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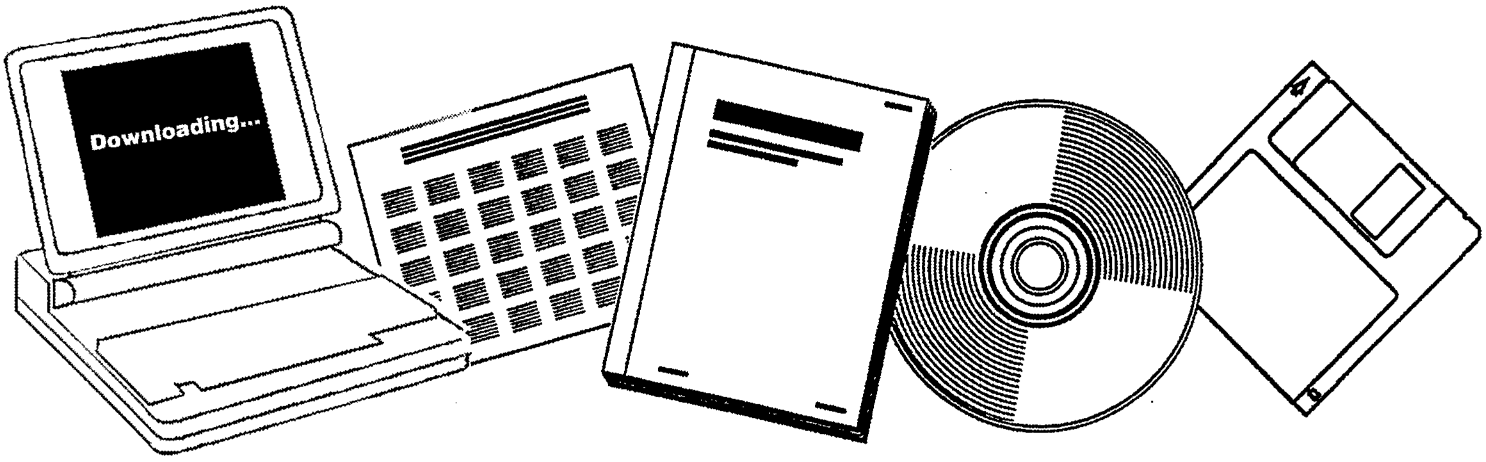
REFINING SYNTHETIC LIQUIDS FROM COAL AND SHALE

NATIONAL RESEARCH COUNCIL
WASHINGTON, DC

NOV 1980



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Refining Synthetic Liquids from Coal and Shale

Final Report
of the
Panel on R&D Needs in
Refining of Coal and Shale Liquids

Energy Engineering Board
Assembly of Engineering

NATIONAL ACADEMY PRESS
Washington, D.C. 1980

NOTICE: The project that is the subject of this report was approved by the Governing Board of the National Research Council, whose members are drawn from the Councils of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine. The members of the Committee responsible for the report were chosen for their special competences and with regard to appropriate balance.

This report has been reviewed by a group other than the authors according to procedures approved by a Report Review Committee consisting of members of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine.

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The study culminating with this report was performed under contract number E(49-18)-1216 between the U.S. Energy Research and Development Administration and the National Academy of Sciences.

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The purpose of this study was to determine the status of research and of technology for refining liquids from oil shale or coal, to recommend areas for future research and development emphasis, and to make recommendations on the roles of government and industry in these areas. Refining is the link between the primary production of liquids from these solid hydrocarbon sources and the supply of liquid fuels meeting the requirements of the various consumers. Therefore, parts of this report are devoted to discussions of liquefaction technologies and the corresponding liquid compositions, the committee's view of coming changes in demand for various types of liquid fuels, and the possibilities for evolution in end-use equipment. Today's refining technology for these synthetic liquids adds hydrogen to eliminate elements other than carbon and hydrogen and thus produce substances similar to petroleum hydrocarbons. Because the manufacture and use of hydrogen are the major sources of energy consumption and expense in refining these liquids, the technology and research needs, ...

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PREFACE

During the 1980s, additions to world petroleum reserves are expected to continue to fall behind production. In this situation, these dwindling reserves will no longer be adequate as the only source of liquid fuels.

Although steps are being taken to supplement the supply of energy from petroleum with energy from a variety of other sources, the need for alternate supplies of liquid fuels for passenger and freight transportation is particularly urgent. The most promising sources for the large quantities of liquid fuels required by the United States are, at present, the ample supplies of coal and oil shale in this country, but the technology for producing and using these synthetic fuels needs to be advanced before full-scale facilities can be constructed and brought on stream. Especially important is a better understanding of the health and environmental impacts of synthetic fuel production and use, and of the means for bringing these impacts down to acceptably low levels.

The National Research Council began to study the problems of converting coal into liquid fuels in 1975, under a contract from the U.S. Energy Research and Development Administration (ERDA, subsequently incorporated into the Department of Energy). On the completion of this study in 1977,[a] ERDA contracted for a follow-on study of the R&D needed for the refining of coal and shale liquids. The results of this study are contained in this report.

In this follow-on study, the National Research Council was asked to undertake the following tasks:

- Survey the state-of-the-art of programs currently underway on the application of petroleum processing techniques to the upgrading of coal and shale liquids.

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[a] The study, titled "Assessment of Technology for the Liquefaction of Coal," was carried out by the Ad Hoc Panel on Liquefaction of Coal, Committee on Processing and Utilization of Fossil Fuels, Commission on Sociotechnical Systems, National Research Council.

- Define the areas in which further research into the upgrading of these liquids would be desirable from a benefit-to-cost standpoint.

- Recommend a course of direction for the achievement of short and long term goals.

In the contract, ERDA also specified the following:

- The primary emphasis of the study should be placed on fuel production, with the production of chemical feedstocks examined only where they may be appropriate by-products in the normal operation of a commercial coal or shale oil refinery.

- Attention should be given to the types of fuel that will be needed after 1985, when synfuel plants are expected to be operating.

- Priorities in the recommended research programs should be clearly described and rationalized with respect to appropriate technical and economic criteria.

Evaluating the processing techniques used in upgrading coal and shale liquids has been the equivalent of shooting at a moving target. When the study began, for example, it was expected that an important use for the liquids would be as boiler fuels. However, as methods for the more complete conversion of coal to distillable fuels were demonstrated, they became the preferred means of removing ash and were incorporated in three of the four plants for demonstrating coal conversion. This report covers both types of liquids, but with emphasis on the distillable synthetic liquids.

This panel did not assess refining costs in detail. Costs of refining synthetic fuels should not differ greatly from conventional petroleum refining. The major cost uncertainties are in the initial conversion steps, not in the refining process.

The study, consistent with its charge, concentrated on the refining of distillable liquids produced by direct liquefaction processes. The panel believes that indirect liquefaction, while potentially important, presents few difficult research and development problems, given its long history and major industry involvement.

AD HOC PANEL ON R&D NEEDS IN REFINING OF COAL AND SHALE LIQUIDS

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CONTENTS

1 SUMMARY

The purpose of this study was to determine the status of research and of technology for refining liquids from oil shale or coal, to recommend areas for future research and development emphasis, and to make recommendations on the roles of government and industry in these areas.

Refining is the link between the primary production of liquids from these solid hydrocarbon sources and the supply of liquid fuels meeting the requirements of the various consumers. But use patterns and combustion equipment are expected to change with time, and the compositions of liquids produced by the variety of raw materials and conversion processes, which differ from those associated with petroleum, will also probably change with time. Therefore, parts of this report are devoted to discussions of liquefaction technologies and the corresponding liquid compositions, the committee's view of coming changes in demand for various types of liquid fuels, and the possibilities for evolution in end-use equipment.

Today's refining technology for these synthetic liquids adds hydrogen to eliminate elements other than carbon and hydrogen and thus produce substances similar to petroleum hydrocarbons. Because the manufacture and use of hydrogen are the major sources of energy consumption and expense in refining these liquids, the technology and research needs for hydrogen manufacture are also considered in this study. Environmental and health problems are given careful attention since the raw liquids are known to contain toxic components.

FUTURE PRODUCT REQUIREMENTS

The major categories of liquid fuels are gasoline, which distills at temperatures below approximately 430°F; middle distillates (kerosene, diesel fuel, and domestic heating oil) which distill below 700°F, and fuel oils which distill above 700°F. Fuel oils are used in electric power generation, industrial heating, and some smaller commercial installations. Because of limitations of natural gas supply, the use of imported fuel oil has increased rapidly. In the long term, it is expected, imports will be displaced by coal and nuclear fission.

However, much existing end-use equipment has long lifetimes and cannot be economically converted to use coal or nuclear fission. For this reason, it would be advantageous to use the high-boiling-point fractions from coal and shale liquefaction with no further refining, or minimal refining, to displace fuel oil in large installations. Development of combustion and handling techniques for dealing with the high nitrogen content, and (in the case of coal liquids) the relatively high content of skin carcinogens, will be required. For smaller installations such as apartment houses and small factories, it is probable that more refined grades will be required.

During this century gasoline consumption is not expected to grow and may decrease as prices increase and more fuel efficient passenger automobiles displace the present fleet. While future use of fuel injection, stratified charge engines, or engines with higher compression ratios may call for adjustments in volatility and aromatic content, it is believed that these requirements can be easily met by applying petroleum refining technology to the lower boiling fractions produced from coal and oil shale once nitrogen, sulfur, and oxygen have been removed. Because of their high aromatic content, these fractions are especially well suited for this use.

The projected increase in use of diesel engines, increased air travel, and continued use of liquid fuels for home heating should result in a considerable increase in middle distillate demand relative to that for gasoline. A high hydrogen content is needed in these fuels to avoid smoke and deposit formation in present equipment and, in the case of the diesel engine, to give satisfactory ignition characteristics. Coal liquids from direct liquefaction processes, because of their low hydrogen content, are at a disadvantage compared with shale oil, which has relatively high hydrogen contents, or with indirect liquefaction products, which normally have very high hydrogen content. Automotive gas turbine, Stirling, or stratified-charge engines, which can tolerate lower hydrogen contents, are not expected to be used widely before the end of this century.

In the long term it is expected that the fraction of total liquid fuel production used in transportation will increase substantially from its present share of approximately 50 percent.

LIQUEFACTION PROCESSES

The two major categories of liquefaction processes are "direct" and "indirect." Direct liquefaction processes involve heating the solid starting material with or without the presence of catalysts, hydrogen, or solvents. Varying fractions of the organic content are converted to liquids and can subsequently be separated from the unconverted solids. Indirect liquefaction refers to a class of processes in which the solid organic material is first converted to a mixture of carbon monoxide and hydrogen by reaction with oxygen and/or steam. After purification, this mixture of gases is converted catalytically to a variety of liquid products, which can include materials such as methanol or hydrocarbons in the gasoline or distillate boiling range. It is anticipated that both classes of processes will see considerable application in the future, with the choice depending on the nature of the raw materials available, the types of products required, and the technological maturity of particular processes. While the liquids produced by indirect liquefaction will require further purification and refining, major problems are not foreseen. This study, therefore, concentrates on the refining problems involved in converting liquids from direct liquefaction processes to acceptable products.

Heating without adding hydrogen or solvents is called pyrolysis. With the western oil shales, high recoveries of the organic fraction can be achieved by pyrolysis, and a variety of retorts have been proposed for this purpose. There is also considerable interest in *in situ* retorting, in which most of the operation is carried out underground. The shale is explosively fragmented, and a flame is propagated downward through the broken stone by pumping air downward. The heat from this flame drives off pyrolysis products, which run to the bottom of the fractured zone, and the flame is fed by the char that remains in the stone. The oil produced is more volatile than that obtained in aboveground retorting, probably due to a higher level of thermal conversion. However, its properties are otherwise quite similar to those of shale oil retorted above ground and do not present significantly different refining problems.

Pyrolysis has also been used in the liquefaction of coal, but the processes developed thus far yield relatively small amounts of liquids (usually less than 30 percent of the coal feed), accompanied by large quantities of char that can be disposed of as a boiler fuel. The liquid is in the form of a very heavy tar that can be used as a low grade liquid fuel or refined to a higher grade fuel.

Higher yields of liquids are obtained by the use of liquid phase processes in which most of the coal is dissolved in a coal-derived recycle liquid which also supplies hydrogen "donors" to upgrade the hydrocarbons in the coal. In general, the recycle liquid is catalytically rehydrogenated either in an external circuit (as in the Exxon Donor Solvent, or EDS, process) or in the presence of the coal and ash (as in the H-Coal and Solvent-Refined Coal II, or SRC-II, processes).

The properties of the liquids obtained depend, of course, on the coal used. They also depend strongly on the amount of hydrogen added during liquefaction. Processes such as SRC-I, which add a minimal amount of hydrogen, produce a relatively high molecular weight tar. A process such as EDS, which consumes a large quantity of hydrogen, can produce a product more than 25 percent of which is in the gasoline boiling range. An alternative, of course, would be to add hydrogen to a product such as SRC-I in a second step; this could be classified as refining. It is not clear how much of the "refining" should take place in the initial liquefaction step and how much outside the liquefaction system *per se*. In all cases, however, these liquids contain unacceptable amounts of nitrogen, oxygen, and polynuclear aromatics, and require further purification.

REFINING TECHNOLOGY

Today's refining technology has been highly optimized for the conversion of a wide variety of petroleum crudes to meet the consumer's fuel requirements. The United States has maintained technological leadership in this field, and American processes are used in the bulk of the world's refining installations. These processes reduce to acceptable values the nitrogen, oxygen, sulfur, polynuclear aromatics, and metals such as vanadium, iron, and nickel originally present in the crude oil. However, the nitrogen, oxygen, and polynuclear aromatic contents of shale- and coal-based liquids are generally higher than those of petroleum crudes, and special process units will be needed to eliminate these undesirable components.

Hydrogenation is the basic technique for dealing with these materials, since by adding sufficient hydrogen all the organic components can be reduced to saturated hydrocarbons and the metals eliminated from the liquid products. Pilot plant studies of several hydrotreating processes have demonstrated the ability to produce satisfactory products from shale and coal liquids. These processes are primarily extensions of the catalytic processes developed for the desulfurization and denitrogenation of petroleum. With some further development, these processes could be used to refine shale and coal liquids, but they require large amounts of hydrogen, higher pressures, and lower feed rates, all of which entail extra expense. More hydrogen is consumed than is stoichiometrically needed for heteroatom removal, methane is produced as a by-product, and a higher level of aromatic saturation occurs. If higher selectivity can be achieved, substantial savings in the energy and expense required for hydrogen manufacture are, in principle, available. A substantial R&D program aimed at reduction of hydrogen consumption is clearly justified. Special emphasis on a search for chemical techniques other than extensions of the conventional catalytic hydrogenation is also needed.

The inorganic contents of synthetic oils vary widely. Those from processes involving distillation contain relatively little, while those produced by filtration or solvent precipitation can contain fairly large amounts. These inorganic materials can cause catalyst deactivation and plugging. Thus, more efficient processes for their removal prior to further catalytic treatment are needed.

Raw shale oil and some coal liquids are too viscous at ambient temperatures to be transported in unheated pipelines. In some cases, viscosity reduction at the liquefaction site may be more economical than pipelining heated oil. Current technology such as coking or visbreaking can be used; however, these processes result in yield losses, and there is an opportunity for improved processes.

The optimum degree of refining at the liquefaction site will depend largely on the particular materials to be handled. In many cases, it may be desirable to refine the liquids to the point at which they can be accepted by conventional petroleum refineries. There are a number of reasons why integrating these new raw materials into the existing large refineries should prove to be an economically optimal route. First, future limitations on total liquid fuel supply will very likely result in some large refineries running at lower total capacity. Second, the refining of coal and shale liquids along with conventional petroleum may well present special opportunities for optimization in the manufacture of products.

A survey of industrial and government laboratory capabilities for carrying out R&D on the refining of coal and shale liquids shows that considerable work is in progress in this area. Responses from 29 companies indicate that more than 2000 persons are engaged in refining and product R&D in industry. About 10-20 percent of this effort is devoted to the refining of coal and shale liquids; however, the personnel and skills involved in petroleum-related process research can be easily transferred to the special problems of coal and shale liquids. Capabilities for applied research and process development are quite limited in governmental laboratories. Considerable relevant basic research is being carried out in industrial laboratories, but the need for new approaches to refining coal and shale liquids calls for an augmented basic research effort.

An increased effort is also needed to define the optimum product composition, taking into account future advances in combustion equipment as well as advances in refining technology. This effort would logically involve fuel manufacturers, engine and equipment manufacturers, and government supported research. Such a program has begun for commercial jet aircraft, but more needs to be done in other areas.

HYDROGEN MANUFACTURE

At present, most refineries do not require hydrogen manufacturing, since by-product hydrogen from gasoline manufacturing is adequate to meet petroleum hydrotreating needs. Large scale introduction of raw synthetic fuels would require manufactured hydrogen, as would most coal liquefaction processes. Hydrocarbon gases are currently the most economic and efficient raw material for hydrogen manufacture, but conservation of this valuable resource will require the use of coal as a starting point for hydrogen manufacture. Using coal as a feedstock is less expensive than producing hydrogen by electrolysis or by current exploratory thermal techniques. While the need for more hydrogen in the refining of synthetic liquids is likely to lead to slightly greater CO_2 generation than in petroleum refining, this is not a major source of atmospheric CO_2. The major source of CO_2 will continue to be the combustion of fossil fuels, including in the future synthetic fuels from coal.

Because of the large amounts of hydrogen that will be required in the future, even a small improvement in cost and efficiency is important. A 10-15 percent reduction in the cost of hydrogen might be obtained by optimizing existing partial oxidation processes for converting coal to hydrogen. An additional 15 percent reduction may be achievable by fully optimizing and developing processes that are further down the road (e.g., air oxidation in multiple-fluidized-bed systems or the use of CO_2 acceptors such as CaO or oxygen acceptors such as Fe).

HEALTH AND ENVIRONMENTAL PROBLEMS

The health and environmental problems posed by the refining of coal- and shale-based liquids and by their use by the consumer must be given careful study. Of greatest importance is the known ability of coal tars to cause skin cancers and possibly other cancers. This toxicity is due to the relatively high content of high-boiling polynuclear aromatic and heterocyclic compounds. Shale oil and petroleum contain less of these substances; however, severe thermal treatment greatly increases their concentrations, and certain heavy fuel oils produced by severe cracking are sufficiently active that special handling is currently required in their refining and use.

While there is considerable experience in the petroleum industry with handling such hazardous materials, introduction of coal- and shale-based liquids will require special attention to potential health problems and to obtaining, through research, a detailed understanding of the hazards posed by carcinogens, co-carcinogens, and mutagens in such liquids. Refining techniques must be capable of reducing this toxicity to an acceptable level. Fortunately, hydrogenation appears capable of converting the toxic materials in these oils to nontoxic hydrocarbons of higher hydrogen content. A survey of research and development on shale and coal liquids in industry and in the national laboratories shows that considerable work is being carried out in anticipation of the need for handling techniques for these materials. Research related to this problem should obviously have a high priority.

In the lower boiling range, the main health hazards have been identified as the toxicity of single-ring aromatics (particularly benzene) and the toxicity, on ingestion, of products such as gasoline and kerosene. These hazards are essentially identical to those associated with today's petroleum-based fuels.

Some raw shale oils have been found to contain amounts of arsenic sufficient to require removal before further processing or use. Handling and disposal of this arsenic is a relatively new refining problem that will require careful attention to avoid exposure during refining and long term environmental risk on disposal.

