as resource availability, present status of processes to convert the resource (i.e., shale rock, coal) to a synthetic crude material, and the anticipated secondary processing required to convert the synthetic crude to a commercial fuel. Since the transition from petroleum derived fuels to synthetic fuel will necessarily be gradual and employ power plants presently using petroleum fuels, factors such as the composition of petroleum crude oil and present petroleum derived fuels and existing petroleum refining technology were also discussed to provide a basis for comparison with corresponding synthetic crudes and liquid products. An effort was made to make these comparisons as much as possible on a chemical composition basis rather than solely on a petroleum technology basis, which it was felt would generate both the greatest insight into alternate fuel problems and provide the resultant information in a more universal language for the reader.

3.1 General Overview of Synthetic Fuel Technology

A variety of processes for the production of liquids from shale rock and coal have been developed at different times and different countries, some of which actually predate the development of the present petroleum based fuel industry. In this section of the report, a brief general history and overview of shale and coal synthetic fuel developments is presented. A detailed analysis of current technology, resource availability and nature of synthetic liquid products is contained in other sections of this report.

In the late sixteenth century and early seventeenth century, the depletion of the once extensive forests used for the production of charcoal for ironmaking led to the development of processes for the production of coke from coal(1-3). In these carbonization processes, the coal was heated in ovens in the absence of added air to produce coke, the earliest form of a coal pyrolysis process. The development of coal pyrolysis processes for the production of illuminating gas began in the eighteenth century. Pitch and tar were often recovered as by-products. Coal tar was used in England to replace American wood tar during the American Revolution. It was not until the middle of the nineteenth century, however, that liquid by-products were generally recovered from coal pyrolysis processes, producing low yields by present standards of light aromatics and coal tars chemicals. The resultant coal derived benzene, toluene, naphthalene, anthracene, phenol, cresols and aniline became the basis for the modern chemical industry, starting with the development of the dyestuff industry in Germany. During World War I coal pyrolysis processes provided both toluene for TNT production and phenol for picric acid production.

Work on the direct hydrogenation of coal under presure was undertaken in Germany starting in 1913(1), and extensive liquefaction research was conducted in Germany during the 1920's and 1930's(4). Coal liquefaction research was carried on in the U.S. during the 1930's and again in the late 1940's and early 1950's(4).

Coal derived liquids may also be produced via the Fischer-Tropsch process where the coal is first gasified to carbon monoxide and hydrogen(5). In 1902, Sabatier and Senderens first reported the synthesis of a hydrocarbon, i.e., methane, by the reaction of carbon monoxide and hydrogen over nickel. In 1913, Badische-Anilin and Soda-Fabrik patented the possibility of producing liquid hydrocarbons and other chemicals such as alcohols, ketones, aldehydes and fatty acids by reacting carbon monoxide and hydrogen over various catalysts. Similarly in 1923, it was discovered that by the use of the proper catalyst and conditions, carbon monoxide and hydrogen can be selectively reacted to essentially only methanol. This work was the forerunner for the present and proposed processes to produce methanol from either natural gas or coal (after conversion to carbon monoxide and hydrogen).

The only present commercial process to produce liquids from coal is in South Africa at the SASOL plant(6). The coal is first gasified to carbon monoxide and hydrogen and then reacted to liquids using Fischer-Tropsch type catalytic processes. Products produced include gasoline, diesel oil, kerosine and waxes. In 1955, its production was indicated at approximately 5,000 bbl per day(6), but was expanded in 1966(7). A number of countries had Fischer-Tropsch processes to produce synthetic liquids, which, however, are not now commercially active(5,8). These processes were operated in France in 1937 (1,000 bbl/day) and in Japan in 1938 (two plants for a total production of 2,500 bbl/day) and in Germany starting in the 1930's (production from nine plants reached a high of 18,000 bbl/day during World War II). Processess for the direct hydrogenation of coal to liquids were built in England in 1935, and in Germany starting in the late 1920's(9,10). The English plant was designed to operate on both coal or creosote oil produced from coal but switched completely to creosote oil during World War II because of bomb hazards. At its peak production in 1941, it produced approximately 5,000 bbl/day of gasoline(9). The largest commercial coal hydrogenation industry to date existed in Germany during World War II where it has been estimated that up to half of Germany's total oil requirements and all of her aviation gasoline were synthesized from coal. Total production from 12 plants using either coal or coal derived tar and pitch was approximately 100,000 bbl/day(9,10).

Shale rock deposits are widely distributed, and the earliest processes involving the pyrolysis of shale rock to produce liquids predates the industrial revolution(12). During the nineteenth century, a wide spread shale oil industry developed replacing whale oil as an illuminant only to itself to be replaced by petroleum. Intermittent and now terminated shale oil industries include those in France starting in 1858, Scotland in 1850, Australia in 1865, Brazil in 1881, New Zealand in 1900, Switzerland in 1915, Sweden in 1921, Spain in 1922 and South Africa in 1935(12-14). It is interesting to note that the Scotish oil-shale industry spanned approximately a hundred years, and in 1890 produced approximately 8,000 bbl/day of synthetic product(14).

At present, commercial shale oil processes are only operated in the U.S.S.R. and in China(12,15). The U.S.S.R. based shale oil industry was established in Estonia in 1921, operated continuously since then, and was expanded by the Russians after World War II(15). The Chinese based oil shale industry was established in Manchuria in 1929, expanded both by the Japanese during World War II and the Chinese during the Korean War and several years ago estimated at approximately a 44,000 bbl/day size(13). Early Estonian emphasis on shale products was for use only as fuels (gas or furnace oil). More recently, U.S.S.R. emphasis is on the production of chemicals(15). Estonian production was cited as 25 million tons in 1973(16), which would be equivalent in size to approximately a 48,000 bbl/day operation (assuming it were all converted to liquids with 30 gallon per ton yield). Products from the U.S.S.R. shale operations include fuel oil, diesel fuel, kerosene, asphalt, benzene, toluene, xylene and specialty products such as solvents, drying oils and paints. The Russian shale oil industry is supported by an active R&D effort.

Major shale rock deposits exist in Brazil and it has been stated that Brazil will establish a commercial sized shale industry(17-18). West Germany has also indicated interest in establishing a shale oil industry(19).

It can be seen that processes for the production of liquids from shale rock and coal have been operated in a number of countries in the world, and actually predate the development of the present petroleum industry. A tar sand process has also been developed, thus, there is no basic technological barrier to the development of coal,shale and tar sand conversion processes by resource owning countries. Because of the difficult solids handling problem it would appear that liquefaction processes, particularly shale rock and tar sand processes, will be located near the source of feed material. Thus, for the purposes of this study, it will be assumed that coal and shale rock derived liquid fuels will be potentially produced in any country possessing the basic resources.

The availability of coal, shale and tar sand resources is discussed in detail in the following section. The U.S. and world reserves of both shale rock and coal are very large. The U.S. contains approximately two-thirds of the world's oil shale reserves. The only other country with shale reserves approaching this magnitude is Brazil which has approximately one-quarter of the world's reserves. Significant deposits, however, are found in the U.S.S.R., China, Canada, Sicily and Africa The major world coal reserves are in the U.S. (approximately one-third) and the U.S.S.R. and China (approximately one-quarter each). Other countries with significant reserves include Germany, U.K., Poland, India, Union of South Africa, Australia and Canada. Tar sand reserves are much smaller than either coal or shale reserves and are essentially found only in two countries (approximately 80% in Canada with the rest in Venezuela).

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3.2 Discussion of Major Synthetic Fuels

3.2.1 Coal and Shale Derived Synthetic Crudes

3.2.1.1 Resource Availability

World and U.S. coal and shale resources are large compared to petroleum. The oil shale resources of the U.S. are very large. The crude oil equivalent of oil shale reserves is approximately 2,000,000 million barrels with about 77,000 million barrels or more that may be easily recoverable (1). The coal reserves are even larger: 1,600,000 million tons with 150,000 million tons minable with present technology (for a detailed discussion see reference 2). These numbers may be compared with the projected U.S. energy consumption of 70,000 million tons of coal equivalent or 300,000 million barrels of crude oil equivalent for the years from 1975 to 1990 (3).

3.2.1.1.1 Coal

Estimated world remaining coal reserves are shown in Table 1, taken from a report of the U.S. Geological Survey by Paul Averitt. Here "producible coal" is based on recoverable reserves defined as "reserves in the ground, as of the date of the estimate, that past experience suggests can actually be produced in the future." These are taken as being seams of 14 in. and upwards in thickness, and at depths not greater than 3,000 ft, and 50% recovery is assumed. The world total of 2.3 million metric tons of producible coal on this basis is somewhat less than that suggested by the World Power Conference, but is still equivalent to 920 times 1965 world consumption.

Total U.S. reserves of coal of all ranks are estimated at 1,567,000 million tons, based on USGS data as of January 1, 1965. Figure 1 shows the location of coal reserves and Table 2 shows the production, reserves and sulfur content of U.S. coals by state (from reference 4). Approximately two-thirds of the estimated reserves may be considered low sulfur coals, largely because more than one-half of the total is composed of low-rank coals (subbituminous and lignite) which generally contain 1 percent or less sulfur. Most of these reserves are in areas in the Western United States which are not highly industrialized, and original reserves of these coals, unlike those in the East, remain virtually intact.

All of the lignitic coal reserves, with the exception of small deposits in Alabama, are situated west of the Mississippi River; about 98 percent of the total is located in North Dakota and Montana.

Reserves of subbituminous coal also are concentrated in the Western States, with about 60 percent of the total occurring in Montana and Wyoming. Most of the remainder is in Alaska, New Mexico, and Colorado. The subbituminous coals generally are low in sulfur, although there are some instances in Montana where sulfur is as high as 2 percent.

Table 1

Estimated Remaining Producible Coal Reserves of the World (1)

Region and Country	Producible Coal 10^9 Metric Tons	Percent of Regional Total	Percent of World Total
Asia			
U.S.S.R.	600	52.3	25.8
China	506	44.1	21.8
India	32	2.8	1.4
Japan	5	0.4	0.2
Others	4	0.4	0.2
Total	1,147	100.0	49.4
North America			
United States	753	94.4	32.5
Canada	43	5.4	1.8
Mexico	2	0.2	0.1
Total	798	100.0	34.4
Europe			
Germany	143	47.5	6.2
United Kingdom	85	28.2	3.7
Poland	40	13.3	1.7
Czechoslovakia	10	3.3	0.4
France	6	2.0	0.3
Belgium	3	1.0	0.1
Netherlands	2	0.7	0.1
Others	12	4.0	0.5
Total	301	100.0	13.0
Africa			
Union of South Africa	34	97.1	1.5
Others	1	2.9	
Total	35	100.0	1.5
Australasia			
Australia	29	99.0	1.3
Others		1.0	
Total	29	100.0	1.3
South and Central America			
Colombia	6	60.0	0.2
Venezuela	2	20.0	0.1
Others	2	20.0	0.1
Total	10	100.0	0.4
World Total	2,320		100.0

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(1) Source: P. Averitt, U.S. Geol. Survey Bull., 1136, January 1960.

Figure 1

Map Showing Location of Coal Reserves

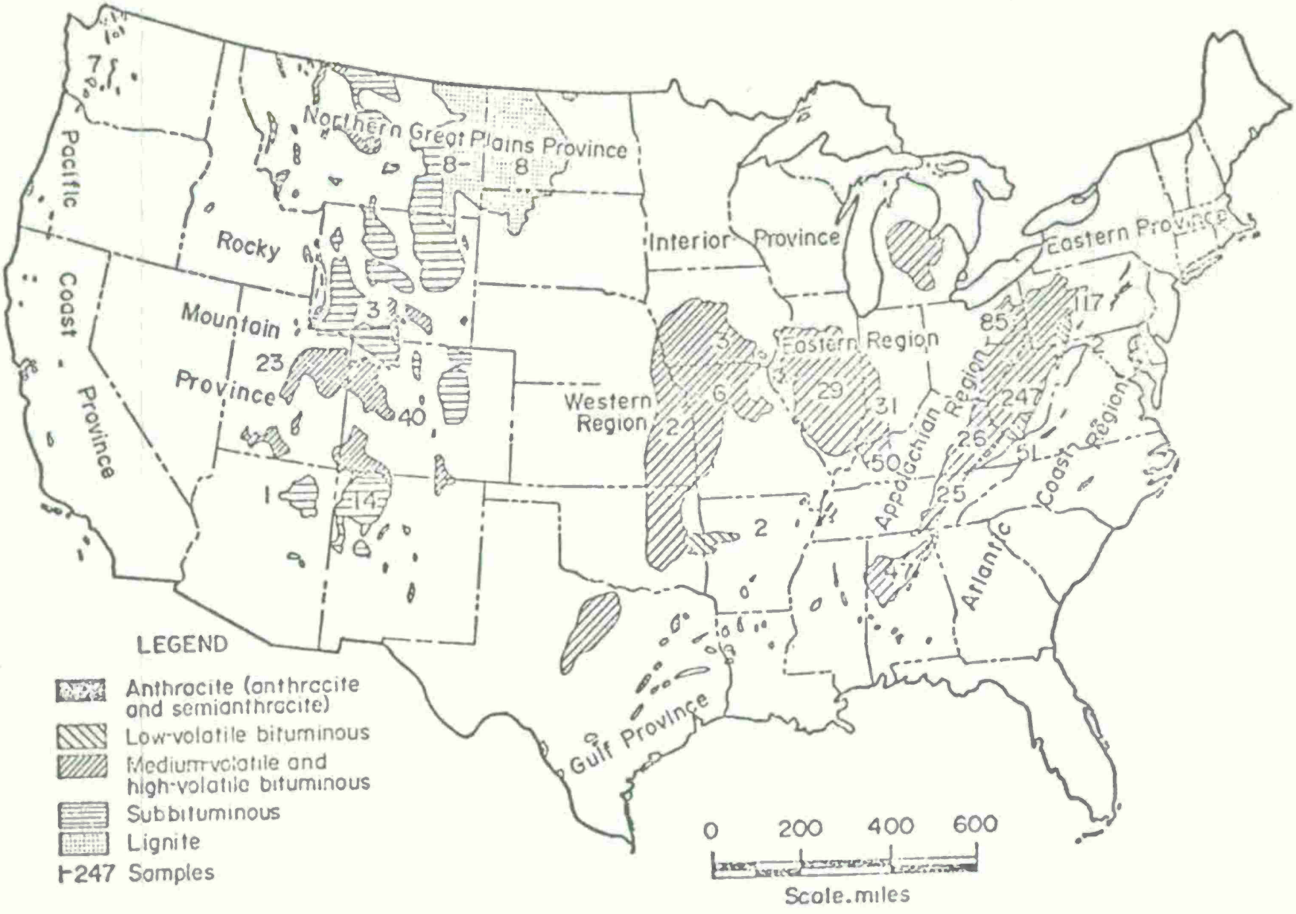

Table 2

Sulfur Content of U.S. Coals by Region(1)

Region and States	Production(2) (M Tons) 1969	Production(2) (M Tons) 1970	Estimated Remaining Reserves (Million Tons) 1965	Bituminous	Sub-Bitum	Lignite	Anthracite	Average for State	Average for Region
Appalachian									1.8
Alabama	17,456	20,560	13,597	1.5	0.5	1.3	0.5	1.5	
Georgia	NA	NA	76	.9				.9	
E. Kentucky	61,584	72,502	29,414	1.0				1.0	
Maryland	1,368	1,615	1,180	3.1				3.1	
Ohio	51,242	55,351	42,024	3.4				3.4	
Pennsylvania	89,104	90,220	70,162	2.6			0.5	2.0	
Tennessee	8,082	8,237	1,859	2.0				2.0	
Virginia	35,555	35,016	10,155	0.9			0.5	0.9	
W. Virginia	141,011	144,072	102,666	1.4				1.4	
Interior Eastern									3.4
Illinois	64,772	65,119	135,889	3.5				3.5	
Indiana	20,086	22,263	34,841	2.9				2.9	
W. Kentucky	47,466	52,803	36,895	3.5				3.3	
Michigan	NA	NA	205	3.8				3.8	
Interior Western									3.7
Arkansas	228	268	2,396	1.5		0.6	2.1	1.5	
Iowa	903	987	6,522	4.5				4.5	
Kansas	1,313	1,627	20,738	3.6				3.6	
Missouri	3,301	4,447	78,760	4.2				4.2	
Oklahoma	1,838	2,427	3,302	2.0				2.0	
Texas	NA	NA	14,880	2.3		1.3		1.8	
Western									.8
Arizona		132							
Colorado		6,025	80,754	.7	.6		0.9	.7	
N. Mexico	4,471	7,361	61,427	.7	.6		0.9	.6	
Utah	4,657	4,733	27,808	1.4	1.3			1.4	
Washington	58	37	5,885	.7	.6	0.9	0.5	.6	
Wyoming	4,602	7,222	120,722	.7	.9			.8	
Northern Plains									.6
Montana	1,020	3,447	221,702	2.6	.6	.7		.7	
N. Dakota	4,704	5,639	350,698			.6		.6	
S. Dakota	NA	NA	2,031			.9		.9	

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(1) Based on USBM I.C.8312, Sulfur Content of U.S. Coals (1966).

(2) USBM Minerals Yearbook-1969 and Preprint-1970.

Of higher rank or bituminous deposits, about two-thirds are located in the states east of the Mississippi River. The coal fields or deposits in Illinois, Indiana, and western Kentucky contain 29 percent of the estimated remaining bituminous-coal reserves, but Illinois alone has the largest bituminous reserves of all states.

The Appalachian Region, which stretches northeastward from Alabama through Tennessee, Virginia, West Virginia, Ohio, and Pennsylvania, is the largest depository of high-rank bituminous coal, with approximately 31 percent of the total remaining reserves. One of the characteristics of the Appalachian Region coals which enhances their value is their ability to coke or agglomerate when heated in the absence of, or with a limited supply of, air. All of the coals are not used for cokemaking, however, because some contain more sulfur than is desired for metallurgical-grade coke. We have more information on the quality of these coals than for any other region in the country. This is due to the many analyses of the coals made by Federal and State agencies in connection with use of these coals, not only for cokemaking, but for light, power, and heat in the industrial, commercial, and residential sectors of the economy. West Virgina ranks second of all states in total bituminous-coal reserves, but first in reserves of bituminous coal among the states in the Appalachian Region. Pennsylvania ranks second among the states in the Applachian Region and third of all states in reserves of bituminous coal.

Deposits of anthracite and semianthracite occur in seven states, but more than 80 percent of the reserves of this rank is found in northeastern Pennsylvania. The sulfur content of Pennsylvania anthracite is generally under 1 percent, with a large proportion of the reserve averaging between 0.6 and 0.7 percent. The small semianthracite coal reserves of Virginia are also low in sulfur, but the Arkansas deposits of semianthracite are relatively higher, ranging from about 1.4 to 3 percent.

When consideration is given to the production of synthetic fuels from coal, the size of the required mine must be kept in mind. To produce 50,000 barrels per day of synthetic crude oil requires approximately 20,000 tons per day of coal. A mine to produce this much coal would require reserves sufficient for approximately 20 years. There are at least 176 such potential mines in the U.S. (5) and probably, if a search were made, many more.

3.2.1.1.2 Shale

Major shale oil world reserves are shown in Table 3. The term oil shale covers a wide variety of fine-grained sedimentary rocks that contain organic material. Upon destructive distillation, much of this organic material is released largely as an oil which is termed shale oil. The rock is only slightly soluble in organic solvents and frequently does not appear or feel oily. It is tough, elastic, resistant to fracture and has essentially no permeability or porosity.

Table 3

Major Shale Oil Reserves(a)

Country or Area	Oil in Place, Million bbl(b)
Argentia	400
Australia (including Tasmania)	270
Brazil	800,000
Balkans and Other Central Europe(c)	340
Burma	2,000
Canada	50,000
Chile	20
China	
Fushun, Manchuria	2,100
Other Deposits	26,000
England	1,000
France	425
Germany (West)	2,000
Israel	20
Jordan	45
Sicily	35,000
Luxembourg	700
New Zealand	560
Republic of the Congo	100,000
Republic of South Africa	130
Scotland	580
Spain	280
Sweden	2,500
Thailand	800
United States	2,200,000
U.S.S.R.	
Estonia and Adjacent Leningrad Area	22,000
Other European U.S.S.R.	13,000
Siberia	80,000
Total	3,340,170(d)

(a) Source: L. W. Schramm and J. D. Lankford, U.S. Bureau of Mines Bulletin 630 (1965).