Refining coal and shale liquids will produce by-products such as ammonia, phenols, and sulfur compounds. These materials are encountered in today's petroleum refining, and technology for purifying wastewater and gas streams is available. However, capacities and efficiencies might require improvement because of the higher nitrogen and oxygen contents of shale- and coal-based liquids.

RECOMMENDATIONS FOR RESEARCH AND DEVELOPMENT

1. More government support should be given to fundamental research on the basic chemistry of refining shale and coal liquids. The potential for carrying out the necessary research exists in the laboratories of industry, the universities, and the Department of Energy, but it needs to be funded at a higher level.

2. Research in the environmental and health areas should be given high priority. The following problems are especially important:

   (a) Establishment of limits on the carcinogen contents of the various classes of fuels.

   (b) Establishment of appropriate handling procedures for the more toxic unrefined materials.

3. Since the capabilities for applied research and development (as distinguished from basic research) are much stronger in industry than in government and university laboratories, major Department of Energy participation in this aspect of the effort is not indicated. The Department should continue to sponsor tests of processes developed by industry, however, as a way of assessing the state of the technology.

4. A reduction in the total cost of refining shale and coal liquids should be a principal R&D objective. The hydrogen required to remove sulfur and nitrogen from these liquids and reduce their boiling points is responsible for a major part of this cost. The R&D necessary to improve the technology for producing hydrogen from coal and coal char should be sponsored by the Department of Energy.

5. R&D aimed at establishing the optimum combination of fuel composition and end-use equipment should be given high priority by government agencies. Full cooperation among government, the fuel industries, and the equipment manufacturing industries is essential.

6. Basic and applied research relevant to the following refining needs is of high priority:

   (a) New methods for removal of nitrogen, oxygen, and sulfur from coal and shale liquids. Selective removal of oxygen and nitrogen is particularly important.

   (b) New methods for removal of metals such as arsenic, titanium, iron, nickel, and vanadium.

(c) Identification of toxic components, determination of their potency, and discovery of new methods for their removal.

(d) New methods for manufacture of hydrogen.

(e) The mechanism of deactivation of the catalysts used in removing nitrogen, oxygen, and sulfur. This will enable the development of longer-lived catalysts.

(f) Mechanisms of the viscosity and solubility changes that occur during storage of coal and shale liquids, and additives to improve stability.

7. Facilities are needed for the experimental refining of synthetic fuels in quantities sufficient for large scale testing.

2 INTRODUCTION

It is likely that synthetic fuels will begin to supplement petroleum-derived fuels in the next few years. This report considers the effects on refining requirements of introducing fuels derived from oil shale and coal. When the production and use of coal and shale derivatives get underway on a commercial scale, we shall begin to see many changes in products and end-use equipment.

An examination of the problem involved in the introduction of fuels derived from coal and shale requires, at the start, an estimate of the type and quantity of liquid fuels that are going to be required in the future. This calls for:

- A projection of the petroleum supply
- A projection of the trends in liquid fuel end use
- A projection of the way fuel composition requirements are likely to change over the years with changes in end-use technology, changes in fuel sources, and changes in refining technology.

The projections that were made in this study were based on the following premises:

- The total supply of liquid fuels will become increasingly limited and expensive with time.
- There will be substantial incentives to substitute other energy sources for liquid hydrocarbon fuels where economically and technically feasible, and consequently important shifts may occur in the types of liquid fuel used.
- Control of health-related emissions will result in an increasingly strict control of sulfur and nitrogen compounds in all fuels, particularly those that are carcinogenic. Attention will also be given to the hydrogen content of fuels because of its relationship to soot formation.

- Research on end-use equipment will increase our ability to use fuels of lower hydrogen content and our ability to burn high-nitrogen fuels with acceptably low NO_x emissions.

- The fuel-producing and end-use systems will be optimized to meet the often conflicting requirements of minimum cost, maximum resource use, and minimal impact on health and the environment.

PROJECTION OF THE PETROLEUM SUPPLY

The annual world production of petroleum is expected to continue to outrun discovery rate during the 1980s and beyond (Figure 1). Taking into account the discovery rate of new reserves and the rate at which available reserves are used, the production rate will begin to limit consumption increasingly severely between 1980 and 2000, with the severity depending on OPEC pricing and production policies (Figure 2).

With the supply of petroleum becoming limited and its price increasing, we should soon begin to see the replacement of liquid fuels with other forms of energy where practical. In stationary equipment, we can expect a switch to solid and gaseous fuels, electricity, and solar energy. In the transportation sector, however, the reliance on liquid fuels is likely to continue for at least 25-50 years with some use of electricity in public transport and automotive systems (General Motors, 1974; Sheridan *et al*., 1976; National Research Council, 1979).

A wide variety of predictions of future petroleum use is available (Dupree and Corsentino, 1975; U.S. Department of Commerce, 1977; National Research Council, 1980). The values used here presume a reasonably orderly world economic system and a drive for conservation tempered by economic considerations and a general reluctance to drastically change present lifestyles. The values imply, for example, a slow phase-out of oil use in power generation, allowing the normal retirement of oil-burning power plants; they also assume a less drastic reduction of fuel use in automobiles than is found in the more extreme forecasts.

An examination of recent U.S. trends in the use of petroleum fuels should help provide an insight into whether other energy forms can be substituted for liquid fuels and, if not, the kinds of non-petroleum fuels that may be required. This is done in Chapter 3.

As the current surplus refining capacity for petroleum-derived fuels becomes supply-limited, the price of petroleum should increase relative to those of other commodities; liquid fuels from shale and coal might then then become an efficient and economical supplement.

MAXIMIZING EFFICIENCIES

With petroleum fuels, the emphasis in efficiency improvement has been placed on the end user because of the relatively low expenditure of

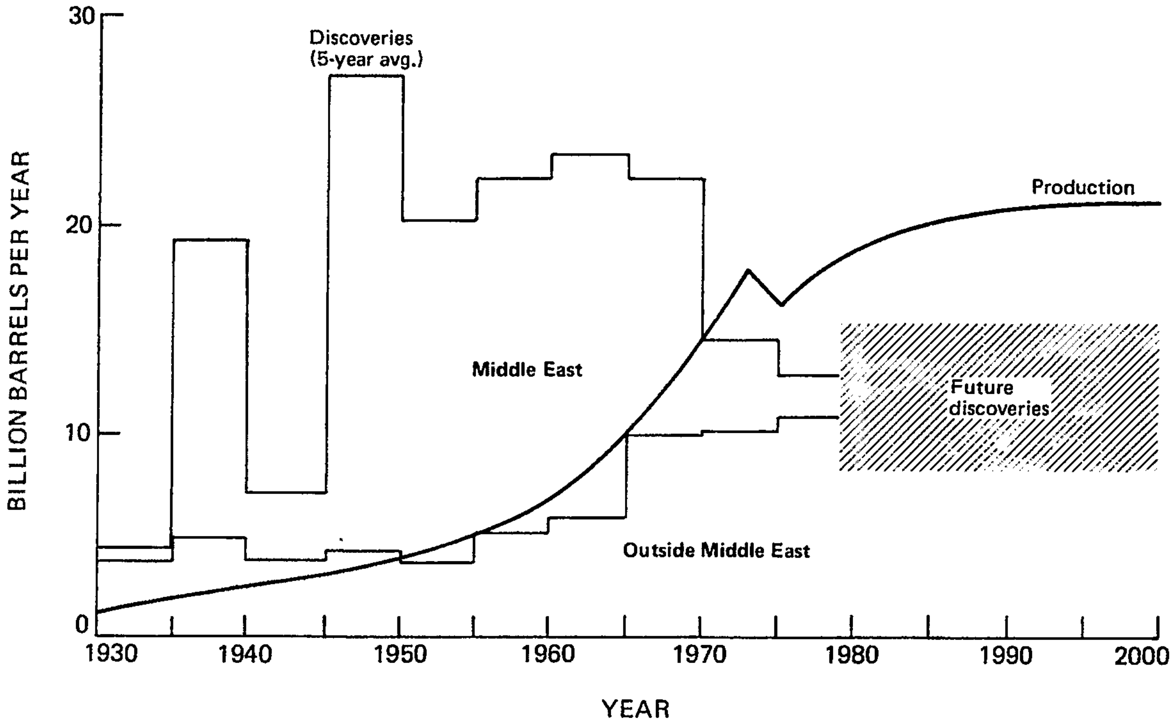

Figure 1 World oil discovery and production rates from 1930 to 2000, excluding the People's Republic of China, the Soviet Union, and Eastern Europe (Exxon, 1980)

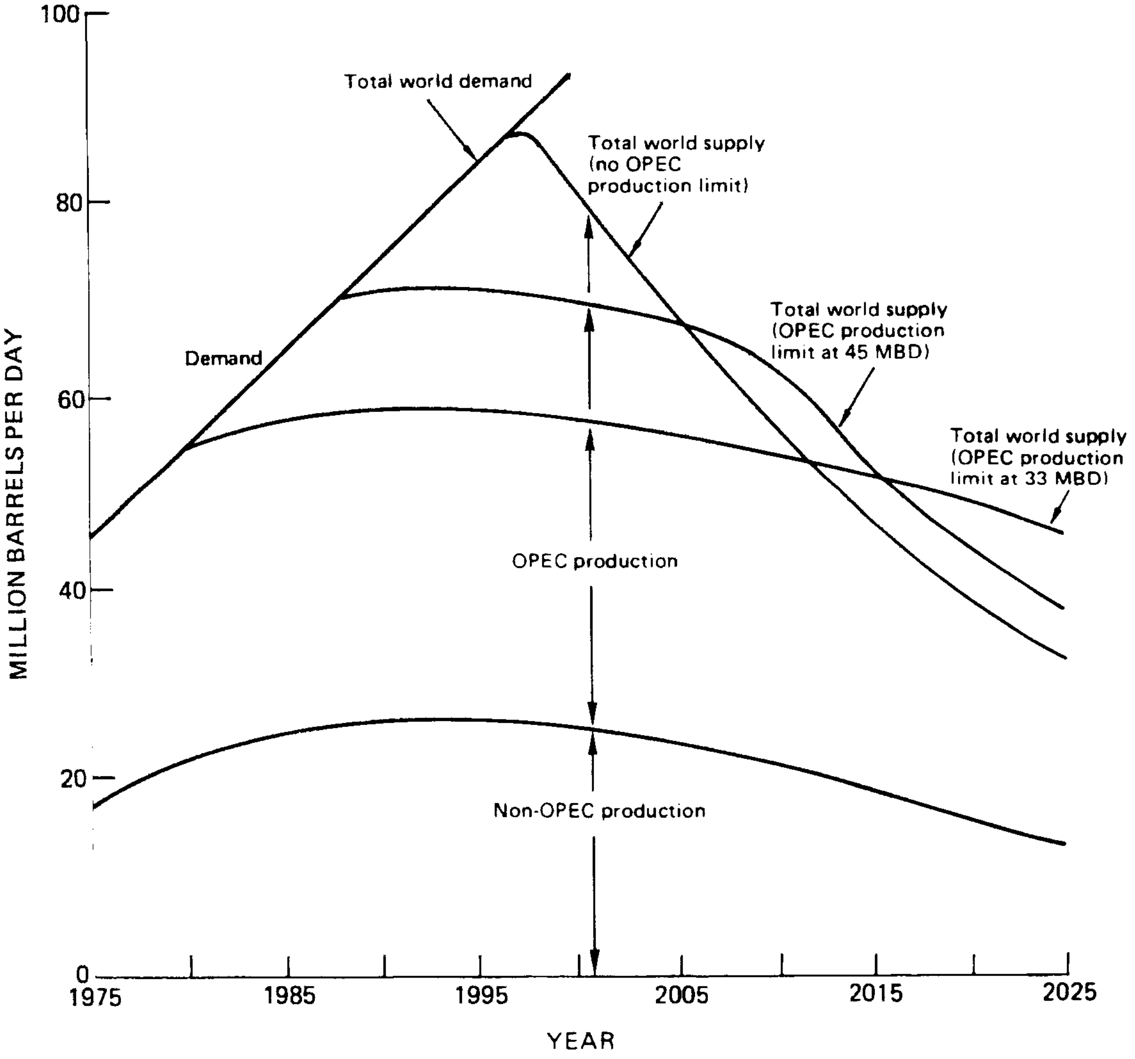

Figure 2 Projections of world petroleum demand to 1999 and supply to 2025 (Workshop on Alternative Energy Strategies, 1977)

energy involved in removing crude oil from the ground, delivering it to the refinery, refining it, and distributing the products to users. The emphasis will change dramatically as we shift from petroleum to oil shale and coal as sources of liquid fuels for transportation. The estimated conversion efficiencies (the percentage of the Btu's in the original feeds that remains in the products) for producing liquid fuels from oil shale and coal are substantially lower than those involved in using petroleum as a source (Figure 3). The energy expended for a given output can vary greatly, depending on the sulfur, nitrogen, aromatic, and ash contents of the coal and shale liquids, as well as their distillation properties and the degree to which these liquids are refined. This also raises the possibility of increasing the overall energy efficiency by modifying or developing engines and stationary combustion systems for the use of shale and coal liquids in the "least

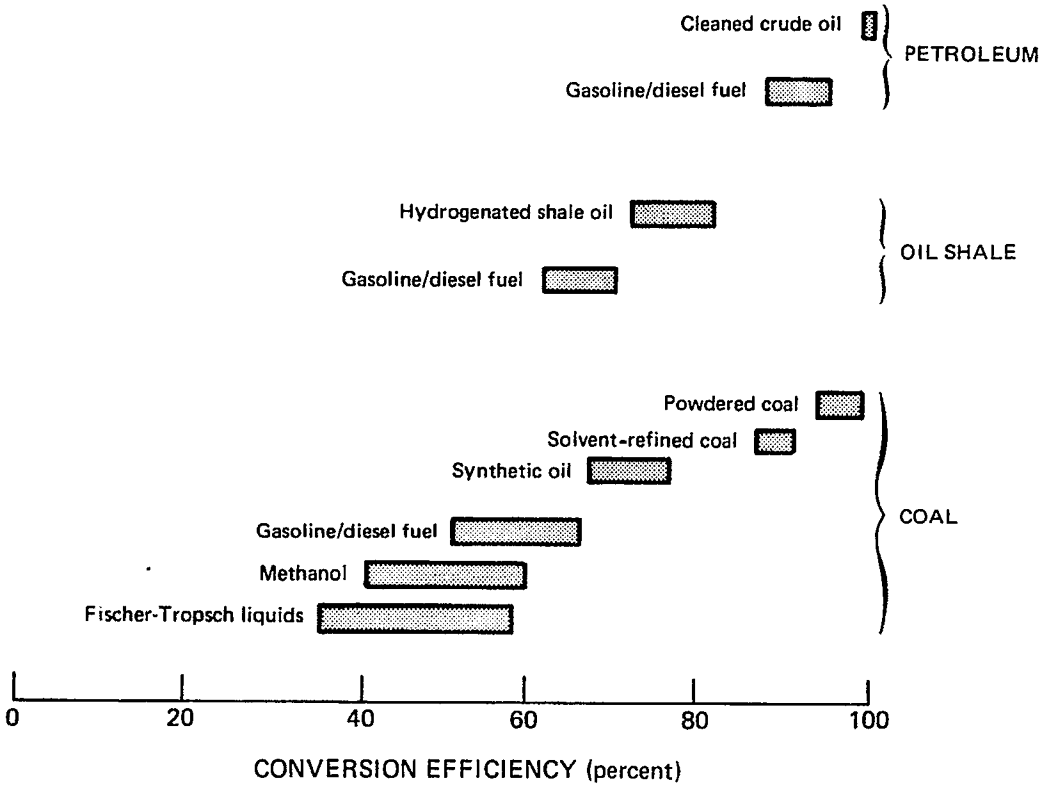

Figure 3 Estimated conversion efficiencies in producing liquid fuels from various sources (Stebar <u>et al.</u>, 1975)

refined" form. In determining the optimum overall systems, however, maintenance and durability must be considered along with the problems of complying with existing federal and state regulations, especially those relating to emissions.

LIQUID FUELS FROM OIL SHALE AND COAL

Pioneer production of coal and shale liquids is expected to begin in the mid-1980s, with substantial production by the end of the century. By the year 2025, there is the possibility that half of the U.S. liquid fuel production will come from these sources. While such predictions cannot be made with any precision, it is nevertheless clear that it will be some time before important quantities of liquid fuel are derived from coal and shale.

There are major differences among the various crude liquids obtained from coal and shale. One is hydrogen content. The atomic hydrogen/carbon (H/C) ratios for coal liquids vary between 1.0 and 1.2, and the atomic H/C ratios for shale oil and petroleum crudes vary between 1.6 and 1.8. Typical liquid fuels in use today fall in the 1.7-1.9 range. While the relatively low hydrogen contents of aromatic fuels may be advantageous for use in engines that require higher octane gasolines, diesel engines and home heating furnaces have difficulty burning fuels in which the H/C ratio is low. Hydrogen can be added to coal liquids to increase the H/C ratios, but this is expensive and wasteful of energy. The thrust of future technology will be toward a more efficient use of hydrogen to achieve a given product composition.

As coal and shale liquids come into use, they will replace petroleum in different applications with varying degrees of suitability, as indicated in Table 1. Petroleum will, of course, be best suited for all its present uses, since these were developed around petroleum, but petroleum components now used for heavy fuel oil will be converted to more highly refined products (e.g., aliphatic petrochemicals and olefins for plastics); these can be produced more economically from the heavier petroleum components than from shale and coal liquids. Coal liquids, because of their high aromatic contents, will be excellent sources of gasoline and could be preferentially used for this purpose; their low hydrogen contents will also make them useful for the production of heavy fuel oil. Shale liquids will generally fit the same use patterns as petroleum and should be useful for the production of jet and diesel fuels.

Coal or coal char can also be converted to a CO/H_2 mixture which can, by catalytic conversion, be made to yield a variety of hydrocarbons, alcohols, and chemicals. If fuels high in hydrogen are required from coal, this "indirect" liquefaction might provide the most appropriate route. Aromatic gasoline components can also be produced by this means.

Table 1 Suitabilities of different feedstocks as sources of various products[a]

	Gasoline	Jet and diesel fuels	Other distillate fuels	Heavy fuel oils	Aliphatic petro-chemicals
Petroleum	X	XX	X	X	XX
Shale oil	X	XX	X	X	X
Coal liquids	XX	0	0	XX	0
CO/H_2-based liquids	XX	XX	X	0	X

[a] XX: very well suited; X: well suited; 0: poorly suited.

The total refining capacity in the United States is not considered likely to increase appreciably for a number of years. There will be little incentive to build expensive new refineries since it should be possible to convert a refinery from petroleum to coal and shale liquids with the addition of hydroprocessing and other facilities. After appropriate feed hydrotreating, existing petroleum conversion and separation processes can also be used for coal and shale liquids.

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3 FUTURE PRODUCT REQUIREMENTS

Nonpetroleum fuels have been considered for transportation many times in the past. Germany produced liquid fuels from coal during World War II and South Africa is doing so today. Oil has been produced from shale in the Soviet Union, Scotland, Brazil, and elsewhere. It is now quite clear that a major effort must be mounted to prepare the United States for the production and use of these fuels during the rest of this century.

In evaluating what must be done to adapt the transportation system in the United States to the use of liquids from coal and/or oil shale, a number of questions must be answered.

- What kinds of liquid fuels will be required during the years ahead? This question can be answered by examining the types of engines and vehicles that will use these fuels. Most of the engines now in use are spark-ignition and compression-ignition (diesel) engines. The conventional fuels used by these engines are gasoline and diesel fuels, both produced from petroleum. New fuels that can be produced from petroleum, coal, and oil shale will be suitable for today's engines only if they closely resemble the gasoline and diesel fuel currently in use. If they differ, however, they may still be usable in modified versions of current engines as well as in unconventional engines such as gas turbines, Stirling engines, and some stratified-charge engines.

- How will the new fuels be introduced? Will the liquid fuels produced from coal and shale be intended for use with conventional as well as new engines, or will they be intended only for use in new engines? If the former is the case, it may preclude radical changes in fuel quality or composition that might allow the overall optimization of costs and energy use. If the latter is the case, it would require the development of new engines and vehicle systems, limiting the rate at which the new fuels could be put to use.

- To what extent can liquid fuels derived from coal and oil shale be substituted for petroleum fuels now used for residential and industrial purposes and for electricity generation by utilities?

UTILIZATION OF LIQUID FUELS

Electric Power Generation

Liquid fuels now used for electric power generation consist mainly of high-boiling-point (No. 6) fuel oil. While this petroleum fraction contains none of the lower boiling fractions used in the major transportation systems, modern refining technology can convert the high-boiling fraction to clean lower boiling fractions more efficiently than it can refine coal and shale liquids. As the liquid fuel demands of transportation increase over the years ahead, we will very likely see a shift of petroleum use from the utilities to transportation, with oil shale and coal providing the fuel for electric power generation. Coal, of course, can be used directly as a utility fuel, but converting existing plants from liquid and gaseous fuels to coal is difficult and expensive. Electric power plants now in operation may be able to switch to relatively unrefined coal liquids and shale liquids more easily than they can switch to coal. The use of liquid fuels makes it easier to meet emission standards.

With new power plants the situation is different. In a new plant, coal and nuclear energy offer the advantage of being more economical than liquid fuels.

The Industrial Sector

The oil now used for industrial purposes is, like utility fuel, composed largely of the higher boiling fractions. The trend in the energy consuming industries will be much like that in the utilities. The use of oil will peak over the near term as it replaces gas and then decline as it, in turn, is replaced by coal.

The Buildings Sector

In commercial and residential buildings, the replacement of gaseous and liquid fuels with coal is not generally practical; the trend toward electric heating will result in the greater use of coal and nuclear power, however. The use of liquid fuels in buildings will therefore level off or slowly decline over the next two decades.

Nonenergy Uses

In contrast to fuel use, the nonenergy use of petroleum and other liquid hydrocarbons (as petrochemical feedstocks, asphalt, etc.) is expected to grow rapidly. For example, the use of plastics to reduce the weight of automobiles should increase, resulting in a lower use of petroleum for operation. Since the production of plastics requires high-hydrogen-content fractions such as naphtha and paraffinic gas oil, the trade-off between plastics for weight reduction and liquid fuel for operation will be an important factor in the overall balance of supply and demand.

Because of its composition, shale oil is a possible substitute for petroleum in the production of olefins for plastics. Coal would have to be put through drastic conversion processes to produce the monomers needed for plastics (e.g., gasification followed by Fischer-Tropsch synthesis).

The Transportation Sector

The quantity of liquid fuel used in the transportation sector is a major percentage of the total quantity produced. While this percentage will decline over the near term, it may increase slowly after 1990 as the increasing use of liquid fuels by trucks and airlines more than makes up for the decline in fuel use by passenger cars.

The future use of fuels by automotive vehicles will depend on the following variables:

- Fuel economy standards for passenger cars, light-duty trucks, and heavy-duty trucks[a]
- The mix of fuels (gasoline or diesel oil) used by each class of vehicles
- The number of miles traveled per year by each vehicle
- The number of vehicles in use
- Vehicle sales and scrappage rates.

Recent forecasts of gasoline demand are shown in Figure 4. There appears to be a general consensus that gasoline consumption will decline during the 1980s as a result of the mandated fuel economy standards. Forecasts have not been made beyond 1990 because of the uncertain nature of the standards that might be mandated beyond 1985.

Two important points should be made about the gasoline demand projections in Figure 4:

- These projections indicate trends; they should not be considered immutable.

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[a] Federal standards for the fuel economies of passenger cars have been established through 1985. Standards for the fuel economies of light-duty trucks have been established through 1982. More stringent standards for later years are likely. Standards have not yet been established for heavy-duty trucks.

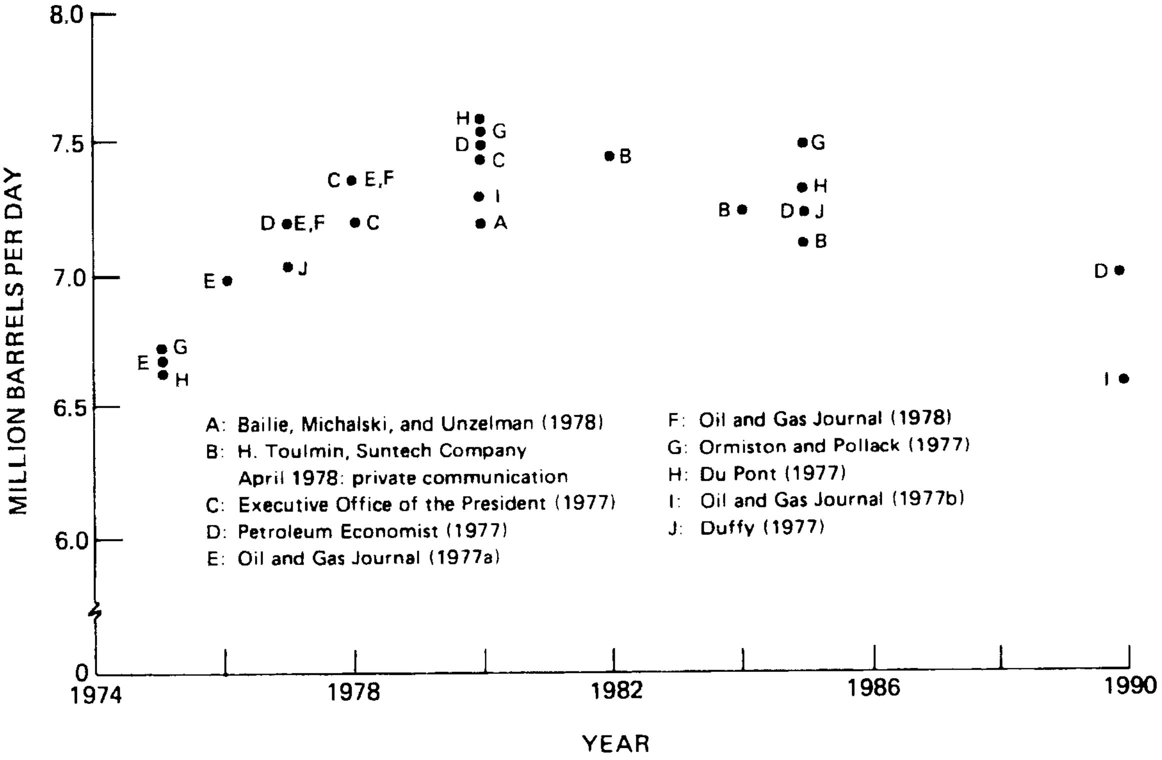

Figure 4 Selected forecasts of U.S. gasoline demand to 1990, in millions of barrels per day

- Essentially all of the gasoline used by passenger cars and light-duty trucks by 1990 will be unleaded, since catalytic converters will be needed to meet federal emission standards. Gasoline used by heavy-duty trucks will probably be leaded as long as emission standards do not preclude its use, but most heavy-duty trucks will probably continue to be built with diesel engines.

The increasing use of diesel engines in heavy-duty trucks, the trend toward diesel-powered passenger cars and light-duty trucks, and the continued use of distillate fuels in trains and aircraft will result in a greater demand for distillate fuels in the future, affecting the gasoline/mid-distillate fuel ratios required from petroleum and nonpetroleum resources.

Projections of fuel use by aircraft vary widely, but it is generally agreed that fuel use in this mode will grow more rapidly than in the other transportation modes.

TYPES OF LIQUID FUELS REQUIRED

The discussion of fuel types can be simplified by dividing them into three major categories, according to their boiling points (Table 2).

Heavy Fuel Oils

The heavy fuel oils are the least refined of liquid fuels. Shale and coal liquids may require the removal of organic nitrogen. The higher boiling fractions must be used in installations where human contact can be carefully controlled, because of their substantially higher carcinogenicity (particularly in the coal-based liquids and the intensely pyrolyzed petroleum-based fractions). The use of heavy fuel oil is now rising rapidly but is expected to fall considerably in the future as it

Table 2 Boiling ranges of fuel types

Fuel types	Boiling range (^{o}F)
Heavy fuel oils	700+
Mid-distillates	350-700
Gasoline	80-440

is replaced in power generation by coal and nuclear energy. Heavy fractions, boiling above 700°F, can then be converted to mid-distillates and gasoline. (The differences between distillate coal liquids and No. 6 fuel oil from petroleum are outlined in Table 3.)

Mid-Distillates

This category consists primarily of kerosene, jet fuel, diesel fuels, and No. 2 (domestic) heating oil. The initial boiling point is set by safety considerations and is defined by a "flash point" specification that ranges between 100°F and 140°F, depending on the application. The final boiling point has historically been determined by freezing point or viscosity considerations, since these fuels are used during the winter and are stored outside.

Kerosene and jet fuel must, at present, have high hydrogen contents to reduce soot formation, in current combustion equipment. This requirement results in an aromatic content specification under 25 percent. The hydrogen content of diesel fuel need not be so high, but it must be high enough for easy ignition in passenger car and truck engines; this limits the aromatic content to around 35 percent. Home heating oil (No. 2) requires still less hydrogen, but in current practice is produced with an aromatic content only slightly (5-10 percent) higher than that of diesel fuels to avoid problems with soot and smoke formation.

In all cases, the nitrogen content must be kept low to avoid sludge and deposits during storage and use. The sulfur content must be kept below 0.5 percent to meet current SO_x emission standards.

Gasoline

Although there is some overlap in the boiling ranges of gasoline and mid-distillates, gasoline is basically a volatile fuel that permits cold starting and reasonably complete evaporation before ignition as a result of the high vapor pressure of its lower molecular-weight components. Unlike mid-distillate performance, gasoline performance is improved by the inclusion of aromatics; consequently, much of modern gasoline refining technology centers on the conversion of paraffin and naphthene into high-octane aromatics.

The conversion requirements of a refinery are determined by the gasoline/mid-distillate ratio. In the past, the large demand for gasoline in the United States has dominated production, the demand for mid-distillates being relatively easy to meet from naturally occurring petroleum fractions and products incidentally produced during gasoline production.

This balance is expected to change drastically in the future. As the end of the century approaches and the rising demand for mid-distillates lowers the gasoline/mid-distillate ratio, the hydrogen

Table 3 Principal differences between distillate coal liquids and No. 6 fuel oil

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Combustion Properties

Coal liquids produce fewer large particulates because fuel can vaporize during combustion.

Coal liquids have a greater tendency to form soot because of their lower hydrogen contents.

Coal liquids produce a more luminous flame due to their lower hydrogen to carbon ratio; this produces a different heat transfer balance.

Emissions

Coal liquids contain less sulfur than most unprocessed petroleum fuel oils.

Coal liquids produce more NO_x because of their higher organic nitrogen content (0.5-1.5 percent compared to 0.1-0.5 percent for petroleum-derived fuel oil).

Conventional oil-burning equipment will generally exceed NO_x and particulate emission standards when using coal liquids, but control technology is being developed.

Toxicity

Coal-based fuel oils contain higher concentrations of skin carcinogens than virgin petroleum and will probably require special handling.

Stability

Coal liquids tend to polymerize and increase in viscosity during storage.

Deposits in atomizing nozzles are a greater problem with coal liquids.

Compatibility

Since mixtures of petroleum-based and coal-based fuel oils form precipitates, separate storage and handling facilities will be required.

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content of the mid-distillates will tend to decrease as a result of the increased use of cracked petroleum stocks and the introduction of fractions from coal and shale liquids (Shearer and Wagner, 1977).

Table 4 gives a projection of changes in the gasoline/mid-distillate fuel ratio, assuming moderate use of diesel engines in passenger cars. Major substitution of diesel engines for gasoline engines could bring a gasoline/mid-distillate ratio as low as 0.6 by the year 2000.

The large shift in this ratio over the years ahead should make it basically easier to meet the demand for high-aromatic, high-octane gasoline (assuming paraffinic naphthas can be used as petrochemical feedstocks). Meeting the demand for high quality mid-distillates, on the other hand, will become increasingly difficult and expensive because hydrogen-consuming processes (e.g., hydrocracking and hydrogenation) will be required. The future would be difficult even if sufficient quantities of petroleum were available as the major refinery feed; the switch to low-hydrogen coal and shale liquids will make the production of conventional mid-distillates even more difficult.

The higher cost of tailoring coal-derived and shale-derived fuels to end-use equipment designed for petroleum products will provide a major incentive to the development of end-use equipment capable of burning low-hydrogen mid-distillates cleanly. Along with this will come the need for refining technology optimized for producing these fuels.

Table 4 Projection of future gasoline/mid-distillate ratios

Year	Gasoline/mid-distillate ratio
1975	1.7
1980	1.5
1990	1.2
2000	1.0
2000+	0.5-1.0

Source: Shearer and Wagner (1977).

When coal becomes a major source of fuel for transportation, the route of char conversion to synthesis gas and then to paraffinic fuels or methanol will offer additional options for adjusting the match between fuel production and consumption.

FUTURE TRANSPORTATION FUELS

The problems likely to be met in developing nonpetroleum fuels for use in transportation during the years ahead are discussed under the following headings.

Gasoline

Gasoline and the spark-ignition (Otto cycle) engine have evolved to their current forms over a period of time. The process has been one of mutual adaptation as gains were made with one or the other, or as requirements changed (e.g., the need for unleaded gasoline when emission standards necessitated the use of catalytic converters). The mutual adaptation between engines and fuels will very likely continue as nonpetroleum fuels come into use.

The standards currently specified by the American Society for Testing and Materials for automotive gasoline, given in ASTM D 439-79, do not completely define gasoline but, rather, describe various characteristics of gasolines for use in cars, trucks, and buses over a wide geographical range.

The key properties described in ASTM D 439-79 for gasoline are the following:

- Octane quality (including the concentration of antiknock additives)
- Vapor pressure
- Vapor-liquid ratio
- Distillation characteristics
- Oxidation stability
- Corrosion characteristics
- Existent gum
- Sulfur content.

The higher nitrogen and aromatic content of coal and oil shale may increase the cost of producing gasoline from these raw materials. If not removed in refining, nitrogen can contribute a small amount to NO_x emissions and interfere with the control of this pollutant. It can also affect the storage stability of gasoline. Aromatics affect elastomers and may be precursors in the generation of polynuclear aromatic hydrocarbons during combustion (although this may not be a problem for engines equipped with catalytic converters).

Diesel Fuel

Diesel engines, now used primarily in trucks, buses, trains, tractors, and stationary engines, may begin to find increasing use in passenger cars as the automotive industry attempts to comply with federally mandated fuel economy and emission standards. Like gasoline, diesel fuels have evolved through the mutual adaptation of fuels and engines over a long period of time, and this interaction will undoubtedly continue when nonpetroleum fuels are introduced.

The standards currently specified for diesel fuel in ASTM D 925-77 are not a complete definition but, like the ASTM standards for gasoline, describe the characteristics required for the use of this fuel under a wide range of conditions. The key diesel fuel properties described in ASTM D 925-77 are as follows:

- Cetane quality
- Distillation characteristics
- Viscosity
- Carbon residue
- Sulfur content
- Flash point
- Cloud point
- Ash content
- Copper strip corrosion.

Nitrogen content will become an important property when diesel fuels are produced from oil shale and coal, since there are indications that high nitrogen contents degrade the stability of diesel fuels and raise the tendency to form acids.

Aviation Fuel

The current standards for aviation gas turbine (jet) fuels are specified in ASTM D 1655-77. Safety problems have led to the current attempt by the military to shift from JP-4 to JP-8. JP-4 is a mixture of naphtha (gasoline) and kerosene; JP-8 is similar to commercial Jet A but has a lower freezing point (-54°F, as against -40°F). The lower freezing point makes the new fuel more difficult to produce.

The amount of jet fuel needed at present can be supplied without difficulty, generally, but the demand is approaching the point at which it could interfere with the production of other mid-distillate products. An increase in jet fuel demand together with an increase in diesel fuel demand will tend to force the use of cracked stocks with higher aromatic contents. The cost and complexity of producing jet fuel over the years ahead could be eased considerably by raising the freezing point (allowing the inclusion of components with higher boiling points) and decreasing the hydrogen content requirement. The latter would be helpful when coal and shale liquids need to be used.

With air transportation particularly vulnerable to the cost and supply of fuel, there is much to be gained from examining the trade-offs involved in the development of aircraft that can use fuels with less stringent specifications. To allow laboratories and contractors to focus on the research, development, and design problems involved in optimizing fuel/aircraft combinations for the future, NASA held a workshop in June 1977 (National Aeronautics and Space Administration, 1977) at which specifications for a new jet fuel for research purposes were agreed upon by representatives of the airlines, the airframe and engine industries, the fuel producers, and various government agencies. The characteristics of this fuel, designated as Experimental Referee Board-Specification (ERBS) jet fuel, are listed in Table 5.

One of the most important changes made was a reduction of the hydrogen content to 12.8 percent; the aromatic content of 35 percent is substantially different from the specified 20-25 percent for Jet A. This change will allow the use of cracked petroleum stocks and materials manufactured from coal and shale, greatly improving the flexibility of jet fuel manufacture.

The second most important change was the raising of the freezing point from -40°F to -20°F, allowing the use of higher boiling point components than those used to produce Jet A and further increasing the flexibility of manufacture.

The characteristics of ERBS jet fuel approach those of a high-quality diesel fuel, but the severe thermal stability requirements will necessitate hydrotreating and the almost complete removal of organic nitrogen. The hydrotreating processes now available will be adequate when petroleum is used as a base, but more efficient processing will be desirable when coal and shale liquids are used to produce this fuel.

The introduction of a low-hydrogen fuel like ERBS jet fuel will require changes in combustion chamber design, since the lower hydrogen content will raise combustion chamber liner temperatures and increase

Table 5 Specifications for "Experimental Referee Broad-Specification" (ERBS) aviation turbine fuel, with data on conventional Jet A fuel for comparison

Specifications	ASTM Jet A	ERBS Jet Fuel	Proposed test method
Composition			
Hydrogen, wt %	--	12.8±0.2	NMR
Aromatic carbon, vol %	25 max	Report (35 typical)	ASTM D1319
Sulfur, wt %			
Mercaptan	0.003 max	0.003 max	ASTM D1219
Total	0.31 max	0.3 max	ASTM D1266
Nitrogen, wt %	--	Report	Kjeldahl
Naphthalenes, vol %	--	Report	ASTM D1840
Hydrocarbon compositional analysis	--	Report	G.C.M.S.
Volatility			
Distillation temperatures, °F			
Initial boiling point	--	Report	ASTM D2892
10%	400 max	400 max	
50%	450 max	Report	
90%	--	500 min	
End point	550 max	Report	
Residue, percent	1.5 max	Report	
Loss, percent	1.5 max	Report	
Flashpoint, °F	105-150	110±10	ASTM D56
Gravity, °API at 60°F	39-150	Report	ASTM D287
Gravity, specific (60/60°F)	--	Report	ASTM D1298
Fluidity			
Freezing point, °F	-40	-20 max	ASTM D2386
Viscosity, cSt[a] at -10°F	--	12 max	ASTM D445
Net heat of combustion, Btu per pound	18,400 min	Report	ASTM D2382
Thermal stability[b]			
Breakpoint temperature, °F	--	460 min	ASTM D3241

[a] Centistokes.