(b) Conversion to barrels of 42 U.S. gallons each is based on shale oil having an assumed specific gravity of 0.92 at 60°F (27.8°C); for an oil of this gravity, one barrel weighs 322 lb.

(c) Includes Bulgaria, Yugoslavia, Albania, Greece, Czechoslovakia, Austria, and Switzerland.

(d) This compares with 12,500 million barrels of world reserves of petroleum.

The organic component of oil shale can be divided into 2 parts, a part that is soluble in organic solvents and a part that is not. It is the insoluble part, generally termed kerogen, which constitutes the bulk of the shale organic matter responsible for shale oil. The composition of kerogen varies considerably from shale deposit to deposit but it is thought to consist of largely cyclic polymeric material probably held together by cross linkages involving hetero atoms such as nitrogen, sulfur and oxygen.

There is no truly typical shale oil but shale oils have some properties in common. In general, most shale oils are black, waxy and possess high pour points. Relative to conventional crude oils, the nitrogen content of crude shale oil is high although the sulfur level is moderate.

Oil shales are widely distributed geographically. However, only certain deposits are considered to be sufficiently rich in kerogen to warrant commercial development. In the U.S. oil shale deposits are found in Tennessee and Nevada but the most important are in the Green River Formation of Colorado, Utah and Wyoming (Figure 2). The Green River Formation has received attention as a possible source of fuels. Within this formation, shale deposits underlie an area of 17,000 square miles in four basins: the Piceance Creek basin of Colorado, the Unita basin of Utah and the Washakie and Green River basins of Wyoming.

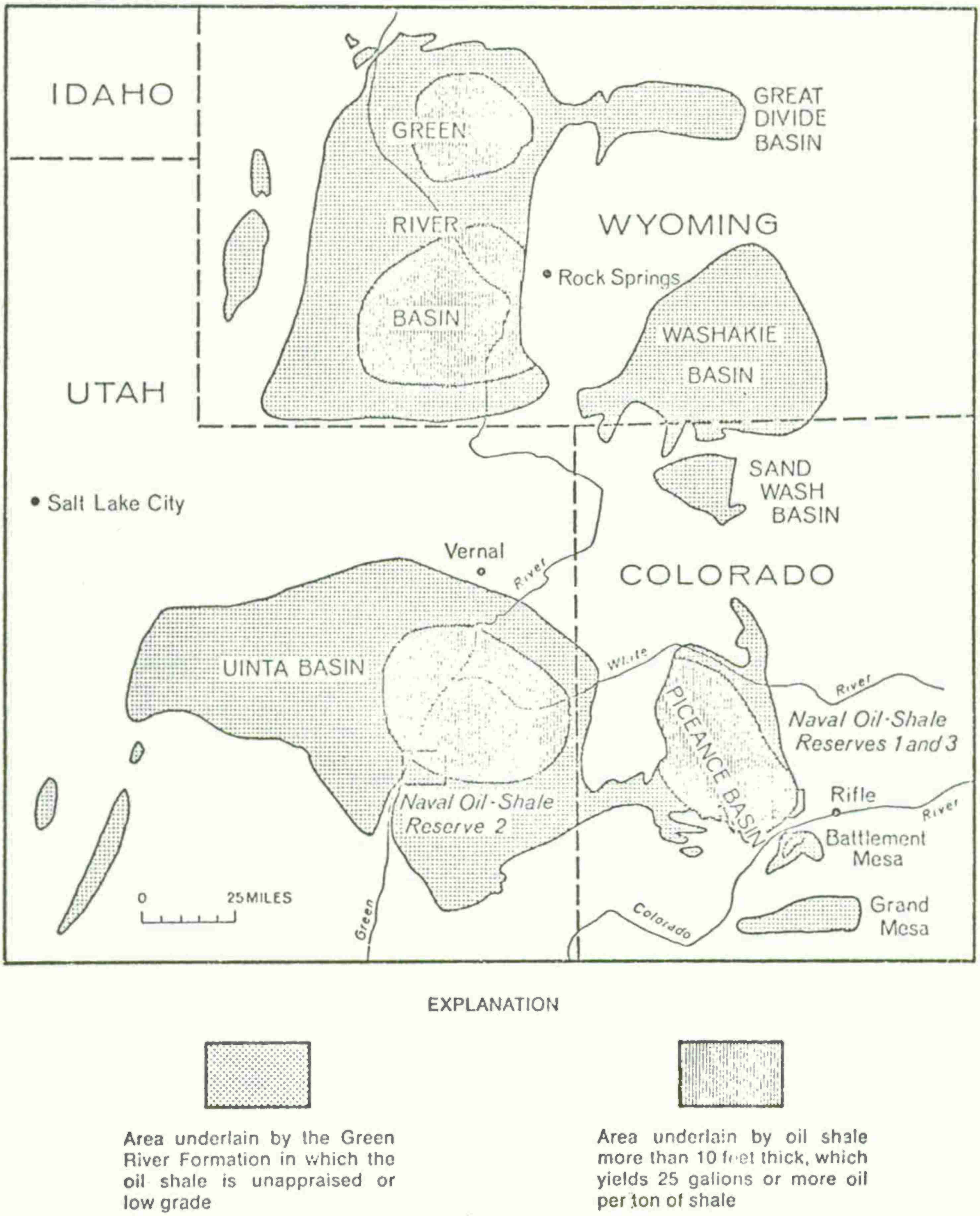
The energy potential of the Green River formation has been estimated to be approximately 1.8 trillion barrels of oil with easily recoverable reserves of 77 billion barrels (2b, 6)(See Table 4). Shale deposits vary in accessability from those at the surface to very deeply buried shales in the Unita basin. The outcrop called the Mahogany Ledge (because of its color) is the location of an experimental mine and consequently has been used to study mining and retorting methods. Most U.S. elemental shale oil analyses come from shale mined here. The oil shales of the Mahogany zone will probably be the first to be developed commercially.

Table 5 presents sulfur and nitrogen data of crude shale oil obtained from shale deposits throughout the world (4). While many of the samples were retorted using different techniques, it has been found that generally the retorting method utilized has relatively little effect on the characteristics of the oil produced unless extreme retorting conditions have been employed (7). Of the deposits listed, only the Green River Formation can be considered to be a possible commercial source of fuels for consumption in the U.S.

Crude shale oil derived from the Green River Formation possesses an unusually high nitrogen level. It has been found that generally the nitrogen content is higher and the sulfur level lower in the higher boiling shale oil fractions. As of this writing, no metal content data for shale oil appear to be available in the published literature. The metals content

Figure 2

Distribution of Oil Shale in the
Green River Formation, Colorado, Utah and Wyoming



Source: Geological Survey Circular 523

Table 4

Summary of Oil Shale Resources and Reserves
Green River Formation - Colorado, Utah and Wyoming

(Billions of Barrels)

	Resources					Reserves @ 60% Recovery			
Location	Class 1	Class 2	Class 3	Class 4	Total	Class 1	Class 2	Class 3	Total
Piceance Basin									
Colorado	34	83	167	916	1,200	20	50	100	170
Uinta Basin									
Colorado & Utah	--	12	15	294	321	--	7	9	16
Wyoming	--	--	4	256	260	--	--	2	2
TOTAL	34	95	186	1,466	1,781	20	57	111	188

Table 5

Sulfur and Nitrogen Content of Crude Shale Oils**

Country	Formation/Location	Sulfur, weight per cent	Nitrogen, weight per cent
United States	Green River, Colorado	0.74	1.78
	Green River	0.69	2.13
	Green River	0.77	1.57
	Green River	0.51	2.10
	Green River	0.67	1.97
	Green River	0.72	1.73
	Green River	0.71	1.89
	Green River	0.64	1.95
	Green River*	1.10	1.73
	Green River	0.66	1.76
	Green River	0.59	1.96
	De Kalb County, Tenn.	3.38	0.88
Australia	Glen Davis, N.S.W.	0.56	0.52
Brazil	Paraiba Valley	0.41	0.98
China	Hwatien Mine, Manchuria	0.19	0.84
Estonia	Kukersite	1.10	0.10
France	Autun	0.51	0.90
	Severac	3.00	0.53
	Severac	3.40	0.65
	St. Hilaire	0.61	0.54
Israel	Um Barek	6.2	1.40
Lebanon	--	1.5	0.6
New Zealand	Orepuki	0.64	0.60
Scotland	--	0.35	0.77
South Africa	Boksburg, Transvaal	0.64	0.85
	Breyten, Transvaal	0.61	--
Spain	Puertollano	0.40	0.68
Sweden	Kvarntorp	1.65	0.68
Thailand	Maesod Area	0.41	1.10

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* Core drilling sample.

** From Ref. 4.

of the crude is of importance in catalytic processing. An unpublished analysis by the Bureau of Mines of shale oil obtained from Green River shale indicates that this oil is high in iron and low in vanadium and nickel. The results obtained were: vanadium, 0 ppm; nickel, 4 ppm; and iron 67 ppm (8). Most of the metals were associated with the asphaltene fraction.

The nitrogen compounds present in shale oil are particularly troublesome in processing and must be removed before shale can be converted into useful liquid or gaseous fuels. Nitrogen removal can be accomplished by severe hydrogen treatment which also reduces the sulfur content to a low level.

3.2.1.2 Present Status of Conversion Processes

The paragraphs below summarize the present status of processes for the liquefaction of coal and shale.

3.2.1.2.1 Coal Liquefaction Processes

The known processes for producing liquid fuels from coal can be grouped into five broad categories: direct hydrogenation, donor-solvent extraction, Fischer-Tropsch synthesis, pyrolysis and solvent refining. Examples of these categories are discussed below.

3.2.1.2.1.1 Direct Hydrogenation Processes

The direct hydrogenation of coal in the presence of a solvent and catalysts was developed in Germany prior to World War II. In this country the Bureau of Mines built and operated a 50 ton per day coal pilot plant from 1949 to 1953 at Louisiana, Missouri. The project died due to indicated unfavorable economics.

Of more recent interest is the H-coal process of Hydrocarbon Research, Incorporated, an adaption of HRI's H-Oil process. The process differs from previous hydrogenation processes in that lower pressure operation can be used, (2500 to 3500 vs. 6,000 to 10,000 psig) and also the H-Coal process uses a fluidized bed comprised of finely ground coal, catalyst solvent, coal extract and hydrogen gas for both liquefaction and upgrading the coal extract (see, for example, reference 9). This process produces 2-3 barrels of crude liquid per ton of coal and has been studied through a pilot stage that handles three tons of coal per day. As in most liquefaction processes, project H-Coal proposes conventional petroleum refinery operations to convert the crude liquid to saleable distillates. Compared to petroleum, the liquid products from coal contain more aromatic and larger amounts of nitrogen and sulfur compounds, thus it is possible that more severe treatment would be necessary for these liquids than conventional petroleum liquids. However, it should be possible to treat tar from coal hydrogenation, and liquefaction in a manner similar to the treatment of petroleum resids.

The Bureau of Mines is developing a process for the hydrogenation of coal (see, for example, reference 10). In this process, hydrogen is reacted with fine coal particles in a fixed catalyst bed at 2000-4000 psi and elevated temperatures. The reaction is carried out under highly turbulent conditions over a cobalt-molybdate catalyst. The expressed aim of the present work is to produce a fuel oil without the use of the excess hydrogen needed to produce a complete synthetic crude.

3.2.1.2.1.2 Donor-Solvent Extraction Processes

Donor-solvent extraction of coal has been under investigation for some time and was also applied in Germany on a semi-commercial scale (Pott-Brocke process, early 1940's). This process differs from direct hydrogenation in that hydrogen is transferred to the coal from an aromatic solvent (itself a coal extract) rather than from gaseous hydrogen. Additional hydrogen is added to the coal extract by catalytic hydrogenation of the filtered extract. In this country Consolidation Coal Company has built a 75 B/D donor type pilot plant at Cresap, West Virginia, under an Office of Coal Research Contract.

The Consolidation Coal Company-donor type process, Project Gasoline (11), had as its objective the conversion and upgrading of coal to gasoline The process consists of solution of coal in a coal-derived solvent followed by separation of the liquid extract from the solid mineral matter. The solid mineral matter is treated to recover solvent and the liquid material is hydrogenated to produce a synthetic crude suitable for processing to saleable liquid fuels via conventional petroleum refining processes. The high H/C ratio in the final product requires additional capacity for manufacturing hydrogen. The Cresap, West Virginia, plant is not currently being operated and Project Gasoline is dormant.

3.2.1.2.1.3 Fischer-Tropsch Synthesis

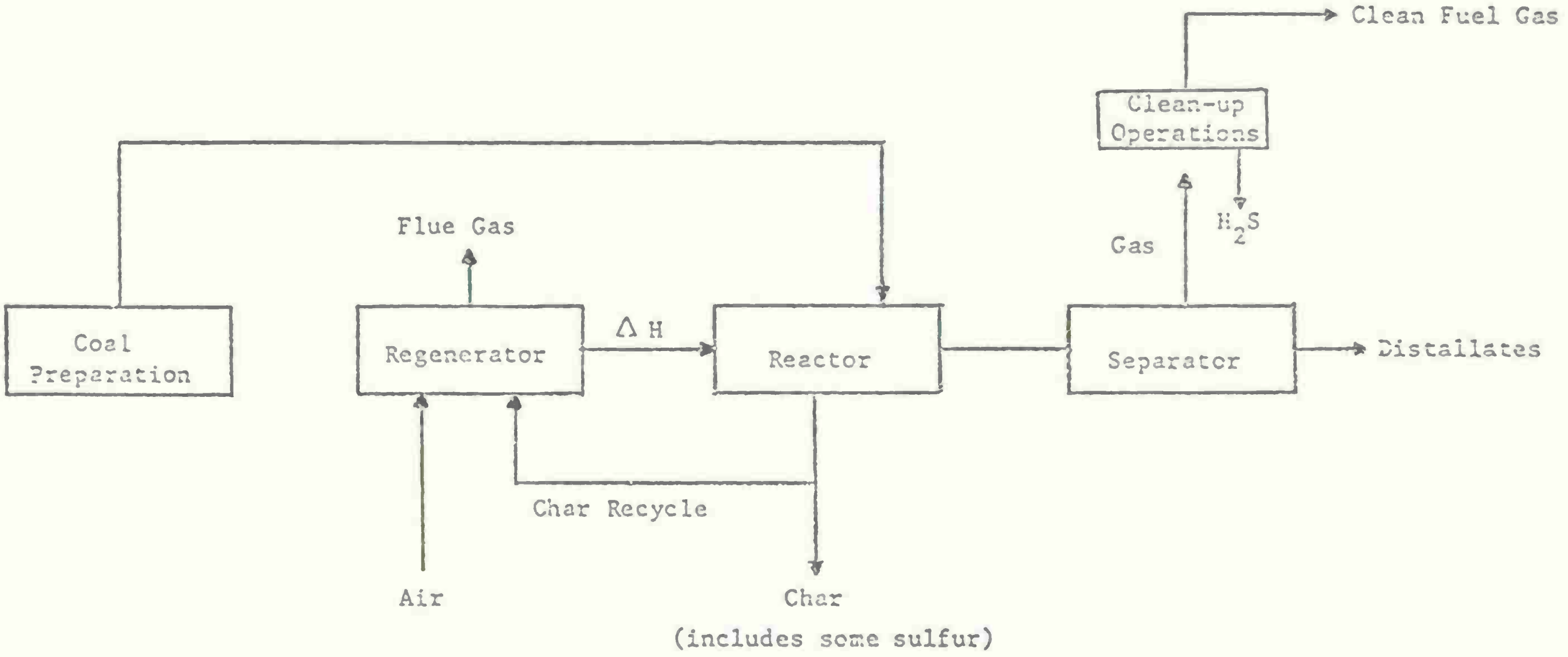
The Fischer Tropsch process for hydrocarbon synthesis is based on gasifying coal to CO and H_2 (synthesis gas) and then reacting these to form hydrocarbons and oxygenated organic compounds. The first commercial plants went into operation in Germany in the period 1936-1939. Others were built during World War II. More recently, the South African State Oil Company started up a facility in 1955 which processes about 1000 tons per day of soft coal to produce both chemicals and fuels. The economics of Fischer-Tropsch synthesis for fuel products are generally considered unfavorable.

3.2.1.2.1.4 Pyrolysis of Coal

An excellent discussion of pyrolysis of coal is contained in reference (12), pgs. 340-674. Hundreds of different types of pyrolysis processes have been proposed and no attempt will be made to go into detail on these. A generalized scheme of pyrolysis processing is shown in Figure 3.

Figure 3

Pyrolysis Processing Sequence



Pyrolysis is presently used commercially in the U.S. to produce coke and coal tar derivatives. Processes involved in this category involve the supply of heat to the coal in order to volatilize and thermally rearrange the hydrocarbon constituents into a fraction relatively rich in hydrogen and a high carbon solid fuel residue. Sulfur is removed either as H_2S from the gas clean-up stage or as a contaminant in the char.

Atlantic-Richfield, under an OCR Contract, did the work on Project SEACOKE, a process in which coal is fed along with oil to petroleum fluid coking units, and the volatile fractions are separated and handled in conventional petroleum refining processes. This process produces solid fuels (coke or char) which can be used as boiler fuel and a liquid product which requires considerable hydrogenation for upgrading.

The FMC Corporation is developing Project COED (Char Oil Energy Development). (See, for example, reference 13). In this multi-stage pyrolysis operation, coal is crushed to a proper size and fed to a series of fluidized bed reactors. Volatiles are recovered by cooling the vapors. The char is extracted at a high temperature from the last stage where its partial combustion with oxygen produces enough hot gases to provide the required heat for the prior stages. This process can be operated to produce pipeline quality gas, liquid fuels, and a low-sulfur char. A 30 T/day pilot plant for demonstration of this process has been constructed and successfully operated for several years. A comparison has been made of desulfurization, denitrification and demetallization of that plant with previous hydrogenation studies (14). A number of processes utilizing fluidized carbonization of coal have been piloted (12, pg. 431).

3.2.1.2.1.5 Solvent Refined Coal

A process for producing a deashed partially desulfurized, "meltable," solid fuel from coal is being investigated by Pittsburgh and Midway Coal Mining Co. under sponsorship of OCR (15,16). A pilot plant has been approved to gather data for further economic and process evaluation. The process uses thermal hydrogenation to liquefy the coal so that the solid ash and unconverted residue can be filtered from the product which is then solidified. Although the product is solid at room temperature, it could theoretically be converted to oil refining type products.

Other organizations are developing coal liquefaction processes. For example, Esso Research and Engineering Company has announced the construction of large pilot unit facilities to liquefy coal by a proprietary process (17).

The suitability of these processes for producing a material that can be up-graded to a particular product has not been investigated in detail. More specifically, no optimization has been made of these processes in an integrated oil refinery producing multiple products.

3.2.1.2.2 Shale Oil Processes

No free world commercial processing plants for the treatment of shale are in operation, although the Department of the Interior has opened bidding on land leases for shale and two bids have been accepted. However, two general approaches are being pursued for the removal of kerogen from the rock. One of these involves underground processing or retorting; its practicality has yet to be demonstrated. The second involves conventional mining followed by above ground retorting. Mining technology is available and prototype retorts for extraction of the kerogen have been tested. A classification of oil shale retorts is given in reference (18) and a description of a number of processes is given in reference (6). The three above ground retorting processes which are most highly developed are (1) the TOSCO hot ceramic ball process which has been operated in a 1000 ton/day pilot facility at Parachute, Colorado; (2) the Bureau of Mines Gas Combustion retort which was developed in the 1960's at Anvil Points, Colorado; and (3) the Union Oil Company process. These retorts are essentially ready for commercial application. A generalized processing scheme is shown in Figure 4.

Currently there is a USN-DOI program to determine the performance capabilities of "military operational fuels" produced from shale liquids obtained from the Parahoe facility at Anvil Points.