[b] Jet fuel thermal oxidation test. Tube deposit rating, 13 or ΔP, 25 mm.

Source: National Aeronautics and Space Administration (1977).

soot emissions on takeoff. The higher freezing point of the new fuel will make it necessary to add heat to the fuel system of long-range high-altitude aircraft and change ground handling facilities in some areas. Preliminary studies sponsored by NASA have indicated the feasibility of dealing with the freezing problem.

The difficulty and cost of retrofitting existing aircraft for an ERBS-type jet fuel will very likely preclude its use in the present fleet. The new fuel must be considered for use over the long term as the next generation of aircraft comes into use. If it is decided not to proceed with the new fuel, the production of the present type of jet fuel from oil shale and coal will require the introduction of hydrogen-intensive processing or, in the long run, the synthesis of paraffinic Fischer-Tropsch liquids from coal.

FUTURE AUTOMOTIVE ENGINES AND THEIR FUEL NEEDS

Table 6 lists a variety of future engine possibilities and their potentials for use in passenger cars, trucks, and farm machinery. Table 7 indicates the relaxation in fuel properties that may be possible with these engines.

A brief discussion of the fuel requirements for each of the engines follows.

Homogeneous-Charge Spark-Ignition Engine (Carbureted)

Since a decrease in the volatility of gasoline impairs vehicle performance, no significant reduction in volatility can be permitted in substitute fuels for carbureted spark-ignition (SI) engines. If a separate fuel and fuel system were used for cold starting, front-end volatility requirements for the main fuel might be relaxed somewhat, but mid-range and back-end volatility similar to that for present-day gasoline would still be required. Dual-fuel systems have never proven practical, however.

The need to maintain fuel octane quality at or near the present level will place an additional strain on the fuel industry over the near term. As it is now, the unleaded octane pool needs to be increased to at least a 91 research octane level from its current level of 88-89 because new cars and light-duty trucks are being designed to use 91 octane fuel.

If spark-ignition engines continue to be designed for this type of fuel, gasoline feedstocks derived from coal and shale liquids will have to be capable of providing the required octane quality. The high aromaticity of coal-derived materials is expected to make it possible to use them for the production of high-octane gasoline if the systems exposed to the fuel are designed with elastomers and other materials that are impervious to aromatics. The high aromaticity of gasoline from coal may make it possible to design more efficient engines with higher octane requirements than those of today (Longwell, 1978).

Table 6 Future automotive engine use[a]

Engine	Small passenger cars	Large passenger cars and small trucks	Heavy trucks and large farm machinery
Homogeneous-charge spark-ignition	XXX	XX	0
Diesel	XX	XXX	XXX
Direct injection stratified-charge	XX	X	X
Gas turbine	0	X	XX
Stirling	X	XX	X

[a] XXX: significant number; XX: moderate number; X: low number; 0: none. Underscore indicates engine currently used in this application.

The need to maintain high octane quality and volatility may preclude major changes in other properties of synthetic fuels, however. Octane and/or volatility requirements may, for example, limit the extent to which the viscosity might be increased. This difficulty could be dealt with by redesigning carburetors, provided the variations between batches of fuel are not excessive. New fuel metering systems, such as the computer-controlled, low-pressure throttle-body injection systems introduced in 1980 and 1981 model cars, may further increase the spark-ignition engine's flexibility in handling fuels of varying viscosity and volatility.

A somewhat higher nitrogen content in a synthetic fuel could probably be handled within the constraints of present emission standards and engine durability requirements, but very high nitrogen and sulfur concentrations in coal and shale liquids may introduce difficulties in the refining processes, just as in the refining of petroleum.

Homogeneous-Charge Spark-Ignition Engine (Timed Fuel Injection)

Fuel volatility requirements may be reduced in timed-fuel-injection engines. In a carbureted engine, the fuel must be volatile enough to aid in the mixing of fuel and intake air in the engine manifold for the proper distribution of fuel to each of the cylinders. The timed high-pressure injection of fuel into each inlet port or cylinder in a fuel-injection engine reduces the distribution problem but a certain degree of front end volatility is still necessary for starting a cold engine. A separate starting fuel of high volatility would allow the volatility specification of the main fuel to be greatly relaxed, but dual-fuel systems have not proven practical to date.

The viscosity of a fuel could be greater and more variable for a fuel-injection engine than for a carbureted engine, but the fuel octane quality would need to be maintained. This could effectively limit an increase in viscosity and decrease in volatility for synthetic fuels, as it does in most cases for petroleum-derived fuels.

This engine's ability to tolerate the higher concentrations of nitrogen, sulfur, ash, and aromatics in synthetic fuels will be the same as that of the carbureted spark-ignition engine, and the same potential interactions of these properties with octane quality would apply.

Compression-Ignition (Diesel) Engine

Diesel engines can use fuels with a wider range of properties than spark ignition engines. Although there is evidence that smoke, particulates, odor, and hydrocarbons increase with lower fuel volatility, the engine could probably tolerate less volatile fuels. The sulfur content of diesel fuels approaches the one percent level in some foreign countries and has been associated with accelerated engine corrosion and wear. As indicated earlier, high nitrogen levels can cause problems.

A high ash content in synthetic diesel fuels would be undesirable, because it could not only increase combustion chamber deposits and contribute to particulate emissions but also clog fuel injectors.

The ignition quality (cetane index) of future diesel fuels should remain at or near current levels, particularly for fuels used in the high-speed diesels produced for passenger cars and light-duty trucks. High aromatic levels can be tolerated in diesel fuels, but they generally decrease ignition quality and increase exhaust smoke.

An increase in viscosity may degrade fuel atomization in the combustion chamber, but higher injection pressures likely in future engines, particularly in open-chamber designs, should counteract the effects of higher viscosity in fuels derived from coal and shale. The lubricity of diesel fuels should remain high to protect fuel-injection system components.

Diesel engines are used not only on the road but also in rail and marine transportation; trains and ships use large, low-speed engines that are more suitable for less-refined fuels, with their lower cetane qualities and higher viscosities.

Table 7 Fuels for future automotive engines[a]

Future automotive engines	"Desirable Fuel"	Volatility	Viscosity
Conventional Engines			
Homogeneous-charge SI engine (carbureted)	Current gasoline	No change	Higher
Homogeneous-charge SI engine (fuel-injected)	Current gasoline	Lower	Higher
Compression-ignition engine (diesel)	Current diesel fuel #1 or #2	Lower	Higher
Unconventional Engines			
DISC (PROCO) engine (stratified-charge)	Current gasoline	Lower	Higher
DISC (Texaco) engine (stratified-charge)	Distillate, current gasoline[d]	Lower	Higher
Gas turbine	Distillate, current gasoline[d]	Much lower	Much higher
Stirling engine	Distillate, current gasoline[d]	Much lower	Much higher

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[a] Assuming "tolerable" relaxations in the properties of future fuels relative to the properties of "desirable fuels." There are reasons to believe that changing fuel properties in the directions indicated may result in an increase in overall energy efficiency; no energy savings would be anticipated for property changes in the opposite direction, and energy losses would probably result.

[b] Cetane rating.

[c] Higher sulfur content could adversely affect performance of catalytic emission control systems, especially the new three-way catalyst systems.

[d] Broad-cut distillate, diesel fuel, kerosene, or jet fuel.

Fuel characteristics					
Aromatic content	Impurity Content			Octane rating	Ignition quality[b]
	Sulfur	Nitrogen	Ash		
Higher	Higher[c]	Higher	No change	No change	--
Higher	Higher[c]	Higher	No change	No change	--
Higher	Higher	Higher	No change	--	No change
Higher	Higher	Higher	No change	Lower	--
Higher	Higher	Higher	No change	None required	None required
Higher	Much higher	Much higher	Higher (not heavy metals)	None required	None required
Higher	Much higher	Much higher	Higher	None required	None required

Stratified-Charge Engines

Stratified-charge engines can be classified according to the method used to achieve stratification of the fuel-air mixture. Although diesel engines incorporate charge stratification, this discussion is limited to spark-ignition engines.

The stratified-charge spark-ignition engines on the road today use a prechamber to separate the rich mixture (where combustion is initiated) from the remaining lean mixture. The fuel requirements of these engines are not significantly different from those of the spark-ignition engines already discussed.

Stratified-charge engines in which fuel is injected into an undivided combustion chamber have the potential for tolerating a wider range of fuel properties than other spark-ignition engines, however. There are two distinct types of engines in this direct-injection category, described next. Neither is available to the public in production automobiles.

Direct-Injection Stratified-Charge (DISC) Engine (PROCO)

In the PROCO ("programed combustion") engine undergoing development by the Ford Motor Company, the fuel is injected halfway through the compression stroke into a high-intensity swirl set up during the air-intake stroke, and the fuel-air mixture ends up (toward the end of the compression stroke) in a cup in the piston where it is ignited. With the relatively high turbulence in the fuel-air mixture, it burns rather quickly and, as a result, detonation (knocking) does not occur at the compression ratios at which it begins to be a problem in conventional spark-ignition engines. Instead of using this feature to lower the octane requirement of the engine, the PROCO engine takes advantage of it by raising the compression ratio to about 11:1, thereby increasing the power output for a given engine displacement and increasing the efficiency of energy use.

The other fuel property requirements for this engine are about the same as for other direct-injection spark-ignition engines.

Direct-Injection Stratified-Charge (DISC) Engine (Texaco)

This engine has been undergoing development by Texaco (and others) for more than 30 years. A high-velocity air swirl set up in the cylinder during induction persists through the compression stroke and, as the piston nears top center, is compressed into a cup in the piston. When fuel is injected into the air (in the same direction as the swirl), a combustible mixture forms almost immediately at the edges of the spray where ignition is initiated (by a spark gap located just downstream of the fuel nozzle).

Although the chemical structure of the fuel influences its ignitability, typical spark energies required for this engine are considerably greater than the theoretical minimum ignition energy. The influence of fuel chemical properties on ignition is, consequently, relatively insignificant in practice.

The problem of unreliable spark ignition that has sometimes been observed with this type of engine cannot be attributed entirely to the properties of the fuel. The degradation in performance of the fuel-injection and spark-ignition systems and the difficulties encountered in operating over wide ranges of engine speed and load are more likely causes. Since all portions of the fuel-air mixture are burned essentially as soon as they are formed, no end gas region exists and the engine has no octane requirement. Since a high-energy spark minimizes ignition delay, the engine has no cetane requirement. Other fuel property requirements are about the same as for the diesel engine.

Open-Cycle Gas Turbine

The open-cycle gas turbine has no octane or cetane requirements. It can use a wide range of fuels; the only essential requirement is that the fuel flow adequately at the lowest temperature encountered in service. Since a relatively long time is available for ignition at start-up (far more than that available during each cycle of a diesel or spark-ignition engine), fuel volatility is relatively unimportant.

The gas turbine can also tolerate significantly higher quantities of impurities (e.g., nitrogen, sulfur, and ash) than those in current automotive fuels and still operate within the constraints of exhaust emission standards, although higher contents of heavy metals could increase corrosion.

Fuels with a high aromatic content would cause higher combustor skin temperatures (because of the increased radiation from the flame) as well as increased soot and smoke formation, but these problems can be solved by redesigning the combustor.

External Combustion Engines:
Stirling, Rankine, and Closed-Cycle Gas Turbine Engines

These continuous-combustion engines should be able to burn any liquid hydrocarbon fuel that can flow adequately at the lowest temperature encountered in service.

SURVEY ON COMPATIBILITY OF FUTURE AUTOMOTIVE FUELS AND ENGINES

To obtain some insight into the problem of matching fuels to engines, letters were sent to a representative group of experts in automotive and petroleum industries, independent research organizations, and universities. A copy of the letter is on the following page, followed by a summary of the comments received.

There was no unanimity on whether "less refined" fuels from coal and oil shale should be investigated for use with current and future engines. Some believed that efforts should be directed toward producing fuels that are essentially identical to the gasolines and diesel fuels in use today. Others thought there was considerable merit in trying to use less refined fuels and that broad-boiling-range fuels should be investigated for use in stratified-charge engines, Stirling engines, and gas turbines. The fuel properties of greatest concern were the sulfur, nitrogen, and aromatics contents.

Many of the respondents believe that spark-ignition and diesel engines will continue as the major automotive power plants through the end of the century, with their fuel needs dictating the kinds of oil-shale- and coal-derived fuels that might be used. They also believe that engines with less stringent fuel requirements (e.g., the Stirling engine and gas turbine) will not see much use prior to the 1990s.

NATIONAL RESEARCH COUNCIL
ASSEMBLY OF ENGINEERING
2101 Constitution Avenue Washington, D. C. 20418

October 28, 1977

Dear Sirs:

At the request of the Department of Energy (formerly ERDA) the National Research Council has formed an ad hoc panel to investigate the research and development needs related to the refining of synthetic crude oils obtained from coal and oil shale. The specific objective of the ad hoc panel and the current composition of the panel are given in the attachments to this letter.

The panel, in reviewing its assignment, has recognized that potentially significant energy and presumably economic savings are possible if future transportation engines can be designed to operate satisfactorily on fuels from coal and oil shale that do not have to be refined to the same extent as current fuels from petroleum.

The major product output from the refinery will be liquid fuel for transportation. To ensure that the refinery is properly designed to support the optimum fuel/engine combinations, anticipating engine changes that could use less well refined fuel that will be in use about 2000 A.D., the panel has decided to ask experts about their opinions on the quality of fuels that will be required for the kinds of engines expected to be in use by then. Considering your background and experience regarding the matching of automotive fuels and engines, would you please project the fuel specifications that you believe will be required for the engines that will power our land-based transportation systems by 2000 A.D. These engines include: spark ignition; diesel; stratified charge; gas turbine; Stirling; and any other engines.

In looking at fuel quality projections, the following should be considered: distillation characteristics; vapor pressure; impurities (sulfur, nitrogen, ash) content; aromatic content; octane and/or cetane quality. This is obviously not an all-inclusive list, and you should include any other fuel properties that you believe will be important. If possible, in assessing the future fuel-engine matches, would you relate your expected changes in fuel properties to those of current specifications (ASTM or other) for the fuels involved.

I would appreciate it if we could receive your response by November 18, 1977. This would give the panel a chance to review and summarize the responses prior to its meeting in early December. I recognize that we are asking you to spend some time essentially peering into your crystal ball. However, I expect that it will turn out to be time well spent if we can get our nation started on the right track toward generating the best fuels for transportation's use in the next century.

Thank you for your cooperation.

Sincerely yours,

John O. Berga
Executive Director

JOB/vs
Attachments

Attachment to letter:

STATEMENT OF TASK

Panel on R&D Needs in Refining Coal and Shale Liquids

The objective of this contract is to define the research and development needs in refining coal and shale liquids to a product slate emphasizing transportation fuels and other distillable fuels.

Survey the program currently underway on processing techniques applicable to coal and shale upgrading. Programs are currently supported by ERDA, Department of Defense, the Electric Power Research Institute (EPRI) and industry.

With the results of the above, define the areas in coal and shale liquids refining and upgrading where research would be desirable from a benefit to cost standpoint and from the standpoint of national needs.

Summary of Responses

Petroleum Company A

- Future motor fuels must meet four basic criteria regardless of source or refining severity: stability, burnability, compatibility, and low emission potential.

- Fuel corrosivity (from chemically active oxygen, sulfur, or nitrogen compounds or compounds that take up water) must be controlled.

- Sulfur, nitrogen, and particulate precursors will need to be controlled because of environmental considerations.

- The metals contents of high-boiling-point fuels must be minimized.

- Crudes from oil shale and coal are likely to contain more troublesome components than petroleum crudes and will very likely require a greater degree of refinery processing.

- Conventional engines of the future (spark ignition and diesel) will require fuels with much the same characteristics as those of current fuels (gasoline and diesel fuel).

- Engines that tolerate fuels of a wider distillation range (e.g., the stratified-charge engine, gas turbine, and Stirling engine) provide greater flexibility in refinery processing.

- It is difficult to forecast engine developments that will permit efficient operation with low emissions on less refined fuels.

Petroleum Company B

- The homogeneous-charge Otto-cycle spark-ignition engine is likely to remain in use for ground transportation until beyond the year 2000. Possible changes in its (gasoline) fuel requirements include (a) a lower Reid vapor pressure, (b) higher 10 and 20 percent evaporated temperatures, and (c) control of the aromatic content. No changes are anticipated in the octane quality, stability, or impurities contents (sulfur, nitrogen, polynuclear aromatics).

- The diesel engine will find increasing use in passenger cars and light-duty trucks through 2000 and will continue to be the engine used most in medium and heavy trucks. Possible changes in diesel fuel specifications include (a) an increase in 90 percent and end-point distillation temperatures (especially if gasoline demand decreases and heavy gas oil is not needed for cracking), (b) a decrease in cetane quality for truck engines if spark-ignition diesel engines come into use, (c) an increase in cetane quality (above 45) for passenger car diesel engines, and (d) the control of aromatic content with constraints on cetane number and emissions (particulates, smoke, and polynuclear aromatics). The stability cannot deteriorate.

- Prechamber (jet-ignited) stratified-charge engines are not likely to find wide application. If used, they will not permit appreciable changes in present gasolines.

- Open-chamber stratified-charge engines may find application. Throttled engines (Ford PROCO) require a fuel similar to current unleaded gasoline; unthrottled engines (e.g., Texaco TCCS) can use either current fuels or a wide range of other fuels without regard to octane or cetane quality. Volatility is not a major concern. Fuel stability and sulfur, nitrogen, and polynuclear aromatic contents will have to be controlled.

- It is very doubtful if either the gas turbine or Stirling engine will find widespread use by 2000. However, either would permit the use of fuels with few specification restrictions.

Automobile Company A

- It is more energy efficient to refine fuel carefully to achieve best engine performance than to attempt to operate with less refined fuels. This applies to gasoline, diesel, and gas turbine engines likely to be in use by 2000.

- Emphasis should be placed on developing the technology needed to refine coal and shale oil into gasoline and diesel fuels that meet the current specifications for these fuels. Refining efforts should concentrate on reducing sulfur and nitrogen contents to acceptable levels.

- Engines may have to be modified to permit the use of fuels from coal and oil shale, particularly because of their high aromatic contents.

Automobile Company B

- The spark-ignition engine will be the principal engine for passenger cars through the year 2000.

- Stratified-charge engines may come into use eventually. The PROCO engine has significant octane requirements, even though it can tolerate variations in fuel volatility and stoichiometry. The TCCS (Texaco) engine has even greater volatility tolerance and presumably no octane requirements.

- To make diesel engines more desirable for passenger car use, starting performance may have to be improved by using lower compression ratios and higher cetane number fuels. If diesel engines achieve widespread use, the sulfur content of diesel fuel may require control.

- Gas turbine and Stirling engines can operate with a wide range of fuels, including fuels with much less hydrogen than current fuels. However, for reasons of customer convenience, supply, and logistics, it is likely that these engines will be designed to use gasoline.

Automobile Company C

- In the future, engines may be able to tolerate less volatile fuels with higher concentrations of sulfur, nitrogen, and aromatics, provided emissions can be held at acceptable levels. Emission constraints may become the main factor in determining the extent to which fuel properties can be relaxed.

- Major changes in engine efficiencies are not anticipated for the fuel changes considered possible.