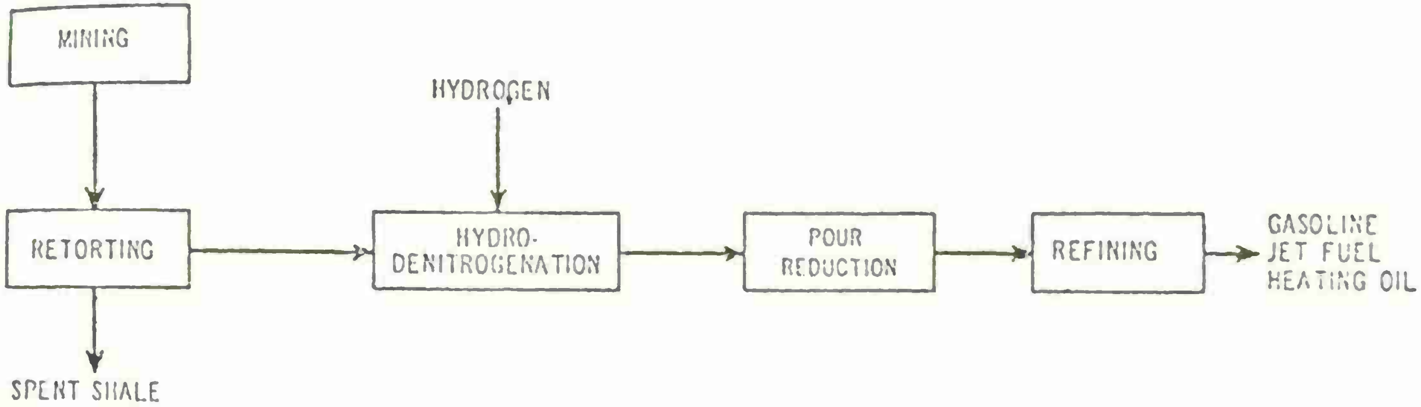
3.2.1.2.2.1 TOSCO II Process

The TOSCO II retorting process was developed by a joint venture between the Oil Shale Corporation, Standard Oil of Ohio and Cleveland Cliffs Iron Company (7).

The retort is a rotary kiln type utilizing externally heated steel balls (1300°F) to accomplish the retorting. Crushed shale of minus 1/2 inch is used and the fines are not removed as they are not detrimental to the operation of the retort. The shale feed is preheated and conveyed through a vertical pipe by flue gases from the ball heating furnace. The preheated shale enters the kiln and is brought up to a retorting temperature of 900°F by contact with the hot balls. A trommel is used to separate the spent shale from the balls which are cycled for reheating. Hydrocarbon vapors flow through a centrifugal separator at the top of the collecting vessel and through an electrostatic precipitator and are then cooled and the liquid sent to a run down tank. After cooling, the liquid and gas products are pipelined to an upgrading facility. Excellent oil recoveries and high shale throughput rate have been reported for this process.

Figure 4

Shale Oil Processing Sequence



3.2.1.2.2.2 Bureau of Mines Process

This process was developed by the Bureau of Mines and has its facilities located at Anvil Point, Colorado (19-21). This pilot plant was set up to demonstrate that low cost shale oil was recoverable from shale. The retort used by the Bureau is a vertical vessel through which crushed shale (a process disadvantage is that shale fines cannot be used) moves downward by the action of gravity. Recycle gas is introduced at the bottom of the retort and is heated by the hot retorted shale as is passes upward through and then exits from the retort. Combustion of a portion of the gas and residual carbon on the spent shale is used to heat the raw shale (1600-1800°F). The upward moving shale oil vapors and gases are cooled by the incoming shale and exit from the top of the retort as a mist. The economics of the process benefit greatly from the fact that it does not require cooling water. High thermal and retorting efficiencies are achieved by the novel manner in which retorting, combustion, heat exchange, and product recovery are carried out.

The crude oil from the retort is too viscous to be pipelined and contains too much sulfur and nitrogen to be processed in a conventional refinery, therefore, it must be upgraded at a nearby plant.

3.2.1.2.2.3 Union Oil Company Process

This process which was developed by Union Oil Company combines an internal combustion retort with a circulating hot gas retort (7). Heat in the combustion retort is supplied by combusting a portion of the organic matter remaining on the retorted shale before the shale leaves the retort and the hot combustion gases are used internally to retort the crushed raw shale. This combustion retort differs from the Bureaus of Mines in that the shale enters at the bottom of the retort. The recycle retort is similar to the combustion retort, but the shale is retorted by hot gas circulating through the retort and an external heater. By balancing the relative amounts of shale processed in each type of retort, fuel gas generation in the combustion retort is used to heat the gas circulated through the recycle retort. The combination of combustion and recycle hot gas retorts allows efficient use of the low Btu gas formed but does require the use of water to cool the spent shale.

3.2.1.2.3 Composition of Raw Products

3.2.1.2.3.1 Synthetic Crude Oils from Shale

Oil shale, as found in the U.S. deposits, is a fine grained, tight rock with very little porosity. The organic matter, which is the source of a synthetic crude from this material, is embedded in the rock and, on the average, comprises about 14% by weight of the shale structure. A typical ultimate chemical composition of the organic fraction of raw shale is as follows(22):

Element	Composition, Weight %
Carbon	81
Hydrogen	10
Nitrogen	2
Sulfur	1
Oxygen	6
Total	100

From a molecular standpoint, the organic fraction of shale is largely comprised of high molecular weight heterocyclic compounds, isoprenoid hydrocarbons, porphyrins and other complex hydrocarbon molecules. As a result, it is a solid with very low solubility in organic solvents. In order to convert this material into a "synthetic crude", it is necessary to subject the organic shale fraction to a destructive distillation or retorting process which thermally decomposes the large molecules into fragments, producing liquid and gaseous products.

The physical properties of the synthetic crude oil produced by the different retorting processes can vary considerably. This is shown in Table 6. In general, the properties of shale oil differ quite markedly from those of a good quality U.S. crude oil being generally heavier, more viscous and possessing higher pour points. In addition, sulfur and nitrogen levels are generally much higher than domestic petroleum crudes. This can be seen in Table 7 which summarizes the sulfur and nitrogen levels of several synthetic crudes produced by retorting Colorado shale.

Table 6

Physical Properties of Synthetic Crude Oils Produced from Shale

Retort Process*	Synthetic Crude Physical Properties Gravity ° API	Pour Point °F	Viscosity at 100°F SSU
N-T-U	19.8	90	280
Pumpherston	25.7	60	50
Gas Flow	16.0	70	660
Royster	19.7	90	230
Gas Combustion	18.6	85	310
High Temperature (1,200°F)	16.5	60	47
High Temperature (1,500°F)	1.6	<5	62
Royster - T.V.A.	9.3	<5	220
Typical Midcontinent Crude Oil	39.0	5	45

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* All crudes produced from Colorado Oil Shale except that produced in the Royster - T.V.A. retort which was from Tennessee shale.

Table 7

Sulfur and Nitrogen Levels of Synthetic Crude Oils Produced from Shale

Retort Process*	Synthetic Crude Sulfur and Nitrogen Content Sulfur Wt. %	Nitrogen Wt. %
NTU	0.7	1.8
Pumpherston	0.8	1.6
Gas Flow	0.6	2.1
Royster	0.7	2.0
Gas Combustion	0.7	2.1
High Temperature (1,200°F)	0.8	2.5
High Temperature (1,500°F)	0.8	3.1
Royster - T.V.A.	3.4	0.9
Typical Midcontinent Crude Oil	<0.2	<0.1

---

* Oil crudes produced from Colorado Oil Shale except that produced in the Royster - T.V.A. retort which was from Tennessee shale.

The type of retorting process is also seen to have little effect on the levels of nitrogen and sulfur in the various synthetic crudes produced. From the standpoint of the production of fuels from shale based synthetic crudes, this means that further processing would be essential to reduce the levels of these elements. Considerable amounts of hydrogen are usually employed to accomplish denitrogenation and desulfurization. Exxon Research and Engineering Company has developed several processes for the reduction of sulfur and nitrogen levels in crude oils of various types and several have effectively been applied to synthetic crudes produced from shale.

Perhaps a more important consideration from the standpoint of utilizing synthetic crude oils for the production of motor and aviation fuels is volatility distribution (distillation curve). Table 8 summarizes pertinent distillation data for several synthetic shale crude oils produced by the different retort processes. It can be seen from these data, that synthetic crude oil produced from shale has a significant fraction of light distillate (400-600°F) which is particularly suitable for further processing into fuels. The volumetric fraction of light distillate product varies from a low of about 13% to a high of about 30% for the Pumpherston Retort process. Though the average light distillate level is somewhat lower than that for a typical mid-continent crude oil, a significant fraction of the synthetic crude oils from shale is suitable for the production of jet fuel. Furthermore, this fraction can be increased significantly by processing techniques such as hydrocracking.

Table 8

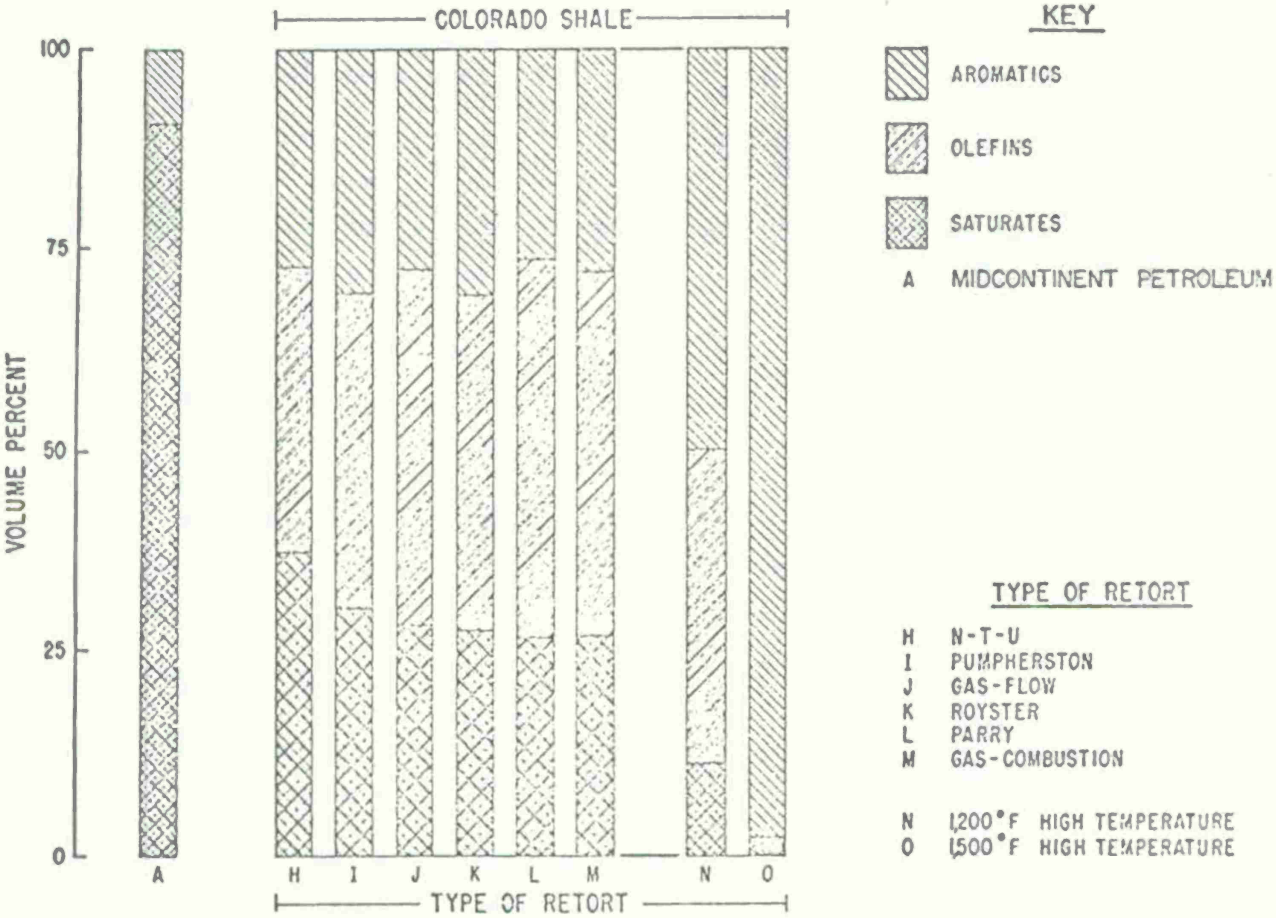
Distillation of Synthetic Crude Oils Produced from Shale

	Distillate - Volume %			
Retort Process	Up to 400°F	400-600°F	600 to 800°F	Residuum
NTU	2.7	15.7	34.4	45.8
Pumpherston	17.6	29.4	40.0	12.7
Gas Flow	1.5	12.8	25.3	60.0
Royster	4.9	13.2	31.6	50.2
Parry	14.9	16.6	27.6	39.9
Gas Combustion	4.4	14.6	31.3	49.7
High Temperature (1,200°F)	39.2	13.5	19.7	27.2
High Temperature (1,500°F)	38.4	15.4	18.3	25.9
Royster - T.V.A.	6.0	24.0	35.0	33.5
Typical Mid-continent Crude Oil	28.4	25.0	18.6	26.3

Another important factor in the consideration of the production of fuels from synthetic crude oil is the relative amounts of different hydrocarbon molecules present in the synthetic crude, i.e., the relative amounts of aromatics, olefins and saturates (paraffins + naphthenes). As can be seen from Figure 5, which compares the hydrocarbon composition of several synthetic crude oils made from raw shale in the U.S. (23) the olefinic composition is quite high varying from about 25 to 50 volume % for the gas combustion process.

Figure 5

Composition of Shale Oil Distillates Below 600°F



Olefinic levels of synthetic crude oils produced from raw shale can be reduced by various hydrogenation processes. Since the removal of sulfur and nitrogen from the synthetic crudes usually involves the same type of processing, denitrogenation, desulfurization and conversion of olefins to saturates can usually be accomplished concomitantly. Typical properties of a synthetic crude oil from shale which has been pre-refined by a hydrogenation process is given in Table 9. Sulfur, nitrogen, and olefinic compound level are seen to be reduced to very low levels.

Table 9

Properties of a Hydrogenated Synthetic Crude Oil from Shale(24)

	Treated Crude*	
Gravity °API	46.2	
Pour Point, °F	50	
Sulfur, Wt. %	0.005	
Nitrogen, Wt. %	0.035	
Reid Vapor Pressure Psi	8	
Viscosity, SUS at 100°F	40	
Analysis of Fractions	C_5-350°F	350-550°F
Volume %	27.5	41.0
Gravity °API	54.5	38.3
Sulfur, Wt. %	<0.0001	0.0008
Nitrogen, Wt. %	<0.0001	0.0075
Aromatics	12	34
Saturates	82	66
Olefins	0	0

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* Based properties of "Syncrude".

3.2.1.2.3.2 Synthetic Crude Oils from Coal

A generalized molecular structure of coal is shown in Figure 6 From this description it can be seen that, chemically, coal is comprised of an extensive network of aromatic rings. The structure is so highly condensed that many carbon atoms have no attached hydrogen atoms. Thus, virtually all of the synthetic crude oils made from coal should be rich in aromatics (particularly condensed ring aromatics). As discussed previously, synthetic crude oils can be produced from coal by a number of different processes involving pyrolysis, hydrogenation or some combination of the two. One additional route, which is somewhat different, involves conversion of coal to carbon monoxide and hydrogen which is then converted to paraffinic hydrocarbons via a Fischer-Tropsch Synthesis process.

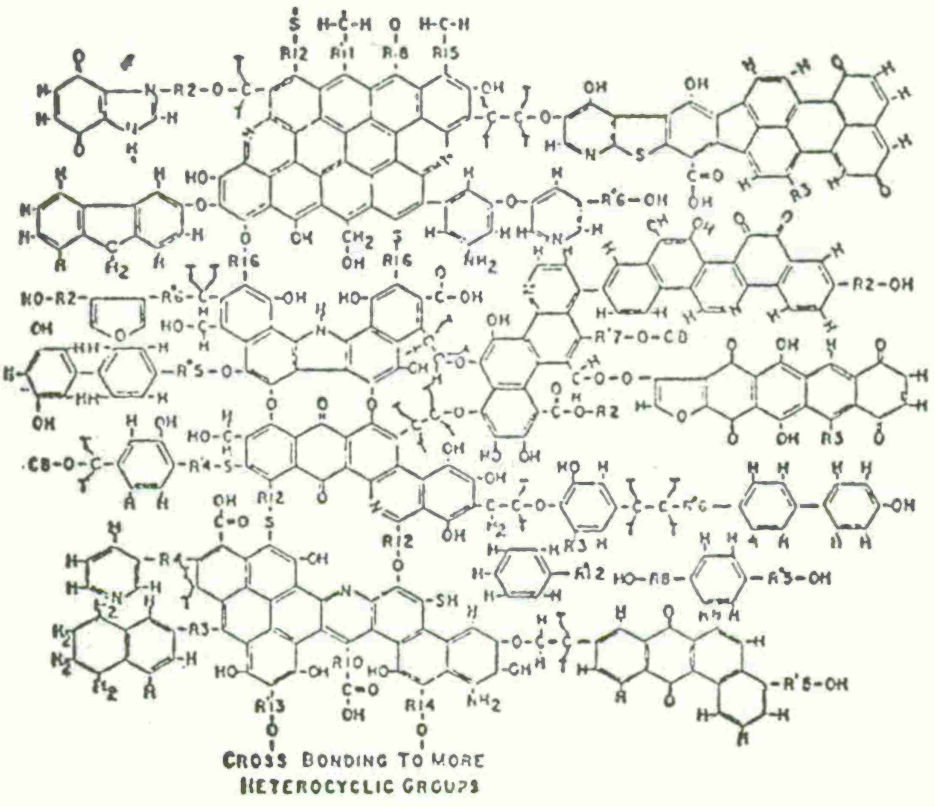
Unlike synthetic crude-oil produced from shale, synthetic crude oil produced from coal will vary considerably based on the type of coal used as well as the extent of hydrogenation employed. However, in general, the synthetic liquid products from coal are much richer in aromatics than shale, lower in olefins, higher in oxygen and lower in nitrogen. Synthetic crude oils made from the direct pyrolysis of coal (without hydrogenation) have been characterized by Jones et al. for the Office of Coal Research (25). Pertinent results are summarized in Table 10.

These synthetic crude oils are seen to be generally quite low in quality, having low hydrogen levels, high oxygen, nitrogen and sulfur levels, very high pour points and low gravity. Most of the chemical compounds formed from the breakup of the coal structure, are hetrocyclic aromatic and complex polar. These synthetic crudes are not suitable as refinery feedstock and have to be further treated. Significant improvements in their quality can be made through various types of hydrogenation as hydrotreating processes. Typical examples of the types of changes (upgrading) brought about by hydrogenation are shown in Table 11.

Figure 6

Molecular Structure of Coal

(It's mostly aromatics, and very unlike oil.)



R°N = Alicyclic rings of N carbons.
RN = Alkyl side chain of N carbons.
R'N = Unsaturated alkyl side chain of N carbons.
CB = Cross bonding by O or S to new heterocyclic groups with side chains.
T = Tetrahedral 3 dimensional C—C bonds, C—O bonds and C—S bonds.

Table 10

Composition of Synthetic Crude Oil Produced by the Pyrolysis of Coal

Composition or Property Ultimate Analysis Wt. %	Synthetic Crude From Utah Coal	Synthetic Crude From Illinois No. 6 Coal
Carbon	82.5	78.7
Hydrogen	9.3	7.5
Oxygen	7.2	10.9
Nitrogen	0.8	1.0
Sulfur	0.3	2.0
Hydrocarbon Analysis Wt. %		
Saturates	20 {10 paraffins 10 cycloparaffins	3
Aromatics	27	9
Polars	53	88
Gravity °API	11.7	-.4
Pour Point °F	95	75

Table 11

Effect of Hydrogenation on Composition and Properties of Synthetic Crude Oil Produced from Coal

Property	Synthetic Oil* Produced by Pyrolysis	After Hydrogenation 3000 psig, 800°F
Gravity °API	-7.7	30
Pour Point	100	-150
Composition, Wt. %		
Carbon	81.1	87.5
Hydrogen	7.1	12.3
Oxygen	8.2	0.1
Nitrogen	1.1	0.05
Sulfur	2.4	0.01

---

* Illinois No. 6 coal.