- The engines of the future, in order of decreasing likelihood, are the homogeneous-charge spark-ignition, diesel, stratified-charge, gas turbine, Stirling, and Rankine engines. The engines fall in the same order when listed according to their increasing tolerance to variations in fuel specifications.

- In evaluating future fuel-engine matches, the following factors must be considered: combustion, performance, cost, durability, emissions, safety, convenience, and fuel and resource consumption.

- Spark-ignition engines will require volatility and octane quality similar to that of current gasoline. Fuel-injected spark-ignition engines may have less stringent volatility requirements than carbureted engines. They might also tolerate more viscous fuels if octane quality is not compromised.

- Diesel engines could probably tolerate less volatile fuels if emissions of particulates, smoke, hydrocarbons, and odor were acceptable. Higher sulfur, nitrogen, and ash contents may not be acceptable because of emission and engine durability problems, however.

- Cetane quality should remain at or near current levels.

- The PROCO-type direct-injection stratified-charge engine requires a fuel similar to the unleaded gasoline now available. The Texaco-type engine has less stringent fuel requirements, particularly for octane quality; its fuel requirements resemble those of diesel engines (except for cetane quality).

- The open-cycle gas turbine engine has a wide fuel tolerance, the most stringent requirement being that the fuel flow adequately at the lowest temperature encountered in service. Fuels with high aromatic contents could lead to higher soot and NO_x emissions.

- External combustion engines (e.g., Stirling, Rankine, and closed-cycle gas turbines) should be able to burn any liquid hydrocarbon fuel that can be pumped at the lowest service temperature and still meet environmental and engine life constraints.

- Special concern should be given to distillate fuels for railroad diesel engines that are designed for ASTM 2D fuel. This type of fuel must remain available for as long as these engines are in operation, which may be 20 years or longer. Future railroad diesels could be designed to use ASTM 4D fuel, if environmental constraints can be met.

Automobile Company D

- There is no clear indication of the benefits in process cost and energy savings that can result from reducing fuel properties in terms of cetane, octane, distillation ranges, freedom from impurities, and so on.

- For today's diesel engines, the most desirable fuels are the ones with the highest cetane quality, minimum sulfur, minimum aromatics, etc. For gasoline engines, the most desirable fuels are the ones with the highest octane, minimum octane improving additives, etc. Engines have useful lives of 10-20 years, especially in industrial and agricultural applications. Thus, fuels similar to current fuels will have to be sold until the year 2000, since no major changes in engines are anticipated, at least through the early 1980s.

- Some stratified-charge, gas turbine, and Stirling engines do not have octane or cetane requirements. However, fuels for these engines will need to remain liquid at normal ambient temperatures (-30°F to 120°F) and be seasonally blended. These engines cannot tolerate fuel impurities that could cause corrosion or unacceptable levels of exhaust pollutants. If unacceptable hydrocarbon pollutants are not generated (even in small quantities), however, higher aromatic levels can probably be tolerated.

Independent Research Laboratory A[a]

- Distillation characteristics of fuels for Stirling and gas turbine engines can vary from those of gasoline to those of No. 2 diesel fuel. A broad-cut fuel could be used. An open question is whether these engines can tolerate tank-to-tank variations in distillation characteristics.

- Vapor pressure restrictions required by evaporative and refueling emission standards could restrict the light-end content of all fuels.

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[a] Comments were confined to Stirling and gas turbine (Brayton cycle) engines.

- Impurities will need to be controlled. Fuel-bound nitrogen may need to be restricted so that its contribution to NO_x emissions does not exceed 0.2 gram/mile (assuming a NO_x standard of 0.4 gram/mile). Sulfur may have to be controlled to the level of current gasoline since the lean operating Stirling and gas turbine engines are likely to oxidize all fuel sulfur to SO_2 or sulfates. Ash content will need to be controlled to lessen engine wear and particulate emissions. Trace metals such as vanadium may also need to be controlled.

- Control of the aromatic content will make it possible to reduce carcinogenic emissions.

Independent Research Laboratory B

- With the decline in the supply of petroleum fuels forecast for the near future, the following sequence of events is expected to occur:

  1. The introduction of conventional engines that are less sensitive to fuel quality (e.g., stratified-charge engines and engines with closed-loop systems)

  2. The introduction of hybrid fuels (alcohol-gasoline blends, carbonaceous diesel fuels)

  3. The introduction of other engines (e.g., gas turbines)

  4. The end of 100 percent petroleum fuels

  5. The introduction of either unconventional engines (e.g., external combustion types) or unconventional fuels (e.g., nonpetroleum compositions)

  6. The introduction of unconventional engine-fuel systems (e.g., an external combustion engine and frangible solid fuels).

- From 1985 to 2000, the fuels used for highway transportation are likely to be gasoline, diesel fuel, broad-cut fuel, gasoline-alcohol blends, and carbonaceous hydrocarbon slurries. These fuels will be obtained primarily from petroleum with inputs from coal, oil shale, and biomass.

- From 1990 to beyond 2000, the transportation fuels are likely to be solids, gels, and slurries or emulsions obtained from coal, oil shale, and biomass. Pure and mixed alcohols and pure synthetic liquid hydrocarbons from these sources are doubtful. Hydrogen, methanol, and ammonia are all unlikely fuels.

- There will probably be two octane grades of unleaded gasoline in use in the year 2000. Metallo-organic antiknock agents will probably not be permitted, and the nitrogen and oxygen content of material from syncrudes will need to be limited. Since engines produced between now and 2000 are likely to be less volatility-sensitive, the constraints on volatility could be relaxed in 2000 or shortly thereafter, allowing the use of higher boiling fuels. If closed-loop systems are widely used as a means of controlling air-fuel ratios, the carbon/hydrogen ratio of the fuel will become a less important variable.

- Both 1-D and 2-D diesel fuels are likely to survive beyond 2000. A broad-cut fuel may become an alternative to 1-D fuel, however. Fuel stability may require tighter control.

- Broad-cut fuels may come into use because they can reduce refinery energy losses and increase refinery yields; they can reduce refinery energy losses because energy does not have to be expended to increase either octane or cetane quality. Broad-cut fuels can be used in some stratified-charge and gas turbine engines and may also find use in future diesel engines.

- Mid-distillate hydrocarbons containing up to 20 percent suspended carbonaceous particles would be attractive fuels for use in diesel, gas turbine, stratified-charge, and Stirling engines. The carbonaceous particles would be obtained by pulverizing the products from the solvent refining of coal. Research must be done to prove the fuels which offer the best cost-energy potential.

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4 COAL LIQUEFACTION PROCESSES

There are both direct and indirect routes for the conversion of coal to high-quality transportation fuels. In the indirect routes, the molecular structure of the coal is completely destroyed and the simple molecules of CO and H_2 that result are used to build molecules of combustible liquids. In the direct routes, the coal molecules are broken down into lower boiling hydrocarbons while preserving as many as possible of the original chemical bonds in the coal.

The products of the two routes have different refining characteristics. The liquids from the direct processes resemble petroleum crudes and can be refined in much the same way into high-quality transportation fuels. The liquids from the indirect processes vary from process to process and differ in character.

This chapter deals primarily with the refining of coal liquids obtained by direct routes. The refining of coal liquids obtained by indirect routes is discussed only when it can add perspective to some aspect of the overall problem.

THE ROLE OF HYDROGEN

Central to any discussion of the conversion of coal to liquids and ultimately to high-quality transportation fuels is the important role of hydrogen. Hydrogen is required not only to increase the hydrogen/carbon (H/C) ratio from that available in coal to that required in the end-products, but also to remove the undesirable heteroatoms (N, S, and O) present in the coal molecules.

The problem with the H/C ratios of coal products can be seen in Figure 5. In refining petroleum crudes, the most common method of increasing the H/C ratio is to reject carbon as a low-hydrogen coke or residuum (Figure 5). This practice plays a varying role in coal conversion processes. In some processes (such as pyrolysis), a liquid with a higher H/C ratio is produced for further refining, and a char with a lower H/C ratio than the coal is rejected. However, in the case of coal, so much hydrogen is needed that at some point in the liquefaction

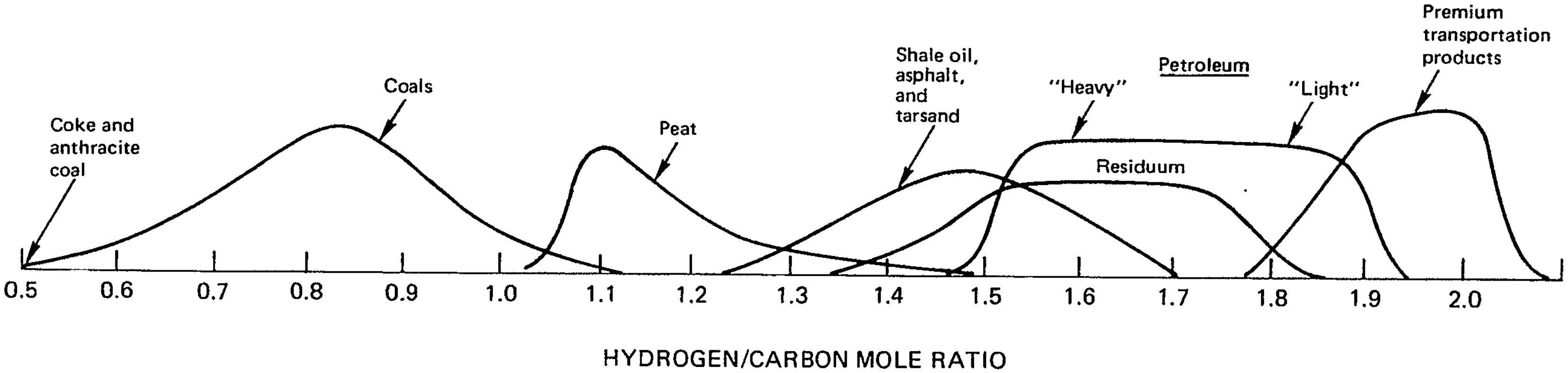

Figure 5 Hydrogen/carbon ratios for various hydrocarbon sources and end products (Whitehurst, 1978)

and refining processes, catalytic hydrogenation is necessary to add hydrogen and remove heteroatoms.

Processes currently in use for hydrogen production ultimately involve the reaction of steam with carbon, either directly or as carbon monoxide or a hydrocarbon. These processes, described in Chapter 7, are both costly and energy inefficient. Thus, increasing the efficiency with which hydrogen is used in the liquefaction and refining processes is critical to reducing the overall cost of converting coal to transportation fuels.

COAL PYROLYSIS

Pyrolysis processes that operate at high temperatures are able to convert about a third of the coal feedstock to liquids and gases that have higher H/C ratios than the original coal, carbon being removed in chars that have lower H/C ratios.

The Char Oil Energy Development (COED) process (Jones, 1975) is a typical example. In this process, coal is pyrolyzed in a series of fluidized beds, with the temperature increasing from bed to bed. In the operation of the COED pilot plant diagramed in Figure 6, bed temperatures were 500°F, 850°F, 1000°F, and 1650°F, the temperature being increased by the addition of oxygen.

The properties of typical products of the pyrolysis of Pittsburgh No. 8 coal are shown in Table 8. The figures indicate that the addition of a large amount of hydrogen would still be required to increase the H/C ratio to that of premium transportation fuels and remove the remaining heteroatoms. It should be noted that the gas produced had an overall H/C ratio of 10.9 because of the large quantities of hydrogen and methane that resulted. This represents a loss of valuable hydrogen that could have gone toward increasing the H/C ratio of the liquid. The liquid had an API gravity of -5°, a pour point of 100°F, and a viscosity of 70 centipoises at 210°F; its physical and distillation properties resemble those of a petroleum crude somewhat, but it has a much lower H/C ratio. (See Figure 7). The high nitrogen content of this liquid would present refining problems.

The char from this process could be used as a boiler fuel but would be high in sulfur if a high-sulfur coal were used as the feedstock. The char could also be gasified and the syngas used as a fuel gas, converted to hydrogen by the shift reaction, or converted to liquid fuels by one of the indirect conversion processes.

Pyrolysis carried out in a hydrogen atmosphere (hydropyrolysis or hydrocarbonization) could improve the liquid yield, thereby improving product quality and reducing the sulfur content of the liquid product and char, but this would require markedly higher pressures, the addition of hydrogen, and higher equipment costs. In addition, the production of methane would be increased.

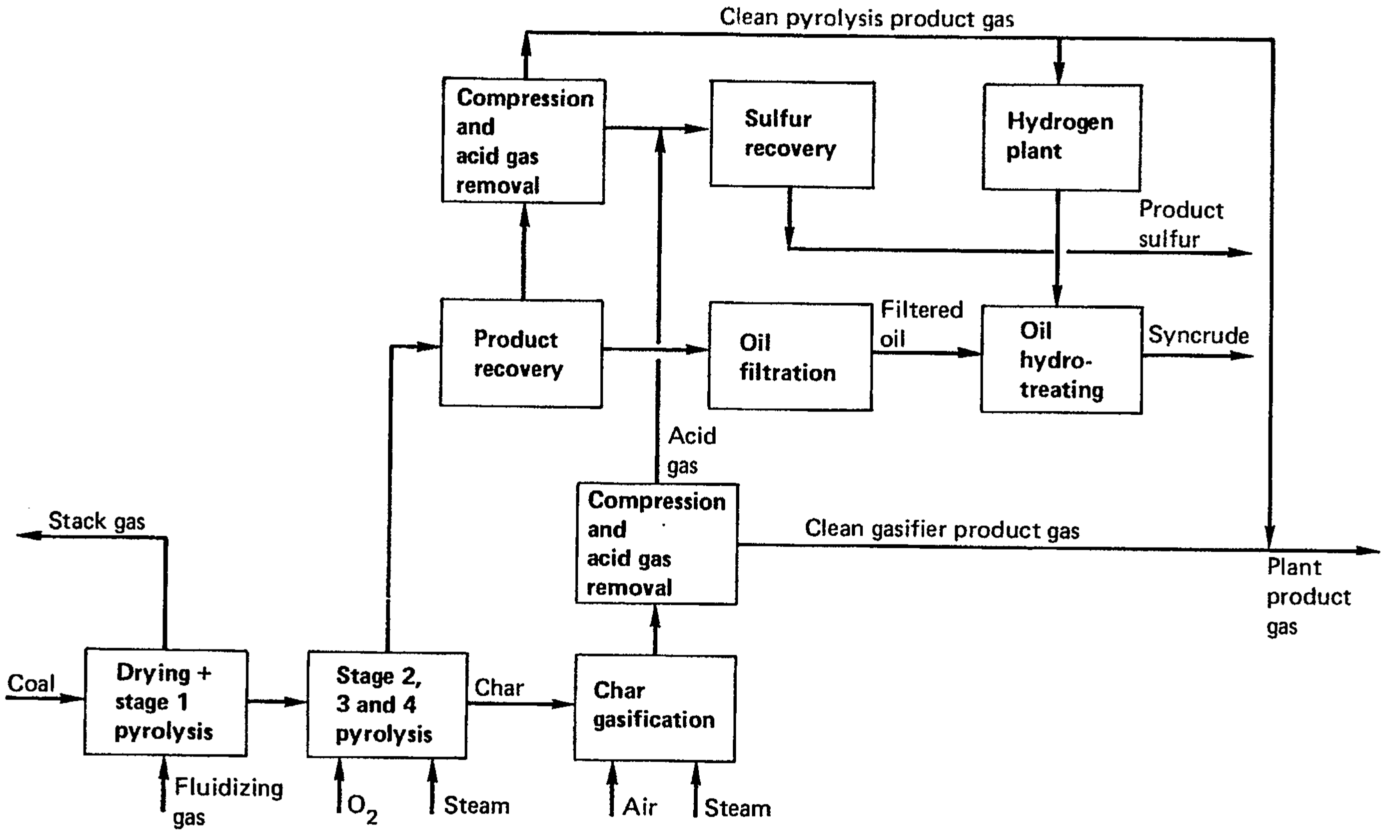

Figure 6 COED coal liquefaction process, with char gasification (Jones, 1975)

Table 8 Properties of coal feed and products from COED pyrolysis (Pittsburgh No. 8 coal)

	Coal	Oil	Char	Pyrolysis gas
Yield	--	0.85 barrel per ton	1,266 pounds per ton	3,675 standard cubic feet per ton
Hydrogen/carbon ratio	0.83	1.12	0.31	10.9
Composition, wt %				
Carbon	76.2	82.68	76.9	--
Hydrogen	5.3	7.73	2.0	23.75
Oxygen	6.7	2.2	1.9	--
Nitrogen	1.4	6.50	1.2	--
Sulfur	3.8	0.85	4.3	--
Ash	6.6	0.04	13.9	--
Carbon monoxide	--	--	--	29.50
Methane	--	--	--	38.26
C_2+ gas	--	--	--	8.49
Pyrolysis oil				
Gravity, °API at 60°		-5		
Pour point, °F		100		
Viscosity, centipoises at 210°F		70		
Distillation temperatures, °F				
Initial boiling point		385		
5%		415		
10%		460		
20%		550		
30%		630		
40%		730		
50%		795		
60%		860		
End point		905		
Recovered, percent		70		
Residual, percent		30		

Source: Jones (1975).

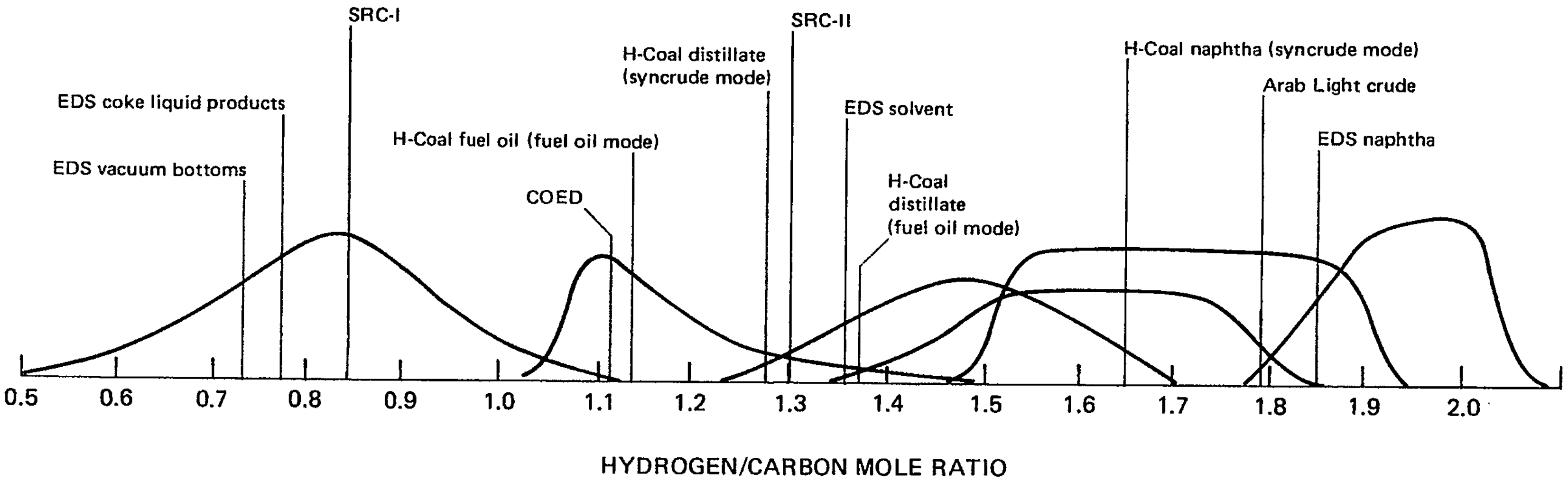

Figure 7 Hydrogen/carbon ratios for products of coal liquefaction pilot plants, with Arab Light crude for comparison (adapted from Whitehurst, 1978)

SOLVENT PROCESSES WITHOUT THE ADDITION OF CATALYSTS

If an appropriate fraction of the liquid product obtained from the heating of coal is returned to the reaction zone, it improves the conversion of the coal to a liquid by acting as a solvent and also by aiding the shift of hydrogen and the rearrangement of chemical bonds within the coal molecule. In most of the processes making use of these effects, a high-pressure hydrogen atmosphere is maintained in the reactor in which the coal is dissolved.

In Solvent-Refined Coal (SRC-I and SRC-II) processes (Sullivan et al., 1979; Synthetic Fuels, 1979), the temperature in the dissolving vessel is maintained at about 850°F and the pressure at 1000-1500 psi, depending on the particular coal and process used, with the required hydrogen provided from an outside supply. By returning part of the liquid produced to the dissolving vessel, the coal is converted to a product that is fluid at the temperature in the vessel. The time required varies from a few minutes to about an hour, depending on the particular process and the product characteristics required.

In the SRC-I process shown in Figure 8, the solvent is taken from the vacuum distillate fraction boiling below 1000°F. Contact times are about 30-60 minutes. Although the H/C ratio of the product (Table 9) does not differ very much from that of the coal used, considerable hydrogen is consumed (Table 10), the quantity equaling that in the gases produced. The ash is removed from the product by filtration or solvent precipitation. Table 9 shows the physical and chemical characteristics of a typical SRC-I product (solid at room temperatures), and Table 10 shows typical yields. To be upgraded, this product must be hydrogenated further.

When the contact time in the SRC-I process is reduced to about 5 minutes, the H/C ratio in the product remains about the same as that in the coal feedstock, but the hydrogen consumption and gas production are lowered. If this product were then de-ashed and hydrogenated in a separate ebullating-bed reactor (e.g., an LC-Fining or H-Oil reactor), the net result would be a good syncrude and an overall reduction in hydrogen consumption (Kleinpeter et al., 1979; Longanbach et al., 1978; Schindler, 1980).

In the SRC-II process (Figure 9), the dissolving conditions are more severe; temperatures and pressures are higher, and contact times are longer. The solvent is a portion of the slurry bottoms rather than a distillate product as in SRC-I, and the product is sufficiently volatile to be removed by vacuum distillation. The product is liquid at room temperature and the hydrogen consumption is greatly increased over that of SRC-I, as is the gas production. In contrast to SRC-I, the H/C ratio of the liquid is increased over that of the original coal. Physical and chemical properties of a typical SRC-II product are given in the second column of Table 9. The amount of high-boiling-point product

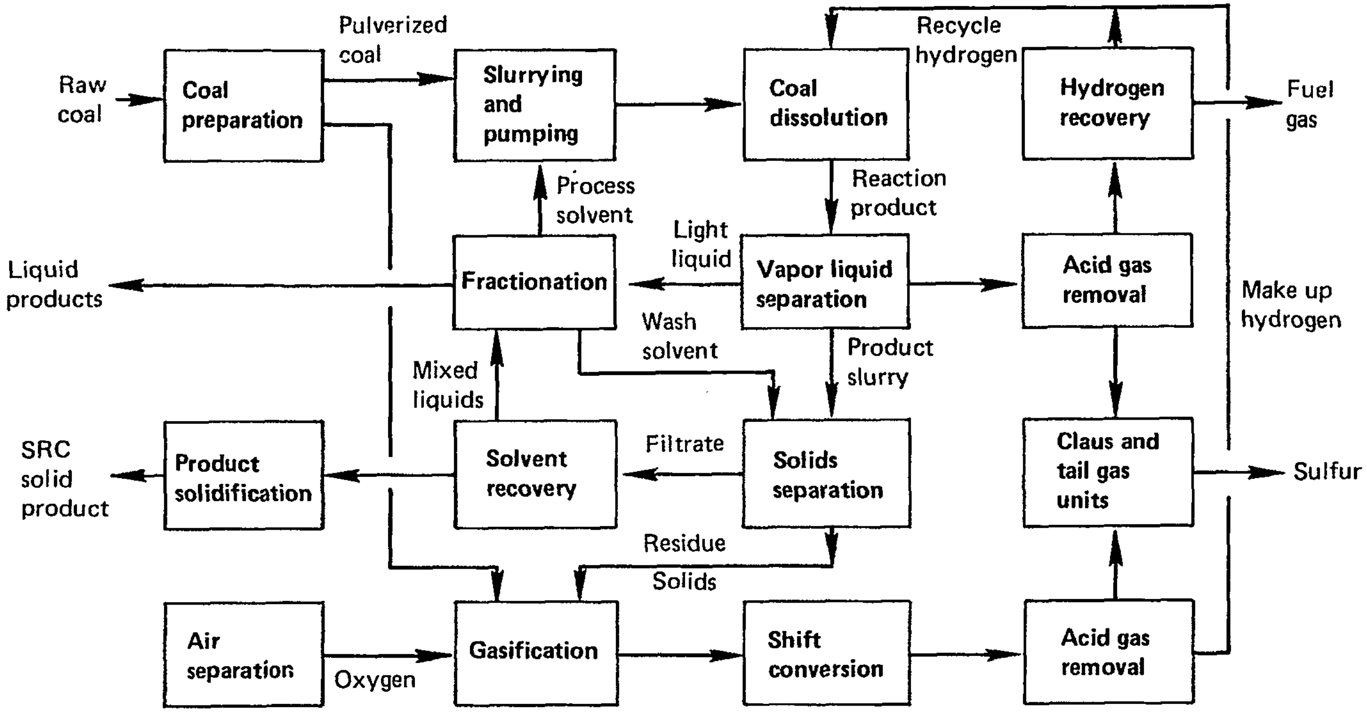

Figure 8 SRC-I process, without the addition of catalysts (Sullivan et al., 1979; Synthetic Fuels, 1979)

Table 9 Properties of SRC-I and SRC-II products

	SRC-I	SRC-II
Gravity, °API	-14.6	18.6
Hydrogen/carbon ratio	0.85	1.3
Composition		
Hydrogen, wt %	6.1	9.1
Oxygen, wt %	4.5	3.8
Nitrogen, wt %	2.0	0.85
Sulfur, wt %	0.9	0.3
Ash, wt %	0.22	0.004
Aromatic carbon, wt %	81	58
Chloride, parts per million	50	50
Nominal boiling range, °F	900+	160-800
Distillation temperatures, °F		
Initial boiling point	159	56
5%	943	189
10%	1017	241
30%	1161	379
50%		424
70%		473
90%		562
95%		642
End point		820
Hydrogen consumption, standard cubic feet per ton	7,400	15,500

Source: Sullivan et al. (1979).

has been greatly decreased over that of SRC-I as a comparison of the two distillate curves in Table 9 shows. The hydrogen to carbon ratio is now 1.3 as shown in Table 9 and Figure 9. Table 10 gives typical yields from this process. Although the boiling range of SRC-II liquids is good for high quality fuel production, the hydrogen to carbon ratio is still a long way from that required for high quality transportation fuels. Some properties of an Arab Light crude are given in Table 11 for comparison.

Table 10 Hydrogen consumption and hydrocarbon yields from various coal liquefaction processes

	SRC I (Illinois No. 6)	SRC I (Kentucky No. 9)	SRC II (Kentucky No. 9)	EDS (Illinois No. 6)	H-Coal (Illinois No. 6)	
					Fuel oil	Syncrude
Hydrogen consumed, standard cubic feet per ton of coal[a]	6,700	7,400	15,500	14,600	13,400	18,500
Process yields, based on coal						
Light gases, pounds per ton of coal						
CH_4	42.6	50.7	116.8	65.6	45.7	51.6
C_2-C_3	52.7	62.7	163.2	102.2	91.4	103.2
Liquid hydrocarbons, barrels per ton of coal						
C_4-380°F	0.26	0.44	0.96	1.53	0.75	1.22
380-650°F	0.35	0.30	1.07	0.21	0.71	0.97
650-1000°F	0.70	0.16	0.20	0.32	0.72	0.71
1000°F+ (SRC)	2.17	2.47	1.11	1.32[b]	1.21[c]	0.74[c]
Total C_4+ liquids	3.48	3.37	3.34	3.38	3.39	3.64
C_4-1000°F liquid, vol %	37.6	26.7	66.7	60.9	64.3	79.6
Hydrogen consumed per C_4-1000°F liquid, standard cubic feet per barrel	5,100	8,200	7,000	7,100	6,100	6,400
Ratio of CH_4 to H_2 consumption, pounds per million standard cubic feet	6.3	6.8	7.5	4.5	3.4	2.8
Ratio of CH_4 to C_4-1000°F liquid, pounds per barrel	32.5	56.3	52.4	31.8	20.9	17.8

[a] As received. Hydrogen externally supplied.

[b] Assumed unconverted coal, 8.2 weight percent of coal. Product coked and coke gasified to produce either hydrogen or fuel gas.

[c] Product gasified to produce hydrogen.

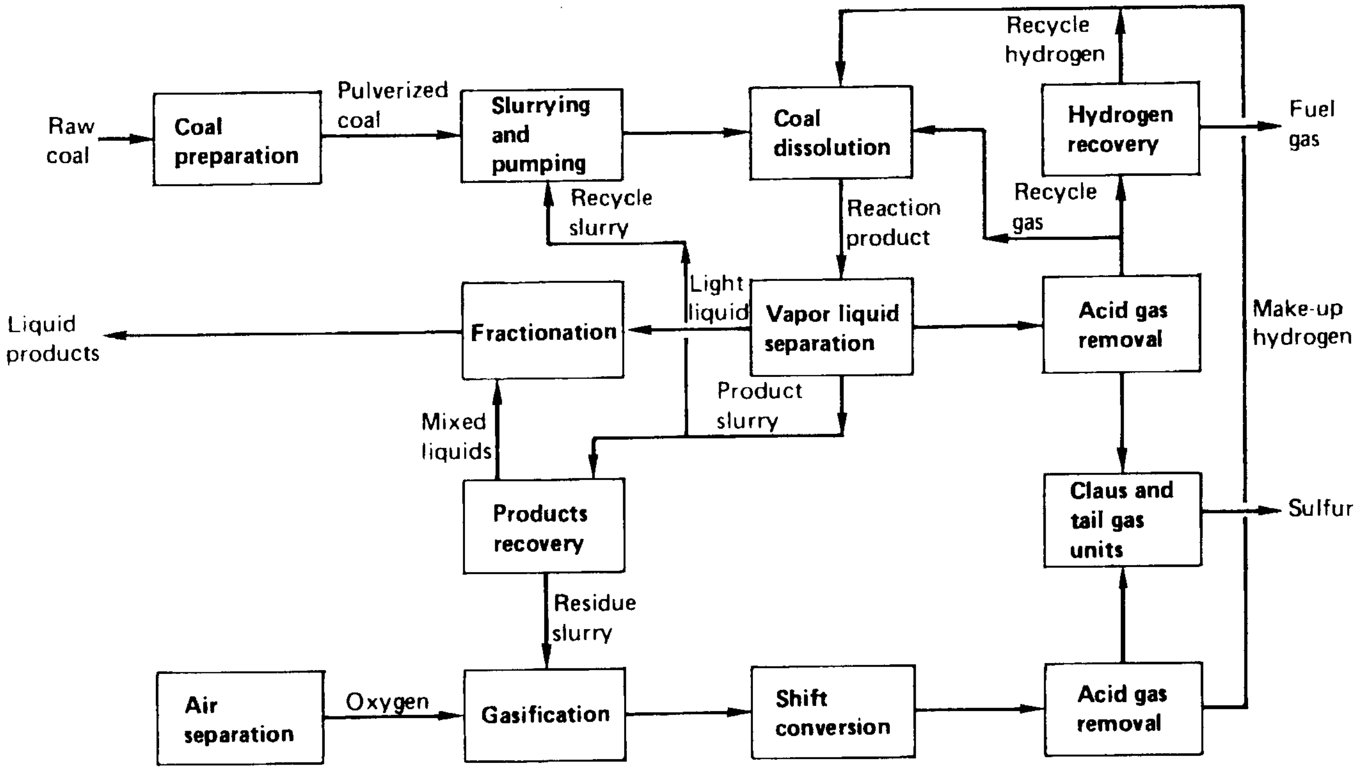

Figure 9 SRC-II process, with catalysts (Sullivan et al., 1979; Synthetic Fuels, 1979)

Table 11 Properties of Arab Light crude

Gravity, °API	34.7
Hydrogen/carbon ratio	1.79
Composition	
Hydrogen, wt %	12.8
Oxygen, ppm	40
Nitrogen, ppm	770
Sulfur, wt %	1.70
Aromatic carbon, wt %	13
Distillation fractions, wt %	
Naphtha, C_5-400°F	26.6
Atmospheric gas oil, 400-650°F	24.9
Vacuum gas oil, 650-1000°F	27.9
Vacuum residue, 1000°F	20.6
Total	100.0

In the past, solvent-refining processes like SRC-I and SRC-II were thought to be noncatalytic, but recent work has shown that the ash of the coal has a degree of catalytic activity that plays an important role in the liquefaction process. The catalytic activity of the ash varies from coal to coal.

SOLVENT PROCESSES INVOLVING THE ADDITION OF CATALYSTS

Although some coal liquefaction processes rely on the catalytic activity of the coal ash alone, this activity is weak. In many of the coal liquefaction processes developed, additional catalytic material is added from an external source.

External catalytic material is generally supplied in one of two ways: (a) by adding the catalyst to the reactor in which the solvent is being hydrogenated prior to its transfer to the coal liquefaction reactor, as in the Exxon Donor Solvent process (Fant, 1978; Epperly, 1978, 1979) or (b) by adding the catalyst to the coal in the liquefaction reactor in the presence of hydrogen, as in the H-Coal process (Stein _et al._, 1977, 1978; Hydrocarbon Research, 1978).

Exxon Donor Solvent (EDS) Process

Figure 10 is the flow diagram from a design study made for a commercial EDS plant. The solvent (a 400-850°F boiling range material) is hydrogenated in the presence of a catalyst and then mixed with the coal to form a slurry that is fed to a liquefaction reactor maintained at a temperature of 800-850°F and a pressure of 1500-2000 psi.

The only catalyst present in the liquefaction reactor is that which is naturally present in the coal ash. The product of this reactor is a slurry of solvent, liquefaction products, unconverted coal, and ash that is then separated by distillation into gas, naphtha, distillates, and a vacuum bottom slurry. The latter is fed to a flexicoker, which contains a coking and gasifying unit. If syngas were produced in the gasifier, it could be used to make hydrogen. In the design shown here, the gasifier produces fuel gas, and the hydrogen required is obtained by the steam reforming of the gas from the distillation unit.

Much of the information for this design was developed from the recycle coal liquefaction unit shown in Figure 11. The properties of its major products (A, B, and C) are given in Table 12. The naphtha stream, with an H/C ratio of 1.85 and a hydrogen content of 13.32 percent by weight, is within the range required for high-grade transportation fuels (Figure 7). However, examination of the flow diagram of the proposed plant, shown in Figure 10, suggests that the naphtha fraction produced should contain less hydrogen than is obtained from the pilot unit, since some of the streams in the commercial plant receive less hydrogenation than the product from the pilot plant. The 1.36 H/C ratio of the 400-700°F solvent of Table 12 also indicates that some further hydrogenation will be required to bring its H/C ratio up to the range of conventional petroleum-derived fuels.

As can be seen from the table, the solvent is highly aromatic and will need to be hydrogenated considerably to produce diesel and jet fuels. Distillate fuels become highly naphthenic after hydrogenation, however, and naphthenic diesel and jet fuels have combustion qualities that may leave much to be desired.

The combined distillate streams from the liquefaction unit, solvent hydrogenation unit, and coker of the commercial EDS plant design of Figure 10 will have a lower H/C ratio and higher aromatic content than the hydrogenated solvent of the recycle unit of Figure 11 (Table 12), because of the differences in the extent of hydrogenation between the two flow schemes. Figure 7 shows how the EDS products compare with the products of other processes. This figure also shows the hydrogen/carbon ratio of the liquid products from a typical coker pilot run with vacuum bottoms.

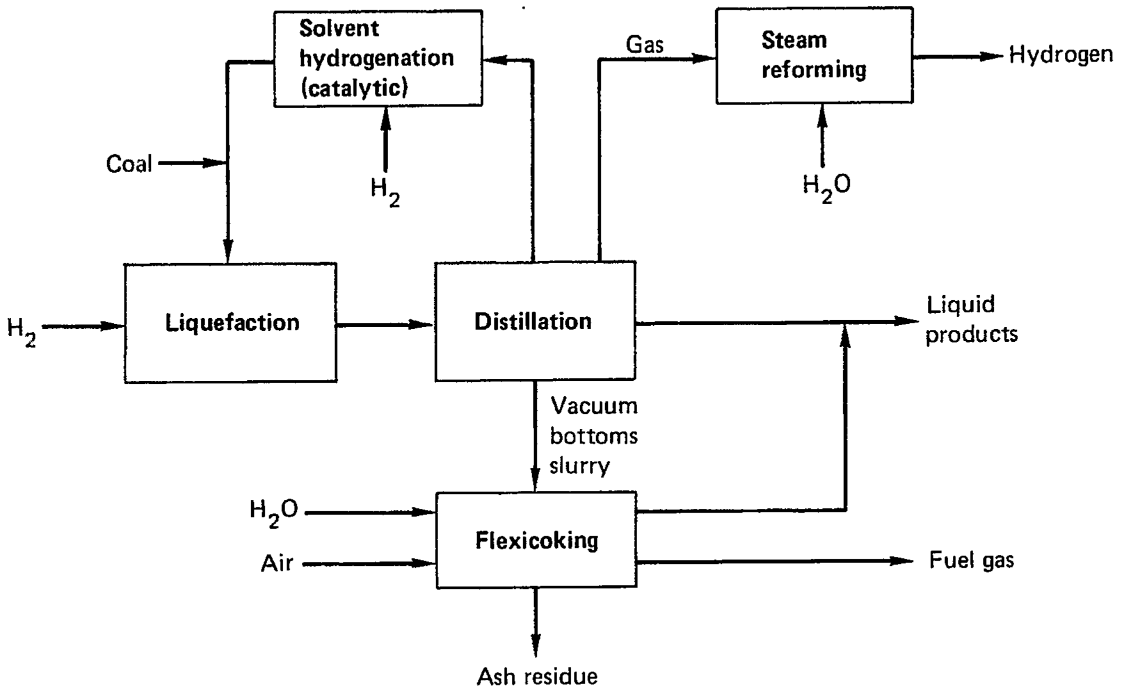

Figure 10 Flow design of commercial coal liquefaction plant based on Exxon Donor Solvent process