Gravity is raised, the pour point is lowered drastically, while more than 98% of the oxygen, nitrogen and sulfur are removed. The hydrogenated synthetic oil could be used with conventional refinery feedstock to make jet fuel.

Similar high quality synthetic liquids can be made by direct high pressure hydrogenation of coal, without using pyrolysis. Properties of some synthetic crude oils made this way are described below.

Quader and Hill (26) have reported the preparation of a synthetic crude oil by the direct hydrogenation of a high volatile bituminous coal from Utah at 500°C and 2000 psi using stannus chloride as the catalyst. After separation of asphaltenes by solvent extraction, the crude oil had the following properties:

Sp.gr.,25°C	0.99
Sulfur, wt. %	0.32
Nitrogen, wt. %	0.61
Tar acids, vol. %	19.0
Tar bases, wt. %	1.5
Distillation	
I.B.P., °C	76
Up to 200°C, vol. %	22
Up to 360°C, vol. %	80
Residue, vol. %	20
Composition of neutral oil, 76° to 360°C, vol. %	
Saturates	42.0
Olefins	5.0
Aromatics	53.0

The production of a light distillate synthetic liquid, suitable for use in fuel, from the direct hydrogenation of a Wyoming sub-bituminous and a Illinois No. 6 coal, has been demonstrated by Hydrocarbon Research, Inc., for the Office of Coal Research (27). The results of this effort are summarized in Table 12.

Table 12

Hydrotreating an H-Coal-Light Distillate Product Can Further Upgrade Quality for Jet Fuel Utilization

		Feed Light Distillate of Synthetic Oil from Coal	Product Fractions	
			(185-390°F)	(390-512°F)
Volume % of total product			65	21
Initial Boiling Point °F		143	219	411
End Point °F		510	404	512
Elemental Analysis	Carbon	87	86	87
	Hydrogen	12	14	13
	Nitrogen	0.2	.003	.006
	Sulfur	0.1	.02	.007
Phenols, wt. %		6.1	nil	nil
Paraffins		19	15	17
Cycloparaffins		61	68	74
Aromatics		20	17	9

Distillate product fractions are formed having properties that make them very well suited for the formulation of fuels. These results are useful in that they illustrate that a continuous upgrading of synthetic oils produced from coal can be achieved by different hydrotreating operations, employing specific catalysts and operation conditions.

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3.2.2 Methanol

Alcohols such as methanol have been used extensively as a fuel in the past (1,2). Methanol's principal use today is a chemical rather than as a fuel because of the economic advantage of cheaper petroleum based fuels(3). There are two potential sources of methanol as a future alternate fuel, i.e., (1) natural gas (CH_4) and (2) coal. The technology for the production of methanol or "methyl fuel" (a predominately methanol blend with other light oxygenated compounds) via reaction of carbon monoxide and hydrogen originted in Germany in 1913 and involves the use of highly selective heterogeneous catalysts to direct the reaction toward methanol and to prevent the formation of methane and higher hydrocarbons as is the case in the Fischer-Tropsch reaction. A number of processes have evolved from this early German work and synthetic methanol for chemical use is produced throughout the world (and with low production levels in terms of typical fuel production) using naphtha and natural refinery and coke oven gas as the starting material(3). Countries with synthetic methanol production include:

The Americas:	U.S., Canada, Mexico, Argentina, Brazil, Chile
Europe:	Austria, Finland, France, U.K., West Germany, Italy, Norway, The Netherlands, Spain, Sweden, Switzerland
Other:	East Germany, Romania, Iran, South Africa, Japan, U.S.S.R., India, South Korea, Taiwan

At present, the production of methanol from methane is only being considered for Persian Gulf based methane where the shipment of liquid methanol could be cheaper than the shipment of cryogenic methane(4). The Persian Gulf and other producing countries have long been concerned by the "loss" of revenue resulting from the flaring of by-product methane during crude oil production. Methanol from Persian Gulf methane is potentially the first synthetic fuel to become available in any quantity in the U.S. The introduction of methanol derived from coal will depend on the rate of development of economic coal gasification processes. Such methanol may be produced as part of a combined SNG-methanol plant.

Methanol potentially has a number of fuel uses(5):

- Regasification to CH_4.
- As a fuel for spark ignition, internal combustion engines, turbine engines or fuel cells.
- Blended (e.g., 10-15%) with gasoline and used as motor gasoline.

Methanol has a low heat of combustion relative to hydrocarbon fuels (i.e., approximately one-half the heat of combustion on a weight basis) and thus requires greater quantities (either weight or volume) for a given energy release. It also has a high latent heat of vaporization relative to hydrocarbons. It has a high octane number and has the potential to produce lower NO_x in spark ignition and gas turbine engines.

Blended with gasoline, methanol faces miscibility and water sensitivity problems. Methanol and benzene are miscible in all proportions down to 3°C, however, only 5% methanol can be dissolved in n-hexane at 0°C. The problem of phase separation is greatly intensified if water is present, e.g., at 78°F less than 0.5% water causes phase separation. Miscibility and water induced phase separation problems, of course, are greater at lower temperatures. Also, the presence of methanol in gasoline greatly increases the vapor pressure of the blend. This could cause significant vapor lock problems if simply added to current gasoline or force the removal of volatiles such as butane and pentane from the gasoline. There are also toxicity and potential emission problems (e.g., higher levels of aldehydes produced) associated with the use of methanol. Metal corrosion and fuel system materials degradation are also potential problem areas.

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3.2.3 Tar Sands

The ultimate potential of tar sands as a petroleum substitute is much lower than that of coal or shale. Estimates of ultimate reserves (1,2,3) indicate that the tar sand potential is only approximately 2% that of coal and 8% that of shale oil. Tar sands even have a lower potential than that of ultimate petroleum crude. As can be seen from Table 13, the majority of tar sand deposits are located in Canada (approximately 80%) and Venezuela (approximately 20%). Other deposits with some small but possible future significance are found in Madagascar and the U.S.

Tar sand is a mixture of sand, water and bitumen (4). Thus, the hydrocarbon portion of tar sand is not strickly speaking a tar (i.e. a thermal residue such as from coal pyrolysis) but rather a heavy petroleum like material. Tar sands generally contain approximately 80% sand with the balance being bitumen and water. Tar sand material generally consists of a sand particle surrounded by a water envelope containing mineral fines which is in turn surrounded by a bitumen film. Removing the hydrocarbon portion of the tar sand thus involves major problems in solids handling and separation. Open-pit methods are used to mine the tar sands and the bitumen is separated from the total sand-water-bitumen mixture by means of a hot water extraction process (5).

Athabasca bitumen (4) is similar to a heavy petroleum crude oil, with a boiling range from 400 to 1000°F. Typical elemental analyses are: carbon, 82 to 84 wt. %; hydrogen, 9 to 11%; sulfur, 4 to 5%; oxygen, 1 to 3%; and nitrogen, 0.3 to 0.5%. Thus, tar sand derived crude in general has more sulfur and less nitrogen and oxygen compounds than shale rock or coal derived crude materials. Thus, the compatability of tar sand crude with present petroleum technology is better than that of shale rock or coal derived crudes. The technology available to process heavy petroleum crude oil (involving problems such as high viscosity, and high asphaltenes, metals and sulfur content) can be used to process tar sand derived crude.

In general, the bitumen is converted into lighter products with carbon numbers in lower, commercial product ranges by some type of a coking process treatment (4,6). The coke fraction of the product is used for fuel and the distillate liquids will generally require catalytic hydrotreating, for example, for sulfur reduction.

Present commercial interest is limited to the athabasca tar sands in Canada (5,7). Here, the Great Canadian Oil Sands Ltd. operates a 45,000 bbl/day plant. In addition, Syncrude Canada Ltd. currently (June 1975) is constructing a 125,000 bbl/day plant. The Syncrude consortium originally consisted of Imperial Oil Ltd., Canada City Services, Gulf Canada Ltd., and Atlantic Richfield. Atlantic Richfield withdrew from the consortium in December, 1974, and construction of the Syncrude plant was halted until it's place in the consortium was taken by the Canadian federal and provincial governments (7,8,9). Prospects for other possible athabasca tar sand plants (i.e. Shell, Petrofina and Home Oil) are unclear in mid 1975 (7).

Table 13

Tar Sand Reserves(1)

Location	In-Place Reserves, 10^6 Barrels
Canada	711,000
Venezuela	200,000
Madagascar	1,800
U.S.A.	2,100
Albania	400
Rumania	25
U.S.S.R.	25

---

(1) Source: Phizackerley, P. H. and Scott, L. O., "Major Tar Sand Deposits of the World," Proc. 7th World Petroleum Congress, Amsterdam, 1967.

References Cited in Section 3.2.3

(1) A. B. Cambel, "Energy, R&D and National Progress," U.S. Government Printing Office, Washington, D.C., 1964.

(2) P. H. Phizackerley and L. O. Scott, "Major Tar Sand Deposits of the World," Proc. 7th World Petroleum Congress, Amsterdam, 1967.

(3) R. A. Baillie and T. S. Mertes, "Sixth Annual Institute on Exploration and Economics of the Petroleum Industry," Matthew Bender and Company, New York, 1968.

(4) Proceedings of the First Athabasca Oil Sands Conference, Kings Printer, Edmonton, Canada, 1951.

(5) J. V. D. Fear and E. O. Innes, "Canada's First Commercial Tar Sand Development," Proc. 7th World Petroleum Congress, Amsterdam, 1967.

(6) Oil and Gas Journal, 65, 69-98, October 23, 1967.

(7) Oilweek (Calgary, Alberta) 26 #5 pages 26, 27 and 32, March 17, 1975.

(8) Oil and Gas Journal, page 39, April 14, 1975.

(9) Forbes, pages 18 and 19, May 1, 1975.

3.3 Present Fuels and Petroleum Processing Technology

Raw materials and intermediate and finished fuels involved in established commercial practice are often discussed in terms of the processing technology used (e.g., a 95 research octane number hydroformate product from a light 160/260 middle east paraffinic naphtha). At present, the exact nature of both the primary processes that will be used to produce syncrudes from coal and shale, and the secondary refining processes that will be selected to change the raw syncrudes to finished fuels is not clear. Thus, discussion of possible syncrudes and products from the process technology point of view would appear difficult and tenuous. In order to provide a fundamental, general basis for analyzing the synthetic fuel problem, it was decided to discuss the problem in terms of the chemical composition of the materials involved as much as possible.

In order to accomplish this, the general physical and chemical composition of present day fuels is analyzed. In Section 3.3.1, the general composition of petroleum is discussed and in Section 3.3.2, information on the composition of individual fuels is treated. Previously in Section 3.2, the general chemical compositions of syncrudes were discussed.

Moreover, the performance of a fuel is ultimately controlled by its chemical composition. This is illustrated in Table 14 where the composition of an aircraft turbine fuel necessary to achieve certain specifications or desired properties is shown.

3.3.1 General Chemical Composition of Petroleum

The composition of a petroleum product such as a fuel is complex and varies widely. A great deal of this variation results from the fact that the composition of the crude oil itself from which the petroleum products are produced varies considerably, reflecting its complex geochemical formation from organic matter over extremely long periods of time. An additional variation in composition is introduced as a result of differences in the refining processes used to produce the product fuel from crude oil. Petroleum refining processes can even add compounds to the fuel which were not originally present in the crude oil. It is difficult to generalize about the effect of refining processes because of the wide variation in the type of petroleum refining operations which can be employed to produce a given product. In addition, variations in operating conditions employed in a given processing unit (i.e., temperature, pressure, catalyst type, space velocity) can also result in significant changes in the composition of the product.

Table 14

Jet Fuel Specifications Versus Chemical and Physical Properties

Specification or Desired Property	Needed Physical and/or Chemical Characteristics
Distillation range API Gravity Vapor pressure at 100°F Freezing point Viscosity Heating value	Correct carbon number range, also influenced by n+i-paraffin, naphthene and aromatic distribution
Existant gums Total potential residue Thermal Stability Pressure drop Preheater deposit code	Level and type of olefins, level and type of trace organic sulfur, nitrogen and oxygen impurities
Total sulfur content Mercaptan sulfur content Aromatic content Olefin content	Correct chemical composition as indicated
Smoke point, smoke volatility index (SVI), luminometer number	Chemical composition, particularly aromatic and condensed ring aromatic content, SVI influenced by percent of lower boiling fractions.
Flash point Explosiveness	Correct lowest carbon number in fuel e.g., 140°F flash point requires fuel with carbon numbers greater than C_9 or C_{10}
Particulate matter	Presence of insoluble impurities
Water separation index Water reaction interface rating	Level and type of organic oxygen trace impurities
Copper strip corrosion	Level and type of trace sulfur and oxygen compounds
Total acid number	Carboxylic acid level in fuel i.e., present of trace organic oxygen compounds

3.3.1.1 Formation of Crude Oil

The almost universal association of oil fields with sedimentary rocks indicates that petroleum originated in sediments. It appears most reasonable to assume that petroleum is derived basically from the organic matter deposited along with the sediments. The presence of optically active compounds, and of chlorophyll-like porphyrins in crude oils support an organic origin. The preponderance of rocks associated with oil fields are of marine, or brackish water environment, which indicates that these environments favor petroleum formation. Rapid oxidation and decomposition of the organic matter would occur in oxidizing environments, so it is likely that the preservation of organic material has taken place in a reducing environment. Three requirements appear to be essential for the source bed: (a) an ample supply of sediment, (b) a favorable environment for organic life, and (c) an anaerobic condition of the sediments on the floor of a marine basin.

The nature of the portion of the deposited organic material which eventually becomes petroleum is unknown, as is the process by which it occurs. Living organisms contain hydrocarbon material, or may form hydrocarbons as part of their metabolism. The organic matter may be acted upon by anaerobic bacteria before it is deeply buried, so that its oxygen, nitrogen, and sulfur content will be reduced to become more petroleum-like.

The effects of temperature, pressure, and geologic time in the transformation of the organic material to petroleum are all dependent on the thickness of the sediments. Recent studies have demonstrated the presence of petroleum-like hydrocarbons early in the depositional history of sediments. Radiocarbon dating has shown these hydrocarbons to be recent. The presence of porphyrins, complex compounds similar to chlorophyll, in crude oils show that petroleums have a low temperature history (less than 392°F). The possible effects of pressure have not been adequately assessed.

Finally, the accumulation of the petroleum is so-called reservoir rocks is unsolved. The mechanism of the transfer from the fine grained source beds to the final storage place is not known; nor is the time in the history of the sediments that the migration occurs.

Studies, largely supported by the American Petroleum Institute (1), have shown that crude oil as would be expected is a very complex mixture of hydrocarbons. Molecular weights vary from the lightest to over 6,000. The nature of these hydrocarbons varies within rather wide limits depending on the origin of the petroleum. In addition to the hydrocarbons, there are also compounds present which contain sulfur, nitrogen and oxygen as well as traces of metal salts. The amount of these non-hydrocarbons also varies widely depending on the oil source. However, they usually constitute less than 10% of the compounds present.

The composition of crude oil generally varies within the following approximate limits:

Carbon	83-87%
Hydrogen	11-15%
Oxygen	Up to 5%
Sulfur	Up to 6%
Nitrogen	Up to 0.5%
Mineral Salts	Up to 0.1%

In general, the source of petroleum is believed to be the remains of marine animal and vegetable life deposited with sediment in coastal waters (1,2). Bacterial action evolves sulfur, oxygen and nitrogen as volatile compounds. These, however, are never completely eliminated despite the ever increasing pressure of sediment. The result of this process is a mixture of hydrocarbons containing varying quantities of sulfur, nitrogen and oxygen compounds, and traces of metals. The properties of this mixture depend on the nature of the source material and the subsequent influential forces which include time, temperature and catalysts. Because these parameters vary from one geological location to another, a wide variety of crude oil compositions result.

3.3.1.2 The Hydrocarbon Composition of Fuels

Both the difficulty in analyzing for the various components present in petroleum and the wide variation in distribution of compounds between different crude oil sources make the question of the detailed hydrocarbon composition of a fuel difficult. The American Petroleum Institute, through its research project 6 has been investigating the composition of petroleum since 1925 (3,4). In Figure 7 is shown a breakdown by compound classes of one representative petroleum (3).

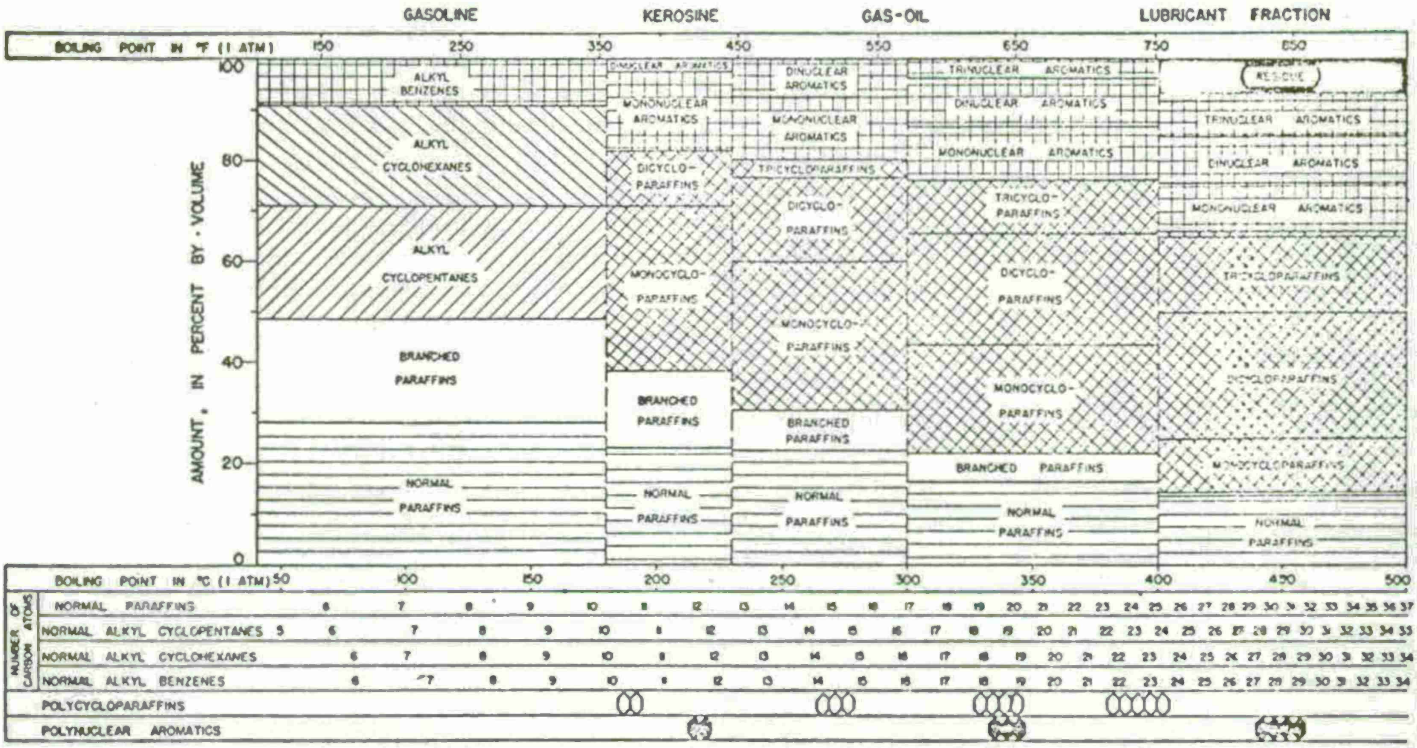
The main compound classes found in fuels are paraffins, naphthenes (cycloparaffins) and aromatics (3,4,5). As illustrated in Figures 8 and 9, the distribution of these compound classes in crude oil is both a function of crude source and carbon number (6,7). In Table 15 is shown a distribution of aromatic compound classes by carbon number in the C_9 through C_{20} range (8).