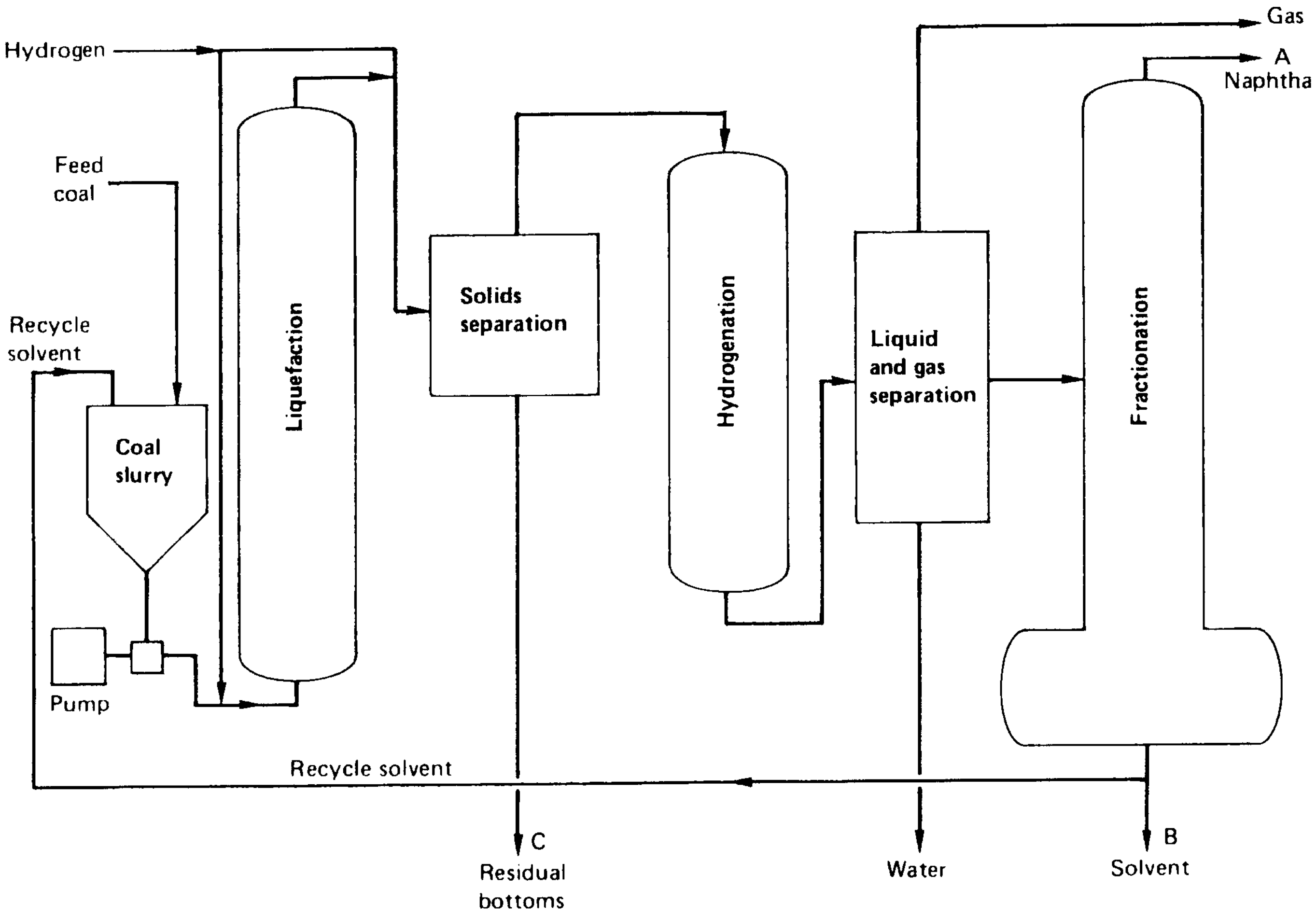

Figure 11 Recycle coal liquefaction process (Epperly, 1979)

Table 12 Properties of coal feed and sample products from Exxon Donor Solvent (EDS) Process (Illinois No. 6 coal)

	Coal (dry basis)	Naphtha C_5-400°F (A)	Solvent 400-700°F (B)	Residual Bottoms (C)
Gravity, °API		42.1	15.7	--
Hydrogen/carbon ratio	0.89	1.85	1.36	0.74
Composition, wt %				
Hydrogen	4.98	13.32	10.18	4.22
Sulfur	4.39	0.012	0.004	2.18
Nitrogen	11.15	0.01	0.04	1.36
Oxygen	15.89	0.46	0.22	12.46
Ash	12.00	--	--	20.61
Aromatic carbon	--	19	53	--
Distillation temperatures, °F				
5%		158	397	89% 1000°F+
15%		206	407	
25%		226	434	
50%		310	501	
75%		362	582	
95%		382	727	

Source: Epperly (1978).

H-Coal Process

In the H-Coal process, the catalyst is added directly to the mixture of coal and solvent, so that the solvent is continuously hydrogenated in the presence of the dissolving coal. A flow diagram of this process is given in Figure 12.

The coal-slurry and hydrogen streams are introduced at the bottom of the ebullating-bed reactor and maintained in a fluidized ebullating state by using a pump to recirculate the liquids. The heat transfer that results from this action keeps the temperature of the reactor contents essentially uniform. The ebullation also aids in handling the solid coal and catalytic material in the reactor. Temperatures of the order of 850°F and pressures up to 3000 psi are used. The products are fractionated, and the vacuum tower bottoms (containing the 950°F+ product,

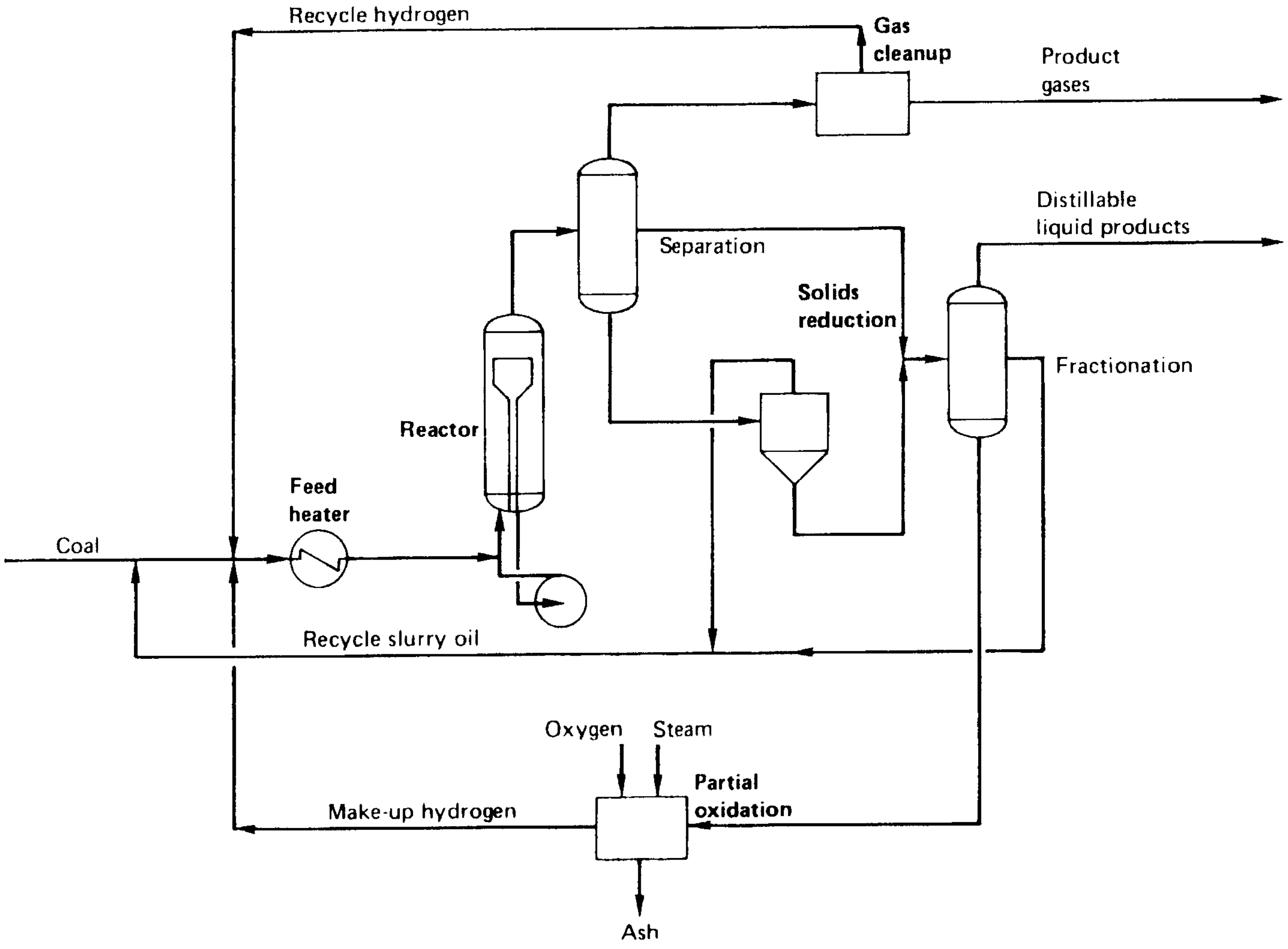

Figure 12 H-Coal liquefaction process (Hydrocarbon Research, 1978)

ash, and unconverted coal) are sent to a gasifier and shift reactor to generate hydrogen for the process.

Two modes of operation are envisioned: a fuel oil mode for the production of boiler fuels, and a syncrude mode to produce material suitable for refining to high quality transportation fuels. The latter is at present considered the more likely for commercial application. The properties and yields of products from the syncrude mode are shown in Table 13; other examples of yields are given in Table 10. Hydrogen/carbon ratios of products of the syncrude mode are approximately 1.28; aromatic carbon analyses show these products to be highly aromatic. Distillation studies show that the syncrude and fuel oil boil at temperatures below 950°F, and contain nothing that corresponds to the residuum of petroleum crude, seen in the Arab Light crude of Table 11. The reason for this is that the higher boiling fraction that corresponds to the residuum is gasified to produce hydrogen for the process. The naphtha from the syncrude mode is highly naphthenic and a good feed for the production of high-octane gasoline in a platinum reformer.

HYDROGEN PRODUCTION AND USE IN DIRECT LIQUEFACTION PROCESSES

In some versions of each of the direct liquefaction processes discussed above, gasification of part of the products (char, vacuum bottoms, etc.) is an essential part of the process, with gas used either as a fuel gas or as a source of hydrogen for the liquefaction and refining processes. In these processes, 30-40 percent of the energy content of the coal is used in the gasifier, with the amount depending on the type of process. When the syngas is used to produce hydrogen to hydrogenate the coal and coal liquefaction products, some of this energy becomes part of the energy of the hydrocarbon fractions, but a substantial energy loss and increase in cost still result.

Table 14 shows the three ways in which the external supply of hydrogen is used in the processes that require it. The added hydrogen (1) hydrogenates the coal and coal products to products containing more than three carbon atoms (C_4+ liquids); (2) produces hydrocarbon gases containing one to three carbon atoms (C_1-C_3 gases); and (3) converts the heteroatoms (S, N, and O) to H_2S, NH_3, and H_2O, permitting their removal from the product.

In Table 14, all the hydrogen in the coal is assumed to end up in the C_4+ liquid. Where a particular atom of hydrogen comes from (the hydrogen gas or the coal) or where it goes (into the gaseous or liquid product) is of course not ascertainable, but this method of accounting is adequate for an overall determination of hydrogen consumption. As seen from the table, essentially no net hydrogen is added to the C_4+ product in the SRC-I process. (In one case, 0.03 pounds per hundred pounds of coal is added, and in the other 0.16 pounds per hundred pounds of coal is lost.) The major portion of the hydrogen consumed goes to the production of C_1-C_3 gases, the balance going to the removal

Table 13 Properties and yields of H-Coal process, syncrude mode of operation (Illinois No. 6 coal)

	Coal feed (dry basis)	Product[a]
Properties		
Analysis, wt %		
Carbon	70.88	88.29
Hydrogen	4.91	9.43
Oxygen	8.57	1.76
Nitrogen	1.47	0.38
Sulfur	3.47	0.14
Ash	10.61	<0.01
Aromatic carbon	--	55
Hydrogen/carbon ratio	0.83	1.28
Kinematic viscosity at 100°F, cSt	--	4.20
Gravity, °API	--	14.1
Yields, wt % dry coal		
Waste gases		6.01
C_1-C_3 gases		10.63
C_4-C_6 gases		4.12
IBP-400°F Naphtha		14.21
400-650°F Distillates		22.26
650-975°F Distillates		6.48
975°F+ Residual oil		19.00
Unconverted coal		5.78
Ash		11.51
Total		100.00

[a] Properties of 350-975°F product; yields include total product yields.

Source: Stein, et al., 1977, 1978; Johanson and Comolli, 1978.

Table 14 Hydrogen use (on a moisture- and ash-free basis) in various coal liquefaction processes

	SRC I (Illinois No. 6)	SRC I (Kentucky No. 9)	SRC II (Kentucky No. 9)	EDS (Illinois No. 6)	H-Coal (Illinois No. 6)	
					Fuel oil	Syn-crude
Hydrogen in coal, pounds per 100 pounds of coal	5.73	5.58	5.58	5.66	5.34	5.35
Hydrogen in C_4+ liquid, pounds per 100 pounds	5.76	5.42	6.27	6.91	5.84	7.04
Hydrogen consumed, pounds per 100 pounds of coal	2.2	2.3	5.67	4.61	3.97	6.10
Net hydrogen consumed by C_4+ liquid, pounds per 100 pounds of hydrogen	0.03	-0.16	0.69	1.25	0.50	1.69
Hydrogen used in heteroatom removal, pounds per 100 pounds of coal	0.62	0.84	1.45	1.51	1.56	1.62
Hydrogen in C_1-C_3 gases, pounds per 100 pounds of coal	1.55	1.62	3.53	1.85	1.91	2.79

of heteroatoms. More of the hydrogen is added to the C_4+ liquids and more goes toward the removal of the heteroatoms in the SRC-II, EDS, and H-Coal processes.

When one examines how the use of hydrogen breaks down on a percentage basis (Table 15), it becomes apparent that a sizable portion of it (32-70 percent) goes into the production of the C_1-C_3 gases. While these gases are valuable products in themselves, they consume a disproportionate amount of relatively expensive hydrogen. Methane, for example, has an H/C ratio of 4, double that of the premium transportation fuels.

The cost of converting coal to transportation fuels could be lowered if the amount of hydrogen consumed in producing the C_1-C_3 gases could be reduced. Short-contact-time experiments on the mechanism of coal liquefaction (Whitehurst et al., 1976, 1977) show that a considerable reduction in gas production is possible.

Another way to reduce the hydrogen requirements of coal conversion processes is to modify end-use equipment to allow the use of fuels with lower H/C ratios. Since such fuels would be highly aromatic, they could be used in spark-ignition engines but might present problems in diesel engines.

DIRECT LIQUEFACTION PROCESSES WITH DECREASED HYDROGEN CONSUMPTION

As pointed out above, a short-contact-time (SCT) version of the SRC-I process can produce SRC liquids with a lower consumption of hydrogen. Lummus is developing a two-stage liquefaction process (Schindler, 1980) in which the product of an SCT unit is de-ashed and passed to an ebullating-bed LC-Fining unit for further conversion. The solvent is obtained from the LC-Fining product and recycled back to the SCT dissolver. Figure 13 is a flow diagram of this process. A comparison of the process' hydrogen consumption (Table 16) with those of other processes (Table 14) shows a substantial improvement.

Reduced hydrogen use has also been achieved in the Lummus Clean Fuels from Coal (CFFC) process (Long et al., 1979) by using a series of plug-flow expanded-bed reactors without any internal recycling (instead of continuous stirred-tank flow, as in H-Coal and LC-Fining). The results obtained with this process are also given in Table 16.

INDIRECT LIQUEFACTION PROCESSES

In the indirect processes, coal and water are first converted to a mixture of CO and H_2 ("syngas"), partial combustion of the coal supplying the heat required and additional CO. This gas is at a higher energy level than the produced hydrocarbons plus CO_2 or H_2O, and can be converted rather easily to hydrocarbons, oxygenated organic compounds, CO_2, and H_2O by a variety of processes, with the further release of

Table 15 Hydrogen use (on a percentage basis) in various coal liquefaction processes

	SRC I (Illinois No. 6)	SRC I (Kentucky No. 9)	SRC II (Kentucky No. 9)	EDS (Illinois No. 6)	H-Coal (Illinois No. 6)	
					Fuel oil	Syncrude
Hydrogen consumed, pounds per 100 pounds of coal	2.2	2.3	5.67	4.61	3.97	6.10
Hydrogen in C_4+ liquid, wt %	1.6	-6.9	12.2	27.1	12.6	27.3
Hydrogen in C_1-C_3 gas	70.4	70.4	62.2	40.1	48.1	45.7
Hydrogen used in heteroatom removal, wt %	28.2	36.5	25.6	32.8	39.3	26.6

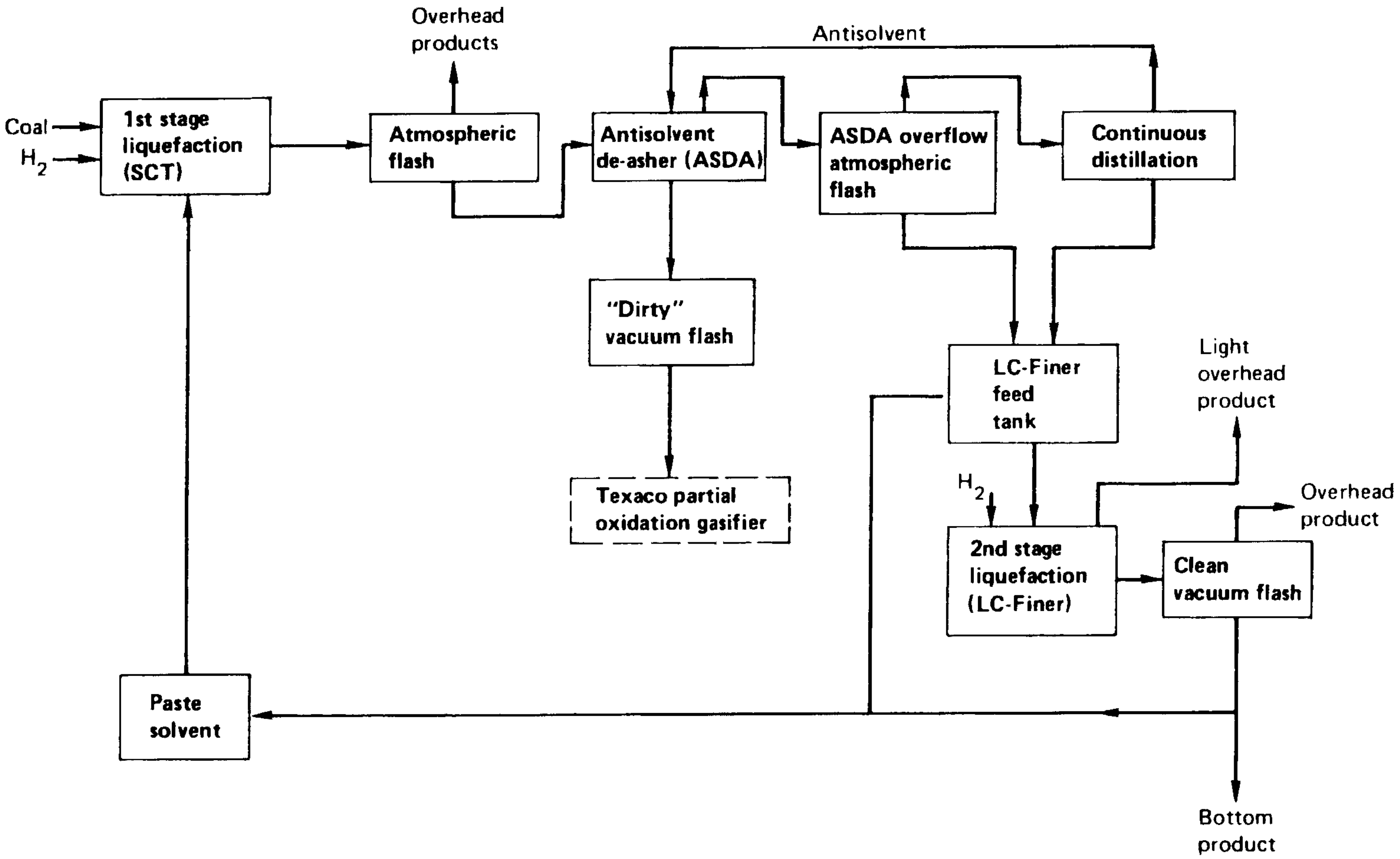

Figure 13 Lummus Two-Stage Coal Liquefaction process (Schindler, 1980)

Table 16 Hydrogen use in two Lummus direct liquefaction processes

Process	Hydrogen use, in pounds per 100 pounds of coal			
	Consumed	In CH_4+ liquid	In C_1-C_3 gas	For hetero-atom removal
Lummus Clean Fuels from Coal process (Illinois No. 6 coal)	3.4	1.24	1.09	1.07
Lummus Two-Stage Liquefaction process (Indiana V coal)	4.4	2.3	0.74	1.36

Source: Long _et al._ (1979); Schindler (1980).

heat. During production of the syngas, the heteroatoms that are not removed with the ash are converted into gases that can be removed from the syngas relatively easily, leaving it free of the sulfur and nitrogen that cause so much trouble in the refining of coal liquids by direct processes. Figure 14 is a flow diagram of a typical syngas plant with a Lurgi gasifier, in which only part of the new gas needs to be shifted to produce the H_2/CO ratio needed for each process.