3.3.1.3 Trace Impurities Potentially Present in Fuels

Compounds containing sulfur, nitrogen and oxygen are present as minor constituents in crude oil. The nature and quantity of these compounds is a function of crude source and of the boiling range for a given crude. Unfortunately our knowledge relative to these non-hydrocarbon compounds is incomplete. It is known that the sulfur and nitrogen contents of crude oil vary widely and that the sulfur content is generally higher than the nigrogen as shown in Figure 10(9). Ball has suggested that as

Figure 7

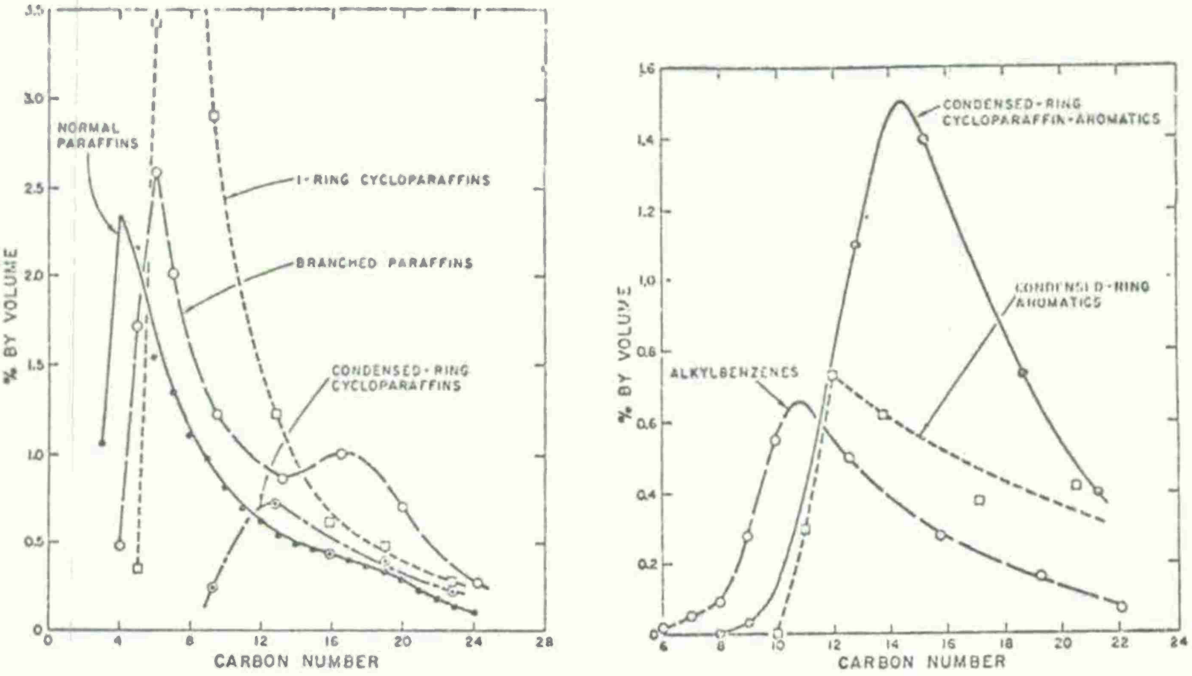
Relative Amounts of Different Types of Hydrocarbons In Several Broad Fractions of One Representative Petroleum



Source: F. D. Rossini, J. Petroleum Institute 44, 97 (1958).

Figure 8

Crude Analyses



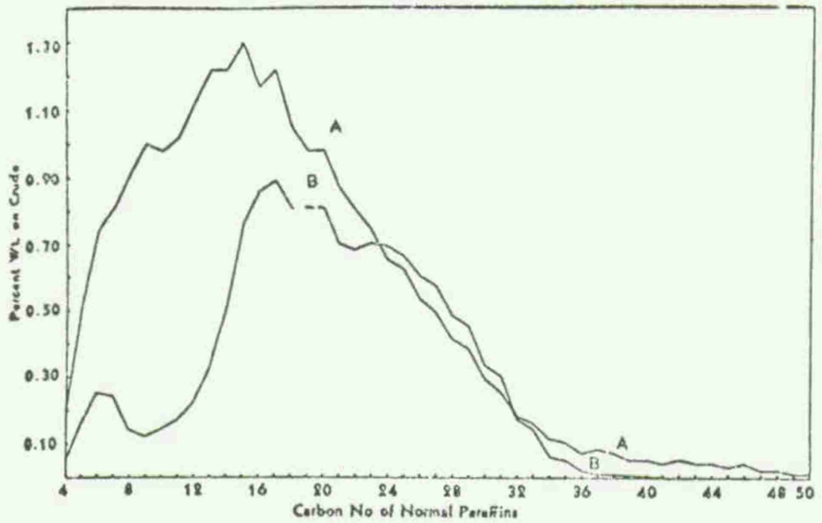
SATURATED HYDROCARBONS BY CARBON NUMBER IN NORTH SMYER CRUDE OIL

AROMATIC TYPES BY CARBON NUMBER IN SOUTH HOUSTON CRUDE OIL

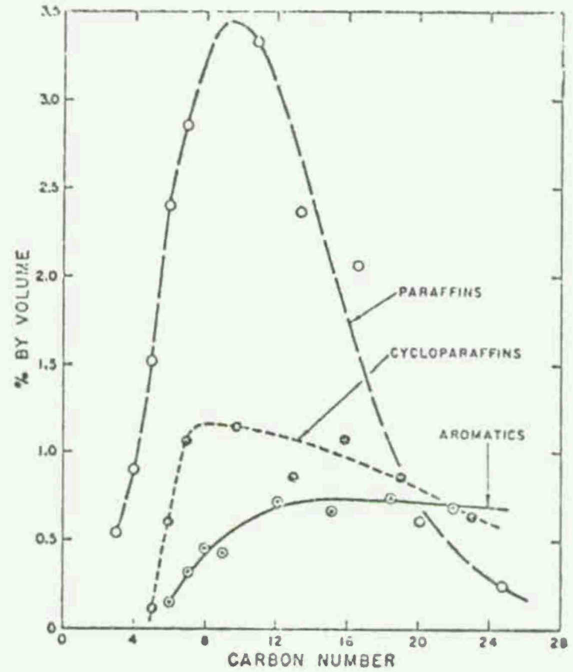
Source: R. L. Martin et al, 6th World Petroleum Congress, Section V, Paper 13, 1963.

Figure 9

Crude Analyses



Normal paraffin carbon number distribution of Libyan (*A*) and Nigerian (*B*) crude oils (% by weight) (1)



HYDROCARBON TYPES BY CARBON NUMBER IN KAWKAWLIN CRUDE OIL (2)

Sources: (1) J. V. Brunoch, Anal. Chem. 38, 1648 (1966).
(2) R. L. Martin et al, 6th World Petroleum Congress, 1963.

Table 15

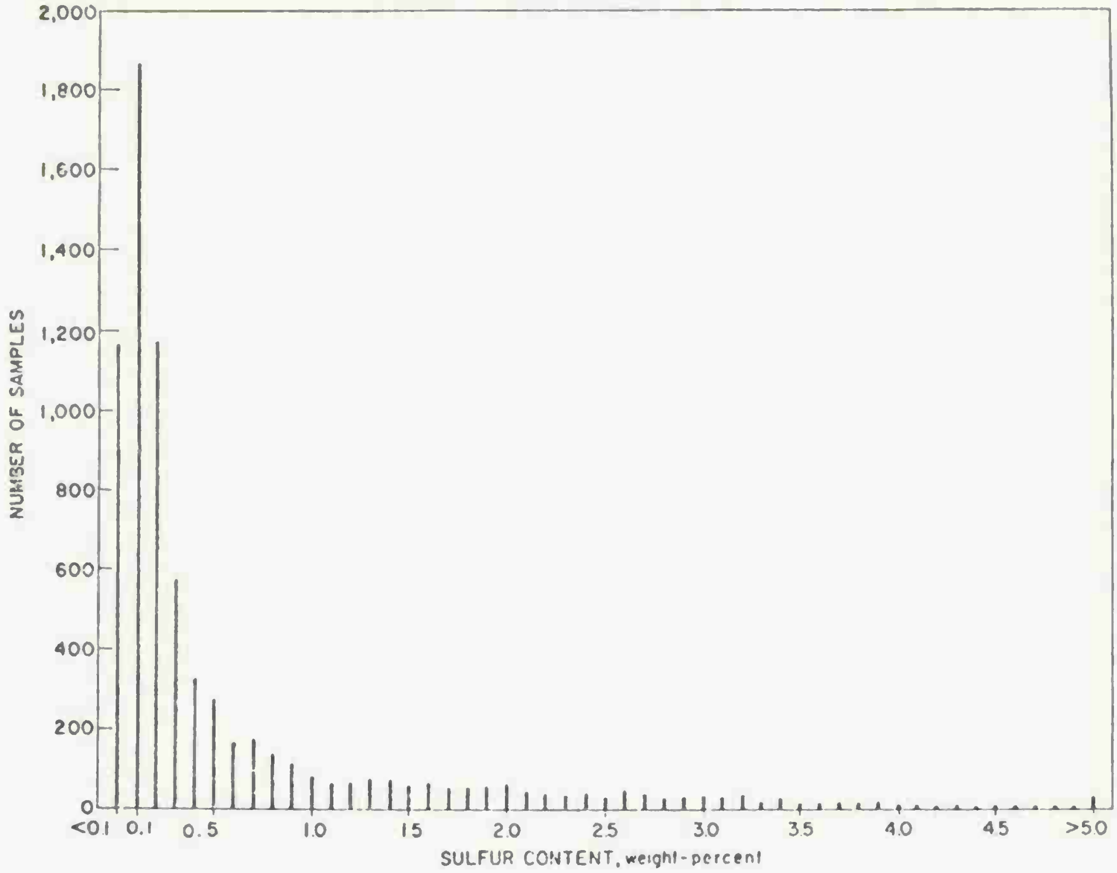
Distribution of Aromatics (Volume Percent)

Compound Type	JP-4	JP-5	Ram Jet	Kerosene	Cat. Cracked Gas Oil(Diesel Fuel Range)	Cat. Cracked Gas Oil(Fuel Oil Range)
Benzenes						
C_9	11.1	1.7	-	0.1	0.2	0.5
C_{10}	4.1	4.6	-	1.4	0.1	1.7
C_{11}	1.1	2.5	0.6	1.6	1.0	1.1
C_{12}	0.5	1.0	0.7	1.0	1.0	5.5
C_{13}	0.1	0.7	0.6	0.8	1.0	4.8
C_{14}	-	0.2	0.7	0.5	1.6	2.1
C_{15}	-	0.1	0.7	0.5	1.0	1.4
C_{16}	-	-	0.7	0.2	0.1	0.7
C_{17}	-	-	0.6	-	0.6	0.3
C_{18}	-	-	0.6	-	0.4	0.1
C_{19}	-	-	0.3	-	0.2	-
C_{20}	-	-	-	-	0.2	-
Indanes						
C_9	-	-	-	-	0.1	-
C_{10}	0.1	0.3	-	0.2	0.3	0.5
C_{11}	0.1	1.0	-	1.0	1.1	2.5
C_{12}	0.1	1.0	-	1.5	2.0	2.0
C_{13}	-	0.4	-	1.2	1.5	1.0
C_{14}	-	0.1	0.1	0.7	1.5	0.9
C_{15}	-	-	0.2	0.3	0.8	0.4
C_{16}	-	-	0.1	0.1	0.5	0.1
C_{17}	-	-	0.1	-	0.3	-
C_{18}	-	-	-	-	0.2	-
C_{19}	-	-	-	-	0.1	-
Indenes						
C_9	-	-	-	-	0.1	-
C_{10}	-	-	-	-	0.1	-
C_{11}	-	0.1	-		0.3	0.3
C_{12}	-	0.1	-	0.1	0.3	0.1
C_{13}	-	0.1	-	0.1	0.6	0.5
C_{14}	-	-	-	0.2	0.6	0.1
C_{15}	-	-	-	0.1	0.4	0.2
C_{16}	-	-	-	-	0.2	0.1
C_{17}	-	-	-	-	0.1	-
C_{18}	-	-	-	-	0.1	-
Naphthalenes						
C_{10}	0.1	0.4	-	0.1	0.2	0.2
C_{11}	0.2	1.5	-	0.8	1.6	2.5
C_{12}	0.2	1.7	-	1.5	4.0	6.1
C_{13}	-	0.4	-	1.0	3.8	6.0
C_{14}	-	0.1	-	0.3	3.5	5.4
C_{15}	-	-	-	0.1	1.7	3.2
C_{16}	-	-	-	-	0.9	0.4
C_{17}	-	-	-	-	0.5	0.1
C_{18}	-	-	-	-	0.2	-
C_{19}	-	-	-	-	0.1	-
Acenaphthenes						
C_{12}	-	-	-	-	0.1	0.1
C_{13}	-	-	-	-	0.9	0.9
C_{14}	-	-	-	0.1	1.2	1.4
C_{15}	-	-	-	-	2.2	1.0
C_{16}	-	-	-	-	1.4	0.6
C_{17}	-	-	-	-	0.6	0.2
C_{18}	-	-	-	-	0.1	-
C_{19}	-	-	-	-	0.1	-
Acenaphthylenes						
C_{13}	-	-	-	-	0.1	-
C_{14}	-	-	-	-	0.3	0.2
C_{15}	-	-	-	-	0.1	0.3
C_{16}	-	-	-	-	0.8	0.1
C_{17}	-	-	-	-	0.5	0.1
C_{18}	-	-	-	-	0.3	-
C_{19}	-	-	-	-	0.1	-
Anthracenes						
C_{14}	-	-	-	-	0.1	0.1
C_{15}	-	-	-	-	0.1	0.1
C_{16}	-	-	-	-	0.6	0.1
C_{17}	-	-	-	-	0.3	-
C_{18}	-	-	-	-	0.1	-
Totals						
Alkanes	30.1	30.0	2.7	41.7	11.6	21.8
Noncondensed Cycloalkanes	32.1	34.6	44.6	37.1	13.0	10.3
Condensed Cycloalkanes	1.6	16.0	44.0	11.9	4.0	3.7
Olefins	1.9	0.0	2.5	2.8	6.6	5.2
Aromatics	19.9	18.0	6.1.	15.6	34.2	18.0
Average Substitutions per Benzene Ring	1.0	1.2	1.0	1.3	not calc.	not calc.

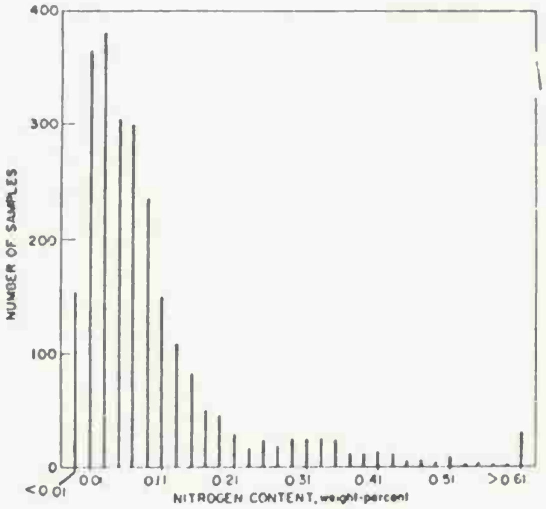
Source: C. L. Kearns et al, ACS Pet. Div. Preprints 3 No. 3, 73 (1958).

Figure 10

Sulfur and Nitrogen Distribution



—Frequency Distribution of Sulfur Content of Crude Oils (7,273 Samples).



—Frequency Distribution of Nitrogen Content of Crude Oils (2,465 Samples).

Source: H. M. Smith, Bureau of Mines Bulletin 642, 1968.

an approximate rule of thumb the nitrogen content of many crude oils is one-tenth that of the sulfur content (10). For high nitrogen content crudes such as California crudes the nitrogen content may be half that of the sulfur. The quantity of both sulfur and nitrogen compounds increase with boiling point of the crude fraction. Petroleum refining processes can often change the nature of such compounds.

3.3.1.3.1 Sulfur Compounds

Sulfur compounds occur in an unusually wide variety in crude oil, and vary extensively as a function of geographic origin (6). Extensive studies of sulfur in petroleum have been carried out by the Bureau of Mines-API Project 48 and by the British Petroleum Company (9-18). In general, sulfur compounds have been shown to increase in concentration with increasing boiling point. The total sulfur content of crude oil varies from practically zero to as much as 14%. Sulfur compound classes identified in crude oil include elemental sulfur, thiols (mercaptans) sulfides and thiophenes. In a review of the Bureau of Mines-API Project 48 work, Rall et al stated that no disulfide has been conclusively identified as present in virgin crude oil (18). Subsequent extensive work appears to have identified a single disulfide in crude oil (17). Disulfides are readily formed, however, by oxidation of thiols, and the most probable source of disulfides and polysulfides in fuel is from the use of Sweetening Processes in the refining of the petroleum. The sulfur compound classes present in crude oil which probably have representative members boiling in fuel range are shown in Table 16.

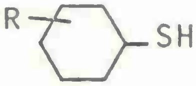
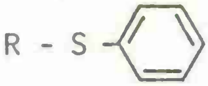
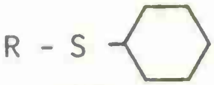
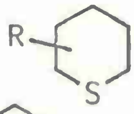
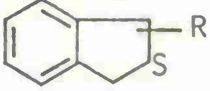
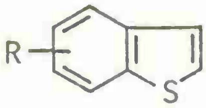
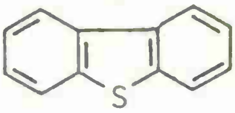
3.3.1.3.2 Nitrogen Compounds

A number of studies have been made of the nitrogen content of petroleum fractions boiling near the fuel range (10,14-28, 34-38). Most of the nitrogen compounds lie in the boiling range above that of jet fuel (10, 24). The nitrogen content, however, rises sharply with boiling point in the upper portion of the distillate fuel boiling range. This is illustrated below for a high nitrogen content California crude (24).

Boiling Range	Wt. % on Total Crude	Total Nitrogen Content, PPM
347 - 392°F	2.4	0
392 - 437°F	3.4	0
437 - 482°F	5.2	130
482 - 572°F	9.6	380

Table 16

Sulfur Compounds Identified in Crude Oil(a)

Class	Structure
Thiols	
Alkyl	R - SH
Cyclic	
Sulfides	
Dialkyl	R - S - R
Alkyl-Aryl	
Akyl-Cycloakyl	
Cyclic	
Thianindans	
Thiophenes	
Alkyl Benzothiophene	
Dibenzothiophene	

(a) Coleman et al ACS Pet. Div. Preprints 15, No. 3, A17 (1970)

If the four fractions shown in the above table were blended to produce a 347 to 527°F cut, the fuel would have a total nitrogen content of 210 ppm. This is higher than that normally found in analyses of such fuels, presumedly reflecting at least in part the effect of the high nitrogen content of California crudes and the effect of refinery treatment. The situation regarding the level and type of nitrogen compounds is also complicated by the fact that refinery processes can either add or subtract nitrogen compounds from fuel boiling range and can also change the chemical composition of nitrogen compounds. For example, processes such as mild catalytic hydrotreating or passing the fuel over an adsorption media such as clay will remove nitrogen and sulfur compounds. In contrast, cracking of higher molecular weight fractions to the fuel range could add more nitrogen to the fuel than would normally be present in a fuel prepared with straight run stocks. In a survey of 34 samples of distillate material, Ward et al (21) confirms this effect of cracking, indicating that straight run cuts show lower total nitrogen than either thermal or catalytically cracked stocks. The distribution of basic and non-basic nitrogen compounds present in the catalytic cracked and thermally cracked stocks were found to be different, indicating that the refinery processes can also alter the distribution of nitrogen compounds present (21).

The classes of nitrogen compounds which have been identified in fuel range petroleum cuts are shown in Table 17. Because of the possible influence of refining processes on types of nitrogen compounds present, the type of petroleum material in which the various classes of nitrogen compounds were found is also identified. The strongly basic pyridine and quinoline nitrogen compounds have been found in both unprocessed material (i.e., crude oil virgin cuts) and fuel range cuts produced via catalytic cracking. Anilines, which are also strongly basic, have only been reported in catalytically cracked products and have not been reported in crude oil. The major classes of nitrogen compounds are pyrroles, indoles, carbazoles, quinolines and pyridines, all of which have been reported in both crude oils and cracked products. A number of studies of the distribution of nitrogen compounds between basic and non-basic types have been made (15,23,33). Richter et al (15) indicates that in a study of 14 widely different crude oils the ratio of basic to total nitrogen varies only between 0.25 to 0.34.

Table 17

Classes of Nitrogen Compounds

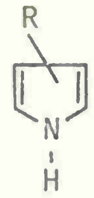
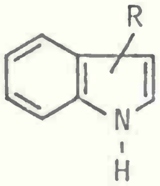
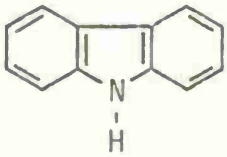
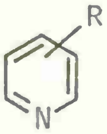
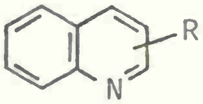
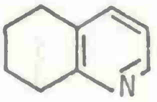
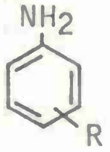
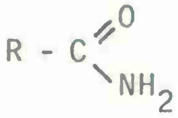
Type	Structure	Petroleum Material Found In	Reference
Pyrrole		374-635°F catalytically cracked product	Sauer et al, I&EC, 44 2606 (1952)
		305-620°F virgin Kuwait	Sauer et al
		480-540°F Cat. cracked cut from California crude	Nixon & Thorpe, J. Chem. Eng. Data 7, 429 (1962)
		410-538°F Cat. cracked cut from California crude	Hendrickson, Pet. Div. Preprints 4, No. 1, 55 (1959)
Indole		374-635°F Cat. cracked	Sauer et al
		305-620°F virgin Kuwait	Sauer et al
		480-540°F Cat. cracked	Nixon & Thorpe
		410-538°F Cat. cracked	Hendrickson
		California crude	Snyder, Acc.Chem.Res. 3 290 (1970)
Carbazole		California crude	Helm et al, Anal. Chem. 32, 1765 (1960)
		374-635°F Cat. cracked	Sauer et al
		305-620°F virgin Kuwait	Sauer et al
		480-540°F Cat. cracked	Nixon & Thorpe
		California crude	Snyder
Pyridine		Crude oil - kerosene cut from California crude	Lochte and Littmann "Petroleum Acids & Bases" Chem.Pub.Co.N.Y. 1955
		374-635°F Cat. cracked	Sauer et al
		305-620°F virgin Kuwait	Sauer et al
		340-430°F Cat. cracked	Nixon & Thorpe
		California crude	Snyder
Quinoline		Crude oil	Lochte and Littmann
		374-635°F Cat. cracked	Sauer et al
		305-620°F virgin Kuwait	Sauer et al
		340-430°F Cat. cracked	Nixon & Thorpe
		California crude oil	Snyder

Table 17 (Cont'd.)

Type	Structure	Petroleum Material Found In	Reference
Tetra Hydro Quinoline		Crude oil 340-430°F Cat. cracked	Lochte & Littmann Nixon & Thorpe
Aniline		340-430°F Cat. cracked 410-538°F Cat. cracked	Nixon & Thorpe Hendrickson
Amides	 $R-C(=O)NH_2$	410-538°F Cat. cracked California crude	Hendrickson Haines et al, 7th World Pet. Congress 9, 83 (1967) Snyder

3.3.1.3.3 Oxygen Compounds

The analytical determination of oxygen in petroleum is more difficult than sulfur and nitrogen, and few direct, reliable analyses of the oxygen content of crude oils are available (38). However, oxygen compounds appear more abundant than nitrogen compounds in crude oil but less abundant than sulfur compounds. It is generally assumed that more oxygen compounds are present in the higher boiling fractions than in the lower boiling fractions, although there is little evidence to support this view. A number of studies (9,27,30-42) have clearly shown that carboxylic acids and phenols are present in fuel range hydrocarbon fractions. Indeed, kerosene and gas-oil petroleum fractions are used as a commercial source of naphthenic acids and phenols. A summary of the classes of oxygen compounds found in fuel range petroleum is shown in Table 18. Very little information is available on the quantity of oxygen compounds present. Some limited data reported (9) indicates that the naphthenic acid content of various kerosenes range from 60 to 750 ppm (as naphthenic acid). Nixon and Thorpe reported that a 340 to 430°F catalytically cracked product contained 0.26 wt. % phenols, and that a thermally cracked material contained higher phenol levels whereas a virgin material contained lower phenol levels (22). In a recent detailed study Snyder reported that a 400 to 700°F California crude contained 0.50 wt. % carboxylic acids, 0.53 wt. % furans (benzofuran and dibenzofuran), 0.32 wt. % phenols and 0.50 wt. % ketones and esters (36).

Hydroperoxides and peroxides are undoubtedly formed in fuels as a result of autoxidative reactions between the hydrocarbon components of the fuel and molecular oxygen.

Table 18

Classes of Oxygen Compounds

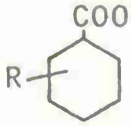
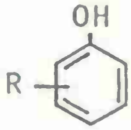
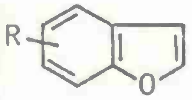
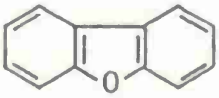
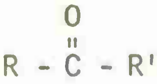
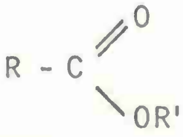
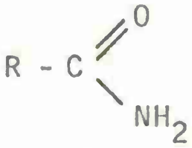
Type	Structure	Petroleum Material Found In	Reference
Aliphatic Carboxylic Acids (Fatty Acids)	$CH_3(CH_2)_nCOOH$	Crude oil	Lochte & Littmann "Petroleum Acids and Bases", Chem. Pub. Co. 1955
		Catalytic cracked product 260-426°F	Gallo et al I&EC 44 2610 (1952)
Naphthenic Carboxylic Acids		Crude oil kerosene fractions	Lochte & Littmann
Phenols		Crude oil	Lochte & Littmann
		Cat. cracked product 260-426°F	Gallo et al
		Thermally cracked naphtha	Field et al I&EC, 32 489 (1940)
		Cat. cracked product 340-430°F	Nixon & Thorpe, J. Chem. Eng. Data 7, 429 (1962)
		400-700°F crude oil cut	Snyder, Acc. Chem. Res. 3 290 (1970)
Furans	 	400-700°F crude oil cut	Snyder
Ketones	 $R-\overset{\overset{O}{\|}}{C}-R'$	Crude oil	Lochte & Littmann
		400-700°F crude oil cut	Snyder
Alcohols	R - OH	Cat. cracked product 410-538°F	Hendrickson, ACS Pet. Div. Preprints 4 No. 1 55 (1959)

Table 18 (Cont'd.)

Type	Structure	Petroleum Material Found In	Reference
Esters		Cat. cracked product 410-538°F 400-700°F crude oil cut	Hendrickson Snyder
Amides		Cat. cracked product 410-538°F 400-700°F crude oil cut	Henrickson Snyder
Hydroperoxides and Peroxides	ROOH ROOR	Reaction product of autoxidation	

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3.3.2 Composition of Fuels

In this section, the general composition of gasoline, diesel fuel and aircraft turbine fuel is discussed in terms of their typical carbon number distribution and aromatic and olefin contents.

In Table 19 are shown the approximate range of carbon numbers of different fuels. Distillation values shown in Bureau of Mines survey were converted to carbon numbers using the data provided by Rossini(1). Gasoline is a very light fuel whose carbon number range primarily falls in the C_4 to C_{11} range with an approximate average carbon number equal to C_7. Gasolines are prepared by blending a variety of stocks, and can have a relatively wide variation in chemical composition(2,3). In general, higher octane number gasolines have higher aromatic contents, because of the high octane number of these components relative to other hydrocarbon classes. It has been estimated that unleaded gasolines will require a substantial increase in average aromatic content to make up for the loss of octane number increase previously provided by the presence of tetraethyl lead(3). It can also be seen that gasoline can contain significant quantities of olefins.

Aircraft turbine fuels vary from a C_4 to C_{15} carbon number range for wide cut JP-4 to a C_{10} to C_{15} carbon number range for high flash point JP-5. Average carbon numbers have been reported as C_8 and $C_{11.5}$ for JP-4 and JP-5, respectively. The average aromatic content for both JP-4 and JP-5 for the period 1960 through 1971 was much lower than allowed by specification, as shown in Table 20. The olefin level was quite low.

In order to provide representative values for the composition of diesel fuels, Bureau of Mines survey results were examined. These results indicate that diesel fuel carbon numbers range from C_9 to C_{21} for Type C-B to C_9 to C_{22} for Type T-T with approximate average carbon number of C_{13} and C_{14} for the respective fuels. Spot analyses shown in Table 21 indicates aromatic levels varying between 18 and 30% and olefin levels varying from 1 to 7%.

Table 19

Fuel Characteristics - Carbon Numbers

Type	Grade	Approximate Range Carbon Number	Approximate Average Carbon Number
Motor Gasoline	Regular (94 RON)(1)	C_4-C_{11}	C_7
	Premium (100 RON)(1)	C_4-C_{11}	C_7
Diesel Fuel(5)	Type C-B (average fuel)(2)	$C_{10}-C_{16}$	C_{13}
	Type C-B (minimum-maximum)(2)	C_9-C_{21}	$C_{11}-C_{14}$
	Type T-T (average fuel)(2)	$C_{11}-C_{18}$	C_{14}
	Type T-T (minimum-maximum)(2)	C_9-C_{22}	$C_{11}-C_{15}$
Aircraft Turbine Fuels	JP-4	C_5-C_{15} (3)	C_8 (4)
	JP-5	$C_{10}-C_{15}$ (3)	$C_{11.5}$(4)

(1) Data from U.S. Bureau of Mines, Petroleum Product Surveys on Motor (Gasoline, #68, Jan. 1971 and #70, June 1971. Distillation values converted to approximate carbon numbers.

(2) Data from U.S. Bureau of Mines, Petroleum Product Surveys on Diesel Fuel Oils, #62 Nov. 1969 and #65 July 1970. Distillation value converted to approximate carbon numbers.

(3) Source: JK Appeldoorn et al "Lubricity Properties of High Temperature Jet Fuels" AFAPL-TR-66-89 Part I 1966.

(4) Source: "Hydrocarbon Fuel Cooling of Gas Turbine Engines" AFAPL-TR-70-41

(5) Since Bureau of Mines product survey results were used to establish representative values, the Bureau of Mines designation for diesel fuel types was employed.

Table 20

Fuel Characteristics - Olefin and Aromatic Content

Type	Aromatics, Vol %		Olefins, Vol %	
	Average	Range	Average	Range
Motor Gasoline (U.S. regular plus premium) Leaded (1)	21	16-34	19	5-25
Motor Gasoline (U.S. regular plus premium) Unleaded (1)	42	37-54	9	1-12
Aviation Turbine Fuel JP-4 (1960-1971) (2)	11.4	<25 (Spec)	1.0	<5 (Spec)
Aviation Turbine Fuel JP-5 (1960-1971) (2)	15.9	<25 (Spec)	1.4	<5 (Spec

(1) Information from "U.S. Motor Gasoline Economics, Vol. 1 Manufacture of Unleaded Gasoline" Prepared for American Petroleum Institute by Bonner & Moore Associates, Houston Texas June 1967. Values are calculated.

(2) Data from U.S. Bureau of Mines, Petroleum Product Survey # 74 "Aviation Turbine Fuels" 1971.

Table 21

Spot Analyses of Diesel Fuel Samples

	Distillation	FIA Analysis Vol%		
Fuel Identification	5% - 95% (FBP)	Aromatics	Olefins	Other
NA (1)	NA	19.5	1.6	
Fairfax 1970 (2)	344(IBP) - 613 (630)	29.9	NA	.31 wt% S
Bayway 1971 (2)	384(IBP) - 576 (602)	24.2	2.0	.08 wt% S
B.P. Sweden	369-630 (647)	18.7	7.0	∿4% n-Paraffins
Esso Belgium	358-729 (731)	26.2	3.6	∿8% n-Paraffins
Texaco Belgium	368-638 (660)	19.5	2.6	∿13% n-Paraffins
Esso Cologne	372-648 (662)	20.1	3.9	∿17% n-Paraffins
Conventional Refined Diesel(4)	see other column	27.0	NA	C_{10}-C_{17} carbon number, 42.7% paraffins, 30.3% naphthenes 2300 PPM S, 13 PPM N, 120 acidity (ppm KOH/g).

(1) Source: G.L. Kearns et al "Composition of Petroleum Products in the C_{12} to C_{20} Range" ACS Petroleum Div Preprint, 3 #3, 73 (1958).

(2) Source: W.A. Herbst, Exxon Research and Engineering Company, Products Research Division.

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3.3.3 Existing Petroleum Refining Technology

The following sections represent a summary of modern crude oil refining.

3.3.3.1 Crude Assay

With few exceptions, available processing methods and additives make it theoretically possible to produce any type of petroleum product from any crude source. Petroleum crudes are selected for the production of given products by the crude assay.

The crude assay is primarily a guide in choosing the proper crude for a given job and, by comparison of product yields, is a measure of the fractionating efficiency of the refinery equipment. The procedure was pioneered by the laboratories of the Exxon Corporation over thirty five years ago and has been generally accepted by the oil industry as the most reproducible technique for crude evaluation.

Briefly, the crude assay involves distillation of twenty five gallons of crude oil in a batch still having approximately fifteen theoretical plates. In the distillation, the crude is split into narrow increments of increasing boiling points up to approximately 1050°F. Vacuum distillation is utilized beyond the gasoline boiling range to prevent thermal decomposition of the hydrocarbons. The appropriate fractions are then recombined, as required, to produce blends which are subjected to physical and chemical tests to determine their quality. These blends do not in all cases coincide absolutely with refinery products but are chosen to provide maximum information with a minimum of effort.

Blends of the fractions are made to evaluate the crude for gasoline, kerosene, gas oil, heavy vacuum gas oil and asphalt. For example, blends of cuts between 300° and 530°F meet the boiling range specifications for kerosene. Such blends are made to test the burning characteristics and jet fuel quality of the kerosene fraction. In addition, the individual incremental fractions are submitted for tests. The quantity of the crude distilling within the boiling range of the desired product is an indication of the value of the crude for producing that product with a minimum of processing.

The quality of two typical crudes for producing kerosene is shown in the following table:

	Crude	
	Lagunillas	Sweden
Crude		
Gravity - °API	17.5	42.6
Sulfur - Wt. %	1.95	0.07
Kerosene		
Yield - Vol. %	9.7	30.4
Gravity - °API	35.6	41.0
Sulfur - Wt. %	0.40	0.02
Smoke Point, mm	17	20

It can be seen that a much larger fraction of the Sweden crude could be put into kerosene than could be obtained from the Lagunillas crude. In a similar way the quantity of a given fuel from synthetic crudes that can be easily obtained will depend to a considerable extent on the nature of the synthetic crude oils.

The crude assay, in summary, allows the experienced refinery expert to choose the proper crude and the proper processing sequence to produce a given slate of products in the most economical way.

3.3.3.2 Refinery Processes

Modern processes for the conversion of petroleum into useful products are usually contained within a petroleum refinery. The function of the refinery is to convert crude oil into products required by the market in the most efficient manner. The methods employed will necessarily vary widely from one refinery to another depending on the crude processed, the nature and location of the market, the type of equipment available and many other factors. However, for simplification, it may be considered that all refining processes fall into one of four basic categories. These are (1) physical cleaning techniques, (2) liquefaction processes, that is, the conversion of one liquid component of petroleum into another liquid, (3) gasification processes and (4) chemical treatment processes. Only the second category will be discussed here since fuels are the principal product of interest.

Basically there are four types of refineries that exist today. These are the hydroskimmer refinery, an ordinary conversion refinery, a maximum conversion refinery and a fuel products refinery with specialties. The hydroskimmer refinery is found quite frequently outside the U.S. where the fractions obtained from crude are essentially in balance with the fuel requirements. A conversion refinery is designed to produce gasoline and distillates with low fuel oil. A maximum conversion refinery is designed to product maximum gasoline and distillates and the fuel oil may decline to zero in such an installation. The final type of refinery is the fuels products refinery with specialties; and this is the type of refinery most used in the U.S. where a wide variety of products are needed. Typical refinery process combinations are shown in Table 22.

Table 22

Typical Refinery Process Combinations

	Crude Distillation	Naphtha Reforming	Distillate Conversion	Residuum Processing	General Product Needs
A - Fuel Products Refineries					
Hydroskimmer	One-Stage	Powerforming	None	None	Product Needs in Reasonable Balance with Crude Fractions
Conversion	Two-Stage	Powerforming	Cat Cracking and/or Hydrocracking	None	Maximum Gasoline and Distillates; Low Fuel Oil
Maximum Conversion	Two-Stage	Powerforming	Cat Cracking and/or Hydrocracking	Coking	Maximum Gasoline and Distillates; Fuel Oil May Decline to Zero
B - Fuel Products Refinery with Specialties	Two-Stage	Powerforming	Cat Cracking and/or Hydrocracking	Coking	Gasoline and Fuel Products; Asphalt Lubricating Oils; Chemical Feedstocks; Grease, Wax; Other Specialties

A schematic diagram of different type refineries is shown in Figures 11 and 12. The higher conversions are obtained by additional processing of the bottoms and/or light ends.

The various units of a maximum conversion refinery will be summarily described in the following paragraphs. Over the years a large amount of research and development has been carried out by the many petroleum companies of the world in developing and perfecting different versions of the major refining processes. Since many of these individual developments are similar except for differences in, for example, catalysts, operating conditions and end products, no attempt will be made to describe in detail the individual developments.

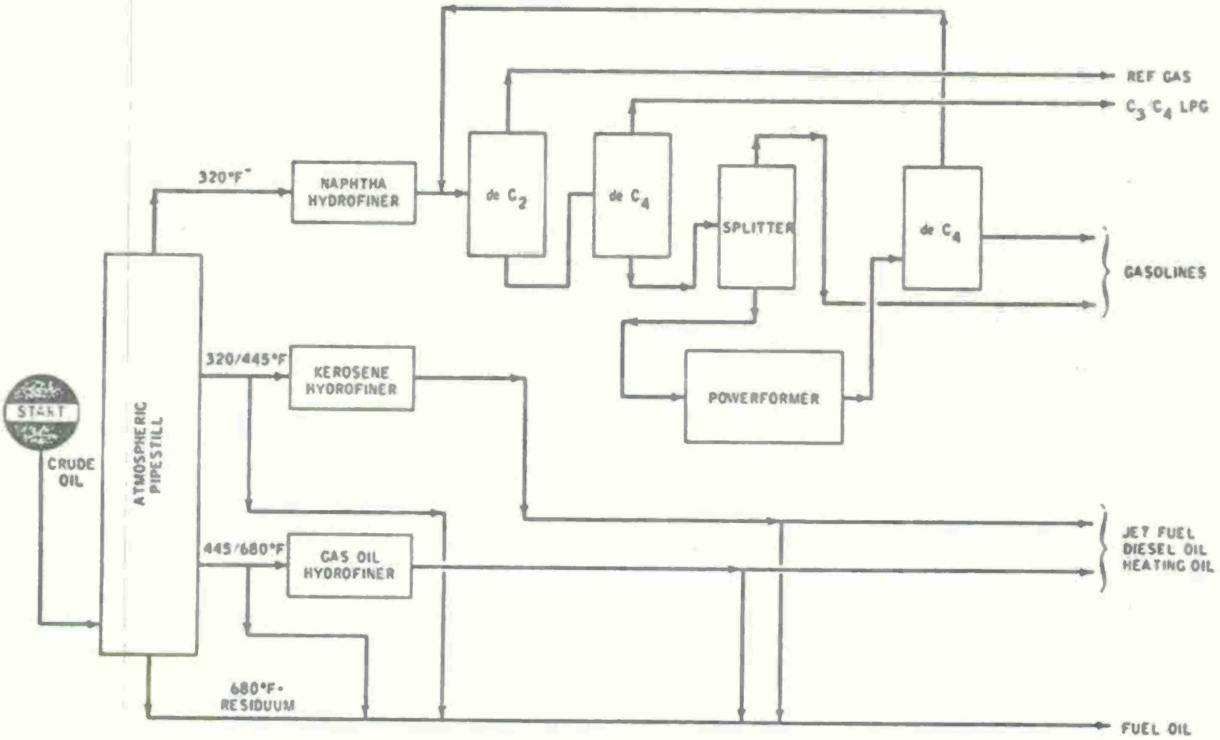
Distillation. Distillation is one of the most important processes in modern petroleum refining. Essentially every petroleum product sold has been processed in at least one distillation unit. Distillation uses differences in boiling points to separate hydrocarbon mixtures. Modern distillation technology involves the use of pipe stills which consist of a fired chamber containing pipes through which the oil to be heated is passed continuously. Preheated oil is pumped to the end of the pipe coil. A hot mixture of liquid and vapor leaves the outlet end of the coil and flows via a transfer line to a fractionating column which separates the products. Pipe stills are operated both at atmospheric pressure and under vacuum.

Catalytic Cracking. In catalytic cracking a catalyst is used to convert large hydrocarbon molecules into smaller ones. Presently, the major emphasis in catalytic cracking involves "fluid beds" in which the feed is contacted with the hot catalyst in a fluid operation. Although catalytic cracking has as its principal aim the production of motor fuels, heavy materials are also produced. The heavy liquids produced in catalytic cracking may be hydrodesulfurized and used as gas oil components or used as fuels or recycled to the feed. A number of companies have developed their own processes for fluid bed catalytic cracking. Processes are offered by Exxon Research and Engineering Company (the originator of the fluid catalytic cracking technique), the M. W. Kellogg Company, Shell Development Company, and Mobil Oil Corporation.

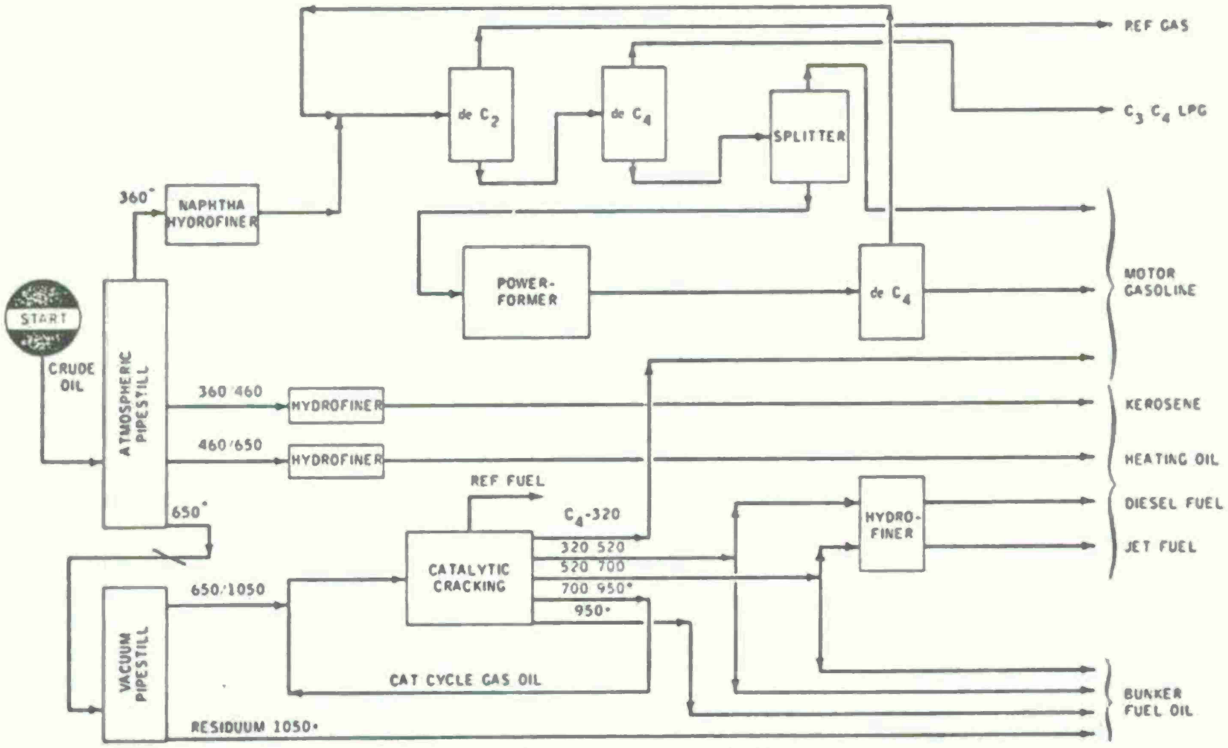
Hydrotreating. Hydrotreating involves the reaction of hydrogen with a feed stock to improve the properties of the material as a fuel or for feed to another process. Hydrotreating is one of the most important techniques in refineries for the removal of sulfur, nitrogen and other obnoxious compounds from petroleum materials. Feed stocks which may be hydrotreated include virgin naphtha, cracked naphthas, heating oils and heavy gas oils and residual oils. Hydrotreating removes such sulfur compounds as mercaptans, disulfides, thiophene and benzothiophene.

Figure 11

Typical Refinery Process Combinations



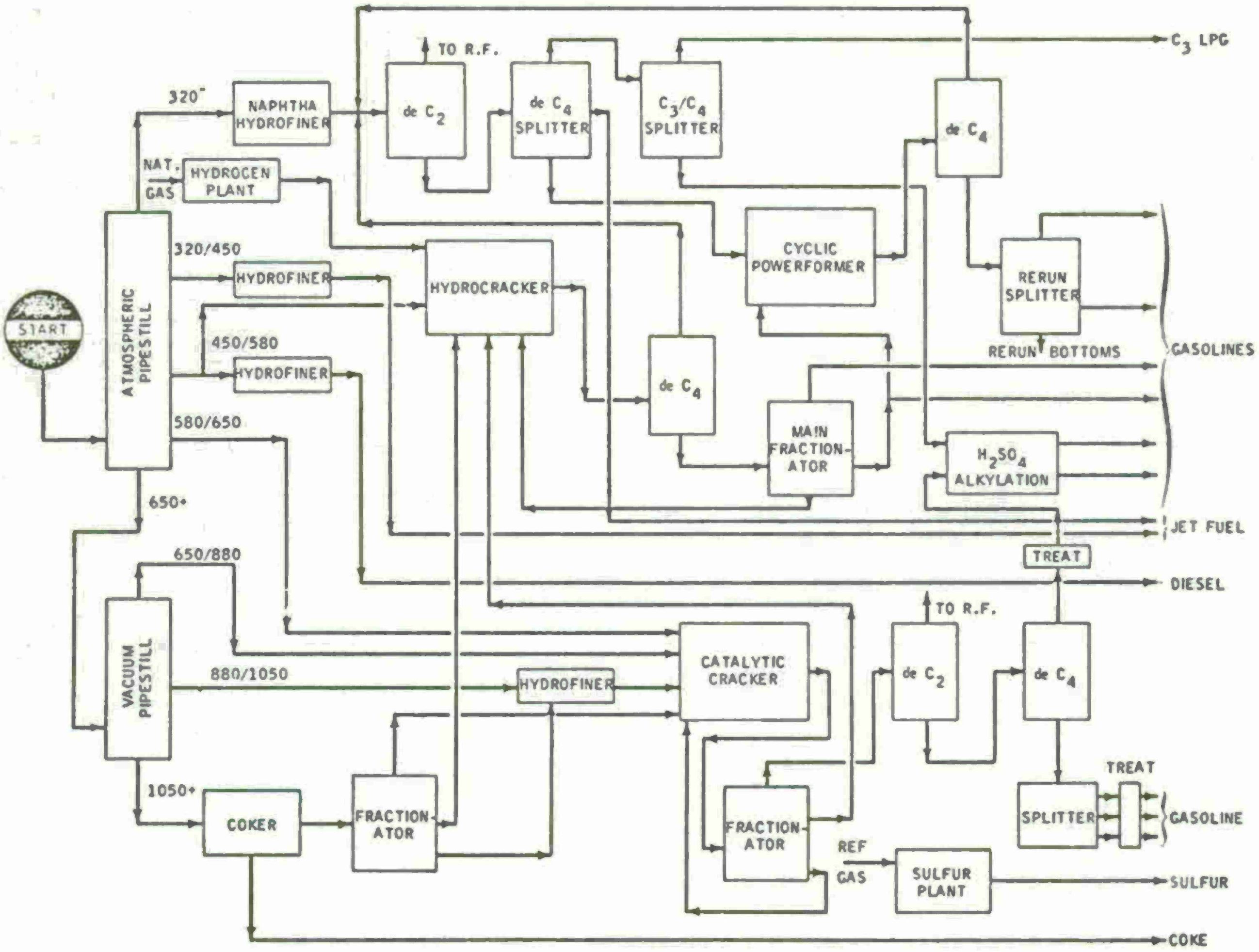
- Typical Hydroskimming Refinery



- Typical Conversion Refinery

Figure 12

Maximum Conversion Type Refinery



Mercaptans and disulfide types are representative of a high percentage of total sulfur in lighter virgin oils such as virgin naphtha heating oil. Thiophenes and benzothiophenes appear as the predominate sulfur form in heavy virgin oils and even more so in cracked stocks of all boiling ranges. Thiophenic sulfur is the hardest to remove.

A number of catalysts are available for use in hydrotreating. These include molybdena on alumina, cobalt molybdenate on alumina, Ni molybdate on alumina and Ni tungstate. Which catalyst used depends on the particular application. A number of hydrotreating processea are available. Licensing is offered by Exxon Research and Engineering Company, Hydrocarbon Research Incorporated and Cities Service Research and Development Company and by Universal Oil Products Company and Cheveron Research Corporation. Sulfur is removed as hydrogen sulfide in these processes.

Hydrocracking. Hydrocracking is a fixed bed catalytic process which cracks and hydrogenates hydrocarbon feeds. The process consumes large quantities of hydrogen and a hydrogen plant is usually necessary to support the operation. Practically any stock can be hydrocracked, including refractory feeds which resist conversion by other processes. The most promising application for hydrocrackers appears to be converting poor catalytic cracking feeds into gasoline or middle distillates. About 10% of the cracking capacity currently in operation in the United States is hydrocracking. A significantly higher percentage is currently being installed in new U.S. refineries, however.

Thermal Conversion. Thermal conversion processes are those which decompose, rearrange, or combine hydrocarbon molecules by the application of heat without the aid of catalysts. Several conversion processes can be further subdivided into two classes: those involving thermal cracking and those involving coking. Thermal cracking will not be considered here since it has been mainly displaced in modern refineries by catalytic cracking. Coking is a process used for conversion of very heavy resids to lighter fuels.

Coking can be divided into two types, fluid and delayed. (FLEXICOKING, a development of Exxon Research and Engineering Company, combines fluid coking with coke gasification to convert 98 weight percent of a vacuum residuum to gaseous and liquid products). In fluid coking the resid is coked by spreading it as a thin film of liquid on the outside of hot coke particles. The resid is then heated in a fluid bed to produce lighter materials which are then subsequently used for fuel oil or feed to a catalytic cracker. A solid product, coke, is a by-product from this operation. The sulfur in the coke feed tends to concentrate in the coke product. This coke product at present is used primarily as fuel. Over 20,000 tons per day of coke is currently produced in the U.S.

Delayed coking is another type process used to upgrade resids. Light ends are removed from the resid by flashing, and the bottoms are heated in a furnace at cracking temperatures. The heated oil enters a soaking drum which provides the long residence time needed for cracking. The heavy ends from the soaking step are recycled. Delayed coking gives higher coke yields than fluid coking. For example, in one case fluid coking gave 18% by weight of coke whereas, on the same feed stock, delayed coking gave 27.3% by weight.

Catalytic Reforming. Catalytic reforming is a fixed bed noble metal (platinum) process for the production of aromatics for high octane components for use in gasoline. Reactions involved over the dual functional catalysts employed include dehydrogenation of naphthenes to aromatics, dehydrocyclization of paraffins to aromatics, isomerization and hydrocracking. Next to catalytic cracking, catalytic reforming is the largest refinery process in use in terms of volume of products produced. In addition to a liquid product for gasoline production, reforming also produces hydrogen which is used elsewhere in the refinery, e.g., for hydrotreating.

Sweetening. Sweetening is a process for improving the odor of kerosene and other petroleum fractions by removing mercaptans (thiols). This is done either by extracting the thiols or by converting the foul smelling thiols (R-SH) to the less odorous disulfide compounds (R-S-S-R). There are a wide variety of sweetening processes.

Doctor Sweetening is the oldest of commercially employed sweetening processes. The reagents employed include caustic, lead oxide and elemental sulfur. Inhibitor Sweetening employs a phenylene diamine antioxidant added during caustic washing. The blend is bubbled with air and the thiols are oxidized to disulfides. It has been shown that Inhibitor Sweetening results in an increase in the peroxide content of the fuel. Other sweetening processes in which thiols are oxidized to disulfides include the Hypochlorite Process and the Copper Chloride Process. In the Hypochlorite Process, in addition to thiol conversion to disulfides, some sulfur compounds are oxidized to sulfones and sulfonic acids which are soluble in the hypochlorite reagent. In the Copper Chloride Process oxygen and the reagent are consumed. The Copper Chloride can be in the form of a solution, slurry or fixed bed. More recently a fixed bed catalytic process for the oxidation of thiols to disulfides without the use of caustic has been introduced (i.e., Mercapfining).

3.3.4 Anticipated Synthetic Crude Processing

3.3.4.1 General Problems

The organic matter present in shale and coal is different from that found in petroleum. Shale organic matter appears to contain a molecular complex of saturated, condensed polycyclic ring systems loosely interconnected with alkyl and heteroatom side chains. Pyrolysis of this matter produces a shale oil containing a large proportion of heterohydrocarbon compounds containing nitrogen, oxygen and sulfur and a large proportion of olefins. Nitrogen compounds found in shale oil include pyrroles, indoles, carbazoles, pyridines, quinolines, amines and amides, while oxygen compounds are rich in phenols and carboxylic acids. Typical coal contains a molecular complex of condensed ring aromatics ranging from single rings up to several condensed rings per cluster. The clusters are joined together by connecting bridges principally short aliphalic groups and ether, sulfide and disulfide linkages. Organic sulfur structures in coal include condensed thiophenes, sulfides, disulfides and thiols. Oxygen structures include phenols, naphthols, ethers, ketones, quinones, furans and carboxylic acids. Nitrogen structures include pyridines, quinolines, amines, pyrroles and carbazoles. Upon pyrolysis coal produces a liquid high in aromatics and containing appreciable nitrogen, oxygen and sulfur.

When compared to petroleum, the hydrocarbon compounds derived from pyrolyzed shale and coal are (1) deficient in hydrogen, and (2) contain higher levels of organic nitrogen and oxygen. Liquid fuels containing compounds similar to those found in present petroleum based fuels can be produced by the introduction of large quantities of hydrogen to saturate olefins and aromatics (as required) and to catalytically remove undesirable heteroatoms. Adjustment in the carbon number distribution may also be required.

The technology to convert coal and shale derived crude oils into present day fuels exists. Such a conversion would involve present petroleum refinery processes, with modified operating conditions. Such existing technology probably would not be optimum for synthetic crude processing and may well be replaced by newer process technology as the introduction of synthetics increases over the years.

There are a number of possibilities for synthetic crude processing, in general, either involving direct or combined (i.e., with petroleum crude) processing.

Direct

- Direct processing of synthetic crude to a single product.
- Direct processing of synthetic crude to a variety of products.

Combined

- Combined processing of both synthetic crude and petroleum crude in an existing refinery.
- Combined processing of both synthetic crude and petroleum crude in new refinery designed specifically for this purpose.

In both the case of the hydrogen deficient stoichiometry problem and the sulfur-nitrogen-oxygen contaminant problem direct processing of synthetic crudes using large quantities of hydrogen to a given product such as present day specification diesel or aviation turbine fuel is considered unlikely on a large scale. On a commercial basis, it is more likely that coal and shale rock crude liquids will be processed in combined refineries designed to handle both these liquids and petroleum crude oil and to produce a spectrum of products in a manner such that minimum hydrogen requirements and minimum capital investment are achieved. Both the exact nature of the refinery processing that will be applied to synthetic crude oil fractions and the detailed chemical composition of the resultant products is difficult to predict at this time.

There are a number of catalytic processes involving treatment with hydrogen which could be involved in fuel production. These processes differ in the types of chemical reactions which are carried out as a result of variations in catalyst type, pressure, temperature and space velocity. For convenience they can be grouped into three classes.

Type	Reactions Carried Out
Hydrotreating (Hydrofining)	Removal of sulfur compounds, nitrogen compounds and oxygen compounds (i.e., phenols and peroxides). The boiling range of the fuel is generally not changed.
Hydroconversion (Hydrocracking)	The process is basically a combination of catalytic cracking (breaking molecules into smaller fragments) and hydrogenation. Heavy boiling components are converted into products which contain fuel range components.
Hydrogenation	Unsaturated compounds (olefins and aromatics) are hydrogenated to saturated compounds of the same carbon number.

Hydrotreating is used to reduce sulfur and/or other impurities and to improve color, odor and stability. A fixed bed cobalt-molybdate catalyst is often used at relatively low temperatures (500-700°F), pressures (200 to 800 pounds per square inch guage (psig)) and hydrogen consumption rates (10 to 1,000 standard cubic feet (SCF) of H_2 per barrel).

Hydroconversion (Hydrocracking) processes came into wide use during the 1960's. A major reason for its rapid growth is the increasing demand for kerosene type jet fuel relative to motor gasoline. The hydrocracking process is basically a combination of catalytic cracking and hydrogenation. A wide variety of feed stocks can be processed. Light and heavy gas oils, often undersulfurized, account for a large percentage of the feed stocks. Operating conditions are more severe than with hydrotreating, i.e., temperature from 600 to 800°F, pressures from 800 to 3000 psig and hydrogen consumption rates from 200 to 1000 SCF of H_2 per barrel. Because of the high pressure hydrogen treatment employed, products from Hydrocracking processes have negligible sulfur, nitrogen and olefin content. Unless operating conditions are severe, aromatic rings are not hydrogenated, but side chains are often removed.

Hydrogenation processes can employ a variety of conditions to achieve the same result, i.e., hydrogenation of olefins and aromatics. Aromatics, for example, can be removed from kerosene for smoke point improvement. Sulfur free stocks can be hydrogenated at mild conditions using active catalysts such as a massive nickel catalyst. Sulfur containing stocks can be hydrogenated at more severe conditions using catalysts not sensitive to sulfur poisoning such as a nickel tungsten catalyst.

3.3.4.2 Processing Synthetic Crude from Coal

Coal pyrolysis liquids which contain appreciable quantities of light aromatics would appear to be most suitable for the production of gasoline. The principal techniques for producing gasoline and distillate fuels from coal liquid products will certainly include some form of hydrogen treatment. Which of the several hydrogen treatments to be selected will depend on the process used to produce the synthetic crude and the full slate of products desired. It is also likely that a thermal treatment will be necessary and probably a cracking unit will be useful.

An example of the treatment of the raw product from coal liquefaction has been given for Food Machinery Corporation's COED process (1). The COED process produces liquid from coal by pyrolysis. The product is a highly viscous oil containing large amounts of sulfur and nitrogen. An analysis of a raw product oil from a Pittsburgh coal is shown in Table 23 (from Ref. 2). Less than thirty percent of the raw product is in the boiling range of kerosene.

The effects of hydrogenating a crude product is shown in Tables 24 and 25 (from Ref. 1).

Table 23

Analysis of COED Oil from Pittsburgh Coal

°API Gravity	-6.8°
Kinematic Viscosity, SUS @ 250°F	188.1
@ 275°F	98.1
% Ramsbottom Residue	15.8
% Quinoline Insolubles	1.0
% Asphaltenes	28
Elemental Analysis, wt.%	
C	82.06
H	7.32
O	7.29
N	1.02
S	2.09
Ash (sulfated)	0.22
ASTM Dist., vol.%	°F
IBP	444
10%	615
30%	777
50%	903
70%	1028
84%	1084

Table 24

Material Balance - Hydrotreating

Oil Source	Illinois No. 6-Seam Coal
Run Duration, hr.	168

Summary Operating Conditions	
Pressure, psig	1750
Temperature, °F.	760
Space Velocity, WHSV	0.50
Recycle Gas, scf/bbl.	78900
Catalyst	American Cyanamid AERO HDS-3A

Yields	Wt.%, Based on Oil and H_2 Input	Vol.%, Based on Oil Input
Syncrude (C_6+)	93.6	112.7
C_4 and C_5	0.4	9.7
C_1- C_3	3.5	-
Liquor	8.0	-

Heteroatom Removal,%	
S	95.3
O	93.6
N	87.7
Hydrogen Consumption, scf/bbl. raw oil	3670

Table 25

Full Range COED Syncrude from Illinois No. 6 Coal

Test	Result
Flash Pt., C.C. °F.	46
Pour Pt., °F.	<-36
Water & Sediment, Vol. %	Trace
Ash, wt. %	<0.005
ASTM Distillation, °F.	
IBP	190
10%	273
50%	518
90%	684
95%	720
Viscosity, cs 100 °F.	3.4
API Gravity	27.2

The product has a much lower viscosity and pour point and has a large fraction boiling in the kerosene range.

To increase the yield of material boiling in the kerosene range, three options are open. These are thermal treatment, catalytic cracking or hydrocracking. A bench scale experiment involving catalytic cracking of a hydrogenated coal oil is described in Ref. 2. Work reported in the literature on catalytic cracking and hydrocracking has usually been designed to maximize gasoline products rather than distillate fuel. It is possible that a more thorough study would indicate that, with less severe conditions, cracking could produce more distillate fuel. Coking of the higher boiling point material from coal liquefaction could also produce more kerosene boiling range material.

Liquid products produced from coal by reacting hydrogen with the coal, could, as in the Hydrocarbon Research Institute (HRI) H-Coal process, the Bureau of Mines Synthoil process or Pittsbrugh and Midway's SRC process, possibly be treated directly. Again coking could be used to increase the jet fuel yield. Some form of cracking may be mandatory for the SRC product since it is a solid at room temperature.

3.3.4.3 Processing Synthetic Crude from Shale

The oil produced from shale is not a very satisfactory material for use in a conventional refinery. It is viscous and contains a high percentage of nitrogen. Like the liquid products from coal, shale oil will be treated by a combination of thermal, hydrogenation and cracking processes.

Hydrogenation of the liquid material improves its properties as shown in Table 26. The quantity of material in the boiling range of aviation turbine fuel has been increased significantly and the sulfur and nitrogen content of the product is much lower.

Reference (3) shows the effect of a sequence of steps in upgrading raw shale oil. These steps are (1) coking, (2) hydrostabilization, (3) hydrodenitrogenation, (4) reforming of naphtha and (5) catalytic cracking of heavy oils. A large fraction of the product is in the distillate range after steps 3 and 5. The results of coking raw shale oil and hydrogenation of the coker distillate are presented in reference (4). The authors evaluated the product as jet fuel and diesel fuel and found a combined yield of 75-78% of the original crude shale oil to the jet and diesel fuels. Finally, high boiling components can be hydrocracked to give lighter materials(5). The conditions used in the hydrocracking gave a high yield of gasoline range material rather than a distillate range material.

3.3.4.4 Hydrogen Production

In the production of finished fuel from coal or shale a large quantity of hydrogen will be necessary. Table 27 gives a breakdown of hydrogen requirements for treating crude liquids from coal and shale to produce a liquid from which a fuel fraction may be obtained. To produce 5 billion gallons per year of fuel would require approximately 6,000 million cubic feet per day of hydrogen for COED liquid and 4,000 million cubic feet per day for shale oil liquid. This assumes that the crude liquid products would give a 20% yield of fuel. These numbers do not include hydrogen that might be used in a finishing step. (The liquid products after the initial hydrogen treatment still contain considerable nitrogen that may have to be removed by further hydrogen treating.) The source of the hydrogen used to up-grade the crude liquids products will depend on the liquefaction process being considered.

Table 26

Properties of Crude Shale Oil and Syncrude(a)

	Crude Shale Oil	Syncrude
Gravity, °API	28.0	46.2
Pour Point, °F	75	50
Sulfur, wt %	0.8	0.005
Nitrogen, wt %	1.7	0.035
RVP, psi	-	8
Viscosity, SUS at 100°F	120	40
Analysis of Fractions		
Butanes and Butenes, vol %	4.6	9.0
C_5-350°F Naphtha		
Vol %	19.1	27.5
Gravity, °API	50.0	54.5
Sulfur, wt %	0.70	<0.0001
Nitrogen, wt %	0.75	0.0001
K Factor	11.7	12.0
Aromatics, vol %	-	18
Naphthenes, vol %	-	37
Paraffins, vol %	-	45
350-550°F Distillate		
Vol %	17.3	41.0
Gravity, °API	31.0	38.3
Sulfur, wt %	0.80	0.0008
Nitrogen, wt %	1.35	0.0075
Aromatics, vol %	-	34
Freezing Point, °F	-	-35
550-850°F Distillate		
Vol %	33.0	22.5
Gravity, °API	21.0	33.1
Sulfur, wt %	0.80	<0.01
Nitrogen, wt %	1.90	0.12
Pour Point, °F	-	+80
850°F-Plus Residue		
Vol %	26.0	None
Gravity, °API	12.0	
Sulfur, wt %	1.0	
Nitrogen, wt %	2.4	

(a) Source: U.S. Energy Outlook: Oil Shale Availability, National Petroleum Council, Washington, D.C. 1973.

Table 27

Hydrogen Required in Production of Fuel

	SCF/Bbl. Liq.	SCF/Gal. Fuel (1)	SCF $\times 10^{-6}$ (2)
COED Coal Oil (3)	3670	437	5986
Shale Oil (4)			
Hydrostabilization	414	219	675
Hydrodenitrogenation	1970	235	3213
TOTAL for Shale Oil	2384	283	3888

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(1) Hydrogen consumed in hydrogenating liquids required to produce one gallon of fuel assuming 20% yield of fuel from crude liquid.

(2) Hydrogen required to produce 5 billion gallons/year of fuel.

(3) Reference 23.

(4) Reference 25.

In the COED pyrolysis scheme of coal liquefaction, 7820 standard cubic feet of gas (on a N_2, H_2O, CO_2, H_2S-free basis) is produced, containing 60.72 vol. % H_2, per barrel of liquid oil(1). Thus, sufficient hydrogen is produced to hydrogenate the oil product. The gas also contains CO and CH_4 which could be used to produce more hydrogen.

In other coal liquefaction processes, where hydrogen is reacted directly in the liquefaction step (e.g., the H-Coal, SRC or Synthoil processes), the product oil could be steam reformed to produce the hydrogen necessary for the process. Alternatively, coal could be reacted with steam and oxygen to produce hydrogen in a gasification step such as the Koppers-Totzek, the Lurgi or the Bamag-Winkler gasifiers. The technology for coal gasification in these reactors has been commercially proven.

In the case of shale oil hydrogenation it is probable that the necessary hydrogen will be produced by steam reforming of the crude product oil or by partial oxidation of the oil.

When considering the production of finished fuels from synthetic liquid oils, hydrogen will represent a major cost factor in up-grading pyrolytic shale or coal oils and is an integral part of coal liquefaction for some processes.

3.3.4.5 Consideration of Refinery Integration

It is unlikely that large numbers of plants would be built to produce only a single product fuel from synthetic crudes. Although in principle this would be possible, the cost would be prohibitive. It is much more likely that a refinery utilizing synthetic crudes would produce a full range of fuel products. This would lend itself to optimization in a manner similar to present day petroleum refining which can be optimized with constraints such as, for example, maximum production of aviation turbine fuel for no more than a given cost.

Two cases would appear possible for production of fuels. The first case would be the processing of synthetic crudes along with petroleum in an existing refinery and the second case would be the processing of synthetic crudes in a grass roots refinery specifically designed for synthetic crudes. The first case is perhaps more realistic for the near future since experience with synthetic crudes in an existing refinery (with, perhaps, additional added units that may be necessary, e.g., for the production of hydrogen) would be very valuable in designing a grass roots refinery specifically for synthetic crudes.

There may be added benefits in refining a mixture of coal or shale liquids along with petroleum crudes. An example of the benefits of integration of petroleum and synthetic crudes can be seen by the following. Typically, synthetic crudes from coal and shale are high in aromatics. Aromatics have high octane ratings and are thus desirable for gasoline production. On the other hand, aromatics are not only not desirable for other fuels such as aviation turbine fuels, diesel fuels and heating oils but may actually reduce the quality of these fuels. In a refinery processing petroleum crudes, catalytic reforming is used to increase the aromatic content of liquids for gasoline production. It is possible that in a refinery utilizing both petroleum and synthetic crudes that the aromatic compounds from shale and coal oil could reduce the extent to which catalytic reforming is necessary for gasoline production while the use of the naphthenic and paraffinic compounds from petroleum crudes would reduce the extent of hydrogenation that crude shale and coal oils require for production of aircraft turbine fuels, diesel fuel and heating oil. Thus, there could be a very beneficial synergism in processing synthetic crude oils and petroleum crude oils in the same refinery. In fact, the mass and energy balances may be such that the diesel and turbine fuels would actually come mainly from the petroleum crude oil and the loss of raw material for gasoline production would be replaced by synthetic crude oils. In any case, a rather detailed examination of the economics would be required before an optimum route to aviation turbine fuels could be obtained.

Finally, a processing step used in producing chemical raw materials may well be employed to optimize an integrated refinery for aviation turbine fuels. This step involves the liquid extraction of aromatics from refinery streams and is used at present to produce benzene, toluene and C-8 aromatics for use as chemical raw materials. This step might be useful for removing aromatics from fuels for use in aviation turbines, diesel engines, etc. and the subsequent blending of these aromatics into streams to be used for gasoline. The inclusion of this step could reduce the use of catalytic reforming for aromatics production for gasoline and at the same time could reduce the use of intensive hydrogenation to remove aromatics in the production of aviation turbine and other fuels.

The many alternates for fuel production in refineries utilizing synthetic and petroleum crudes makes it extremely difficult to predict at this time both the exact nature of the processing steps to be employed and the detailed composition of the products themselves.

References Cited in Section 3.3.4

(1) J. F. Jones, "Project COED - (Char-Oil-Energy Development)," presented at IGT Clean Fuel from Coal Symposium, September 12, 1973, Chicago, Illinois.

(2) J. F. Jones et al., "Char Oil Energy Development," R&D Report No. 56 - Final Report - Contract No. 14-01-001-498 for October 1970 - June 1971 - Appendix II, p. 48, FMC Corporation for OCR.

(3) D. P. Montgomery, "Refining of Pyrolytic Shale Oil," ACS Division of Fuel Chem. Preprints, April 1968.

(4) E. L. Clark et al., I&EC 43, 2173 (1951).

(5) P. L. Cottingham and H. C. Carpenter, I&EC Proc. Des. and Dev., 6, 212 (1967).

4. AREAS FOR FRUITFUL R&D EFFORT

At present, the magnitude of the tasks involved in developing economic synthetic fuel processes are such that much of the current effort in the synthetic fuel area is devoted to the problems of process development per se. At present, there are a large number of possible permutations and combinations of crude synthetic liquids and secondary treatment schemes for these synthetic crudes, all of which could possibly influence the nature, cost and availability of synthetic derived fuel products. Although the ultimate development of synthetic fuels would appear certain as petroleum sources are depleted, the timing and exact nature of the transition remains unclear at the present. In the presence of such a complex situation, it would appear necessary for a fuel user such as the Army (who is dependent on commercial fuel sources and whose power plants of necessity have a long life in use) to conduct a vigorous R&D program to insure the achievement of its objectives.

A number of broad areas where R&D effort relative to synthetic derived fuels would appear potentially fruitful are listed below.

1. Analytical Studies and Forecasts

At present, synthetic fuels are, in general, not a major commercial factor in the world fuel situation. Although the timing for the introduction of synthetic fuels is not clear at present, the magnitude of the effort involved in developing a sizable synthetic fuel industry is such that its introduction even under the most advantageous circumstances would still require in excess of 10 years to accomplish. Thus, at this time, analytical paper studies and forecasts appear highly desirable.

- Analytical studies and forecasts emphasizing the Army's needs and point of view designed to establish the general nature of synthetic crudes and products derived therefrom in advance of their actual introduction. Factors to be analyzed should include the effects of:

    (1) The type of synthetic material used and the type of process employed to produce the synthetic crude.

    (2) The nature of secondary processing of the synthetic crude employed to convert it to a fuel product. Both direct processing and indirect processing involving combined refineries processing both petroleum and synthetic fuels should be considered.

- Generation of data and the development of expertise and background in the synthetic fuel area so as to provide a sound technical basis for an Army input to a national energy policy and to insure maximum integration of the Army's effort with that of other government agencies and private industry.

- Fuel cost and availability studies aimed at providing data for trade-offs between specifications (or composition) and supply-demand and cost factors to insure maximum supply at lowest cost of desired fuels. Such studies should emphasize the maximum production of middle distillate fuel from synthetic sources.

- Encouragement of maximum interactions between experts in the areas of fuels, power plants and process development. This interaction could be effected via joint study efforts or DOD funded workshops.

- Because of the Army's strong interest at present and in the future in middle distillate fuels, analytical studies should be carried out to predict the impact of changes in synthetic fuel developments on nature and supply of middle distillate fuels. For example, the Fischer-Tropsch process can produce an excellent middle distillate fuel rich in paraffins while coal pyrolysis processes generally produce an aromatic rich material more suited for motor or aviation gasoline.

- Much of the current effort has centered on U.S. developments in the synthetic fuel area. In contrast, the only real synthetic fuel industry at present in existence is outside the U.S. Studies to analyze and predict foreign synthetic fuel developments should also be carried out. Both the conventional and emergency fuel situation should be analyzed.

2. Product Quality Studies

Product quality studies should be carried out to help to further define the nature of both unblended synthetic fuels and fuels obtained from blends of synthetic fuels with conventional petroleum fuels. Because of the complexity and uncertainties involved with synthetic fuels, this effort should either be carried out in conjunction with the analytical studies and forecasts effort, or in close coordination with this effort. The object of the studies should be to obtain basic physical and chemical analyses of synthetic fuels and blends of synthetic fuels so as to further elucidate their detailed composition particularly in terms of any difference which from conventional fuels which might cause problems to arise.

3. Storage Stability

Long storage life would appear to be a necessary feature of Army used fuels. The introduction of even small quantities of synthetic fuels into a fuel blended from petroleum and synthetic liquids could have a major deleterious effect on storage life as the storage stability characteristics are generally dominated by the nature of the trace impurities in the fuel, i.e., the nature and level of organic sulfur, nitrogen and oxygen compounds.

The presence of olefins and aromatic hydrocarbons are also generally found to accelerate the autoxidative sediment, gum and deposit formation. Synthetic liquids derived from shale and coal often have a much higher level of nitrogen and oxygen compound impurities than petroleum crudes. For example, nitrogen compounds should be of particular concern because: (1) present diesel fuels and aviation turbine fuels such as JP-5 or Jet A fuel generally contain little nitrogen (e.g., less than 10 ppm for jet fuel and less than 50 ppm for diesel fuels), and (2) with present removal technology such as hydrotreating nitrogen is much harder to remove than sulfur from a fuel. These factors could result in a situation where nitrogen levels are dramatically increased, with the introduction of synthetic fuels, with a severe drop in the quality of fuels during long term storage.

The impact of synthetic fuel components on the storage stability, particularly of conventional middle distillate fuels, should be studied. Studies should investigate the effect of the presence of olefins, sulfur, nitrogen and oxygen containing compounds on the storage stability of fuels and which compound types will occur in the synthetic products and which types and to what level must be removed to provide adequate stability. Techniques should also be studied to develop fuel pretreatment technology to allow the use of marginal or subquality fuels, particularly in an emergency situation.

4. Deterioration, Corrosion and Material Compatibility

Studies should be undertaken to assess possible problems in the deterioration, corrosion and materials compatibility area. Coal liquids, for example, potentially contain high levels of a large spectrum of metals as a result of the high initial metal content of the parent coal. The presence of high levels of organic oxygen compounds, such as carboxylic acids, phenols, ketones, in synthetic fuels could also result in attack on storage containers, leaching the metal into the fuel in addition to damage to storage facilities. Dissolved metals such as copper are known to drastically reduce the storage stability of fuels, whereas the presence of metals such as sodium, potassium or vanadium could cause major problems with turbine blade life of engines used in helicopters as a result of hot corrosion attack. Since future power plants may employ new materials of construction, e.g., new turbine blade materials, changes in fuel composition as a result of the introduction of synthetic fuels should be considered along with compatibility with present fuels and fuel combustion products.

5. Toxicity, Emission and Odor Problems

Potential toxicity problems associated either with handling synthetic fuels or with emissions and/or odors from engines burning synthetic fuels should be considered. For example, Russian workers associated with their Estonian shale operations have reported both toxic effects and carcinogenic activity with shale pyrolysis products. The high organic nitrogen content of synthetic liquids would also be expected to result in increased NO_x emission levels during fuel combustion. Since conventional fuels will be commercially procured, it is anticipated that Army efforts in the toxicity, emissions and odor area will be coordinated with other groups working with conventional synthetic fuels. Consideration should also be given by the Army to potential acute toxicity problems associated with contact with unfinished synthetic derived liquids which might be used as emergency fuels.

6. Combustion

Studies should be undertaken to determine if the composition of synthetic fuels will effect combustion characteristics. Coal derived liquids, for example, are expected to be relatively high in aromatics content. Potential combustion problems associated with normally low aromatics containing middle distillate fuels should be considered.

7. Water Reactivity

The presence of high quantities of organic oxygen compounds including carboxylic acids and phenols in some synthetic crude materials creates a potential water reactivity problem if such materials are added in quantity to a fuel. Studies should be carried out to identify potential water reactive agents in synthetic crude and product fuels and to determine their effect as a function of compound type and level on fuels, and also to identify any interactions with other trace impurities such as nitrogen compounds. Emphasis should be given to the consideration of the effect on diesel type fuels because of their known sensitivity in this area and wide Army use.

Phase separation after contact with water is anticipated to be a major problem associated with the use of methanol in gasoline blends as a conventional motor gasoline fuel. An evaluation of the practicality of the use of such methanol-gasoline blends for Army use as a conventional motor gasoline fuel should be made, along with an assessment of problems associated with such fuels in emergency use. Also, the properties of blends of methanol with synthetic fuel fractions, particularly those containing appreciable quantities of organic oxygen compounds should be evaluated, to assess the effect of the presence of these organic oxygen compounds on the phase separation properties of such blends.

8. Fire Safety

Changes in fuel composition could affect properties related to fire safety such as fuel flammable or misting tendencies under impact. Studies to assess the possibility of problems in this area should be carried out.

9. Other Areas

A number of other areas should also be considered. For example:

- New Opportunities

  Can synthetic fuel properties be a blessing rather than only a problem. For example:

  - A high density fuel for increased range of volumetrically limited systems.
  - Should the phenols present in synthetics such as shale liquids be left in the fuel to function as a natural antioxidant for enhanced storage stability.
  - Should condensed thiophene type sulfur compounds such as alkyl benzothiophenes or dibenzothiophenes which are the most stable of all classes of sulfur compounds (in terms of storage stability) be left in the fuel to insure good lubricity properties.

- Additives

  What new additives will be necessary or desirable.

  - New storage stability additives.
  - New additives for improved cold flow properties of middle distillate fuels.
  - Additive packages for emergency fuels to insure operability.
  - Additives to improve phase separation properties of methanol-fuel blends.

- Emergency Fuel Operability

  Field or on-vehicle pretreatment of emergency fuels involving use of catalysts and/or absorbents.

5. APPENDIX

ADDITIONAL REFERENCES

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This STAF reviews the broad problem of the impact on the U.S. Army of the use of synthetic fuels (defined as a non-petroleum derived fuel) over the time period of 1975 to 2000. The STAF is divided into three basic parts. The first part involves a forecast of which synthetic fuels will have a major impact in the time period under study. In the second part of the STAF, those alternate fuels identified as the most feasible synthetic fuels in the future were subjected to detailed analyses. The third part of the STAF consists of

the identification of a number of areas which appear to offer promise for fruitful R&D in the synthetic fuel area.