The Fischer-Tropsch process used by SASOL in South Africa (Schreiner, 1978) converts the syngas into a complex mixture of hydrocarbons and oxygen-containing compounds that must be refined further to produce the end products required (fuels and chemicals). Table 17 shows the distribution of products from the SASOL plant.

The flow diagram of a typical Fischer-Tropsch plant is shown in Figure 15. In this plant, the reactor operates with a fluidized catalyst. The hydrocarbon products are mostly straight-chain olefins and paraffins, with almost no aromatics. Good diesel fuels are easier to produce from these products than from the highly aromatic products of direct liquefaction, but the use of the Fischer-Tropsch process for producing high octane gasoline presents problems due to the aliphatic nature of the product.

The production of gasoline from coal by the intermediate production of methanol is a simpler process. A flow diagram for such a plant is shown in Figure 16. The syngas is converted to methanol (CH_3OH) in a fixed catalyst bed, and the methanol is converted to high-octane gaso-

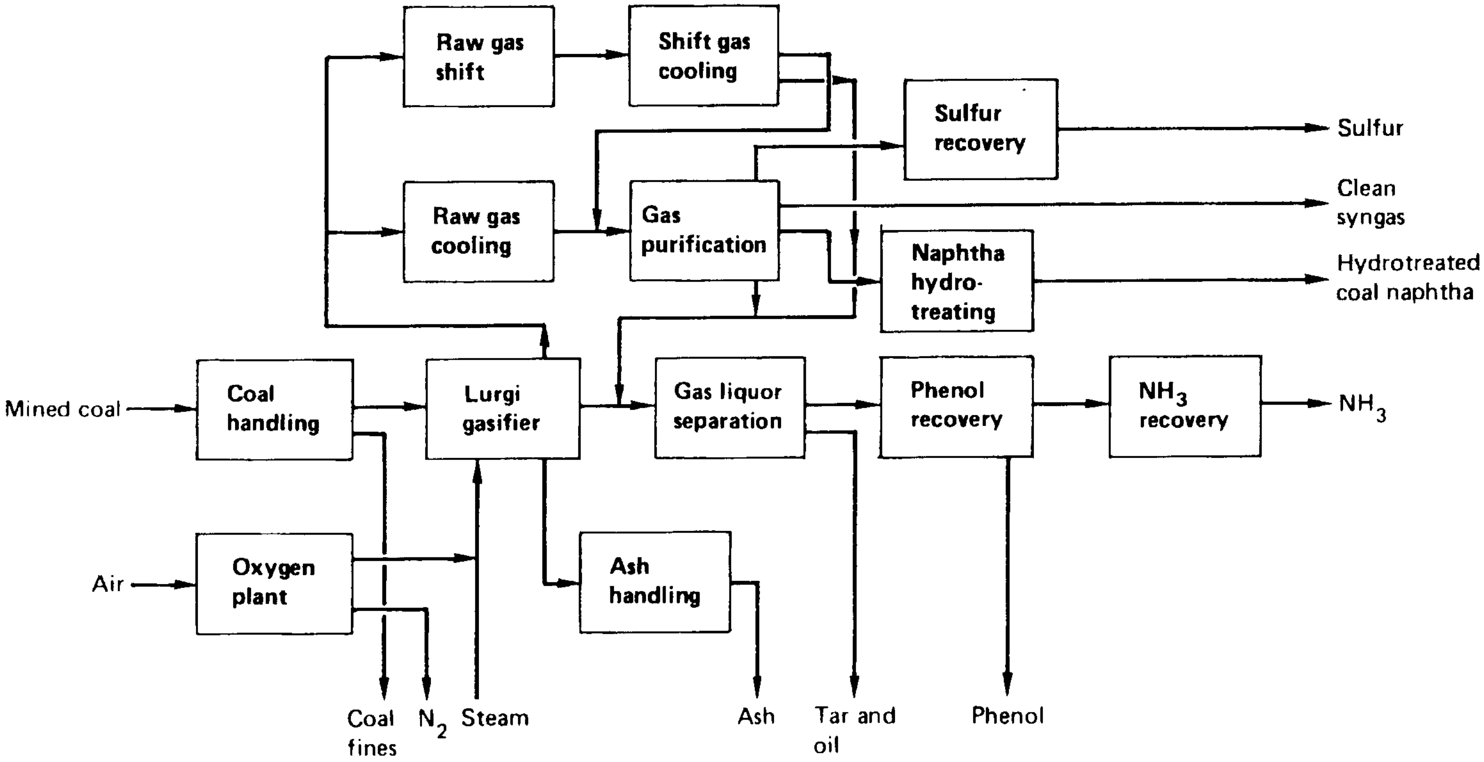

Figure 14 Typical coal gasification process, with Lurgi gasifier (Schreiner, 1978)

Table 17 Product yield of Fischer-Tropsch process

Component	Yield (Percent by weight)
Methane	10.7
Ethylene	3.7
Ethane	6.0
Propylene	11.6
Propane	2.0
Butylene	8.3
Butane	1.1
C_5-400°F	31.9
400-1000°F	13.4
1000°+F	0.6
Subtotal	89.3
Non-acid oxygenates	8.8
Organic acids	1.9
Total	100.0

Source: Hoogendoorn (1973).

line in a single step over a zeolite catalyst. To supply the hydrogen needed for hydrotreating the naphtha obtained from the gasifier, some of the gas is passed to a hydrogen recovery section. The first plant to produce gasoline by this process, to be built in New Zealand, is scheduled to go into production by the mid-1980s. In the methanol-to-gasoline step, the methanol is converted to water, gasoline, LPG, and a small amount of fuel gas. Essentially no materials with boiling points above that of gasoline are produced. Product properties and typical yields are given in Table 18.

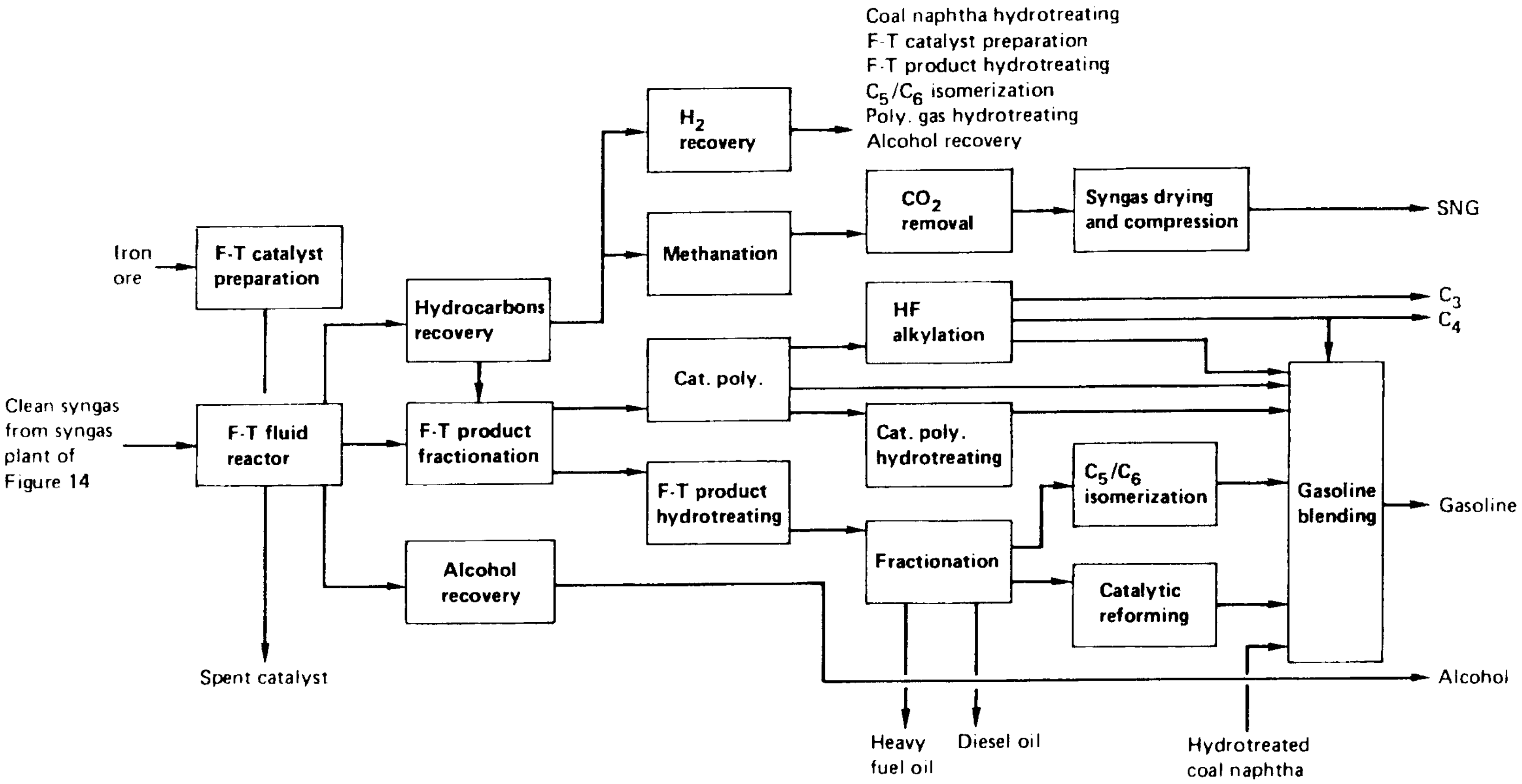

Figure 15 Typical Fischer-Tropsch process (Schreiner, 1978)

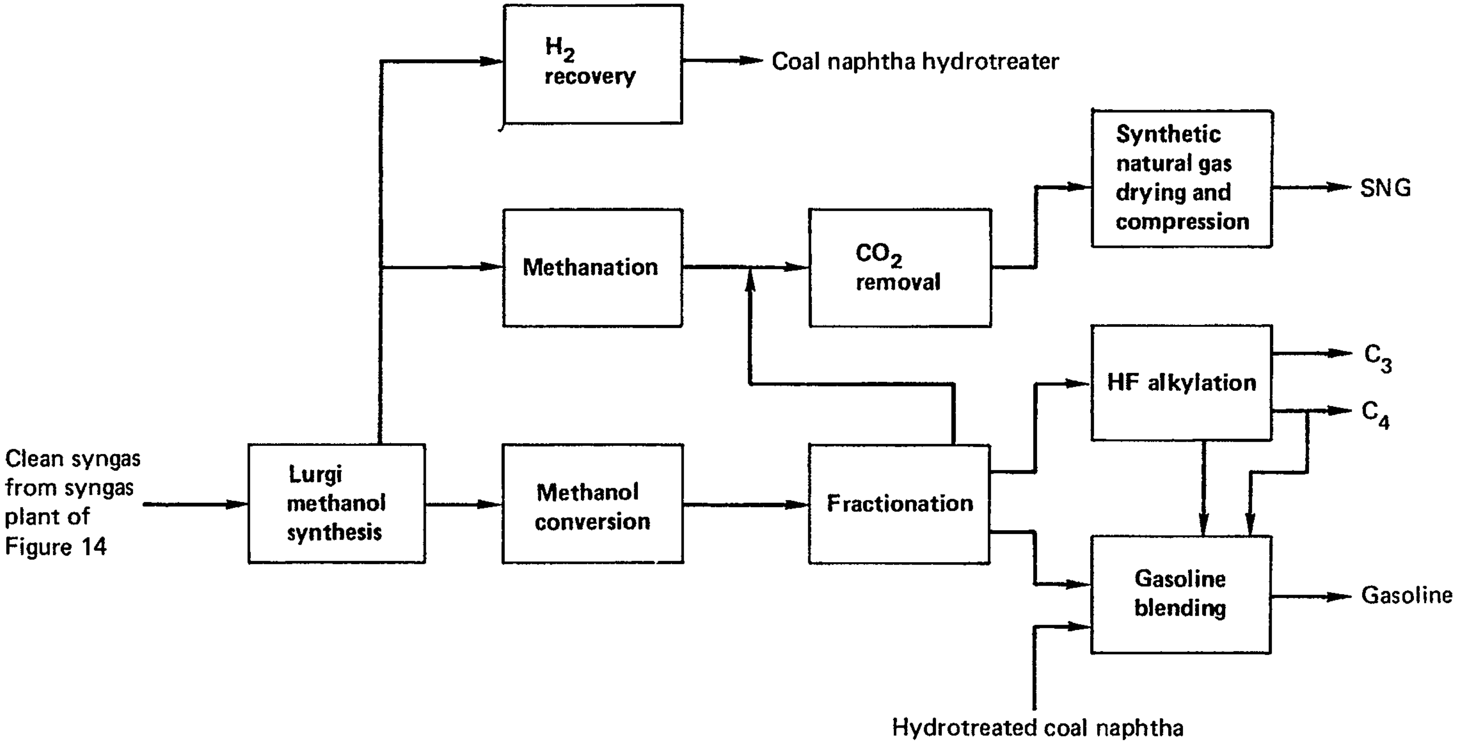

Figure 16 Flow design for methanol-to-gasoline plant (Schreiner, 1978)

Table 18 Typical product yields and properties of methanol-to-gasoline process, using methanol with 17 percent H_2O

Yield, wt % of methanol charged	
Hydrocarbons	43.6
Water	55.9
Hydrocarbon product composition, wt %	
C_1-C_2	1.4
C_3-C_4	18.7
C_5+ gasoline	79.9
Total	100.0
Finished product, wt %	
Gasoline, including alkylate	85.0
Liquefied petroleum gas	13.6
Fuel gas	1.4
Total	100.0
Physical properties of gasoline	
Research octane	
Clear	93
Leaded[a]	101
Reid vapor pressure, psig	9.0
Specific gravity	0.728
Sulfur, wt %	nil
Nitrogen, wt %	nil
Corrosion, copper strip	1A
Distillation temperatures, °F (ASTM)	
10%	114
30%	145
50%	198
90%	330
Composition, vol %	
Paraffins	53
Olefins	12
Naphthenes	7
Aromatics	28
Total	100
Motor octane	
Clear	83
Leaded[a]	90

[a] 3 cc tetraethyl lead per U.S. gallon.

Source: Schreiner (1978).

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5 OIL SHALE EXTRACTION PROCESSES AND PRODUCTS

Oil shale is a layered gray-brown sedimentary rock known as marlstone, formed millions of years ago in freshwater lakes. The oil in the shale is in kerogen, a complex material composed mainly of carbon, hydrogen, oxygen, sulfur, and nitrogen. The large kerogen molecules are bound to each other by oxygen, sulfur, and hydrocarbon bridges in a three-dimensional network that extends through the mineral portions of the shale, binding them together. The amount of kerogen in a given deposit depends on how much organic material was present in the lake beds.

The oil content of shale denotes its quality. Shale with an oil content of 10 gallons per ton (about 4 percent by weight) is considered low-grade shale. Shale with an oil content of 26 gallons per ton (about 10 percent) is considered medium grade, and shale with an oil content of 36 gallons per ton (about 14 percent) is considered high grade.

In considering the ultimate use of shale oil, it is necessary to understand the retorting processes for decomposing and separating the kerogen from the rock. The shale can be retorted either *in situ* underground, or after it is mined and brought to the surface.

It is highly desirable that both types of retorting be developed, since their combined use will lead to optimal resource recovery. A preference of one over the other is not indicated or intended in this report. Neither has yet been demonstrated on a full commercial scale, although the probability of success for both is high.

This chapter deals with the retorting processes that have been brought to the point at which they are being considered for eventual commercialization. The first section of the chapter covers surface retorting, the second section covers *in situ* retorting, and the third section deals with the physical and chemical properties of the raw liquids produced by these processes.

SURFACE RETORTING PROCESSES

Lurgi-Ruhrgas Process

The Lurgi-Ruhrgas (LR) process "distills" hydrocarbons from oil shale by bringing raw shale in contact with hot fine-grained solid heat carriers. The best heat carrier is the spent shale, but rich shales, which deteriorate into a fine powder, must be supplemented by more durable materials such as sand.

In the LR process (Figure 17), the pulverized oil shale and heat carrier are brought into contact in a mechanical mixer such as a screw conveyor. In pilot plant tests, the shale was first crushed to a maximum size of one-fourth to one-third of an inch, but larger commercial units might process particles as large as half an inch (Rammler, 1970). The gas and oil vapors are then cleaned of dust in a hot cyclone; the dust is recycled and the oil is separated by condensation. Retorted shale from the mixer passes through a hopper to the bottom of a lift pipe, with the dust from the cyclone. Preheated air introduced at the bottom of the pipe carries the solids up to the surge bin, during which time they are heated by the combustion of the residual carbon in the shale to about 1,000°F. (If the residual carbon is insufficient for this, fuel gas is added.) In the surge bin, the hot solids separate from the combustion gases and return to the mixer, where they are brought in contact with new oil shale, completing the cycle.

Pilot plant tests have produced high yields. Oil recovery greater than 100 percent Fischer assay has been achieved from Colorado shale with an oil content of about 30 gallons per ton. (The Fischer assay procedure is a rigidly defined test, the results of which serve as a baseline for comparing different extraction processes.) Since no combustion occurs in the mixer retort in this process, the product gas from the mixer has a high calorific value.

As the LR process can handle very small particle sizes, it can be modified for a variety of shale feedstocks. The system is also mechanically simple; only the mixer is of concern because it must operate reliably in a harsh environment. Two serious problems result from the movement of dust through the system, however. One is the accumulation of combustible dust in the transfer lines, increasing the likelihood of fires and plugging. The other is entrainment of dust in the oil produced; most of the dust is removed in the hot cyclone, but some is inevitably carried over in the retort product.

There are ways of dealing with the latter problem. When the crude oil from the LR process is fractionated, the dust concentrates in the heaviest fraction, and can be dealt with by diluting and filtering this fraction or by recycling it to the mixer.

The LR process, developed in the 1950s for the low-temperature flash-carbonization of coal, has been tested on European and Colorado oil shale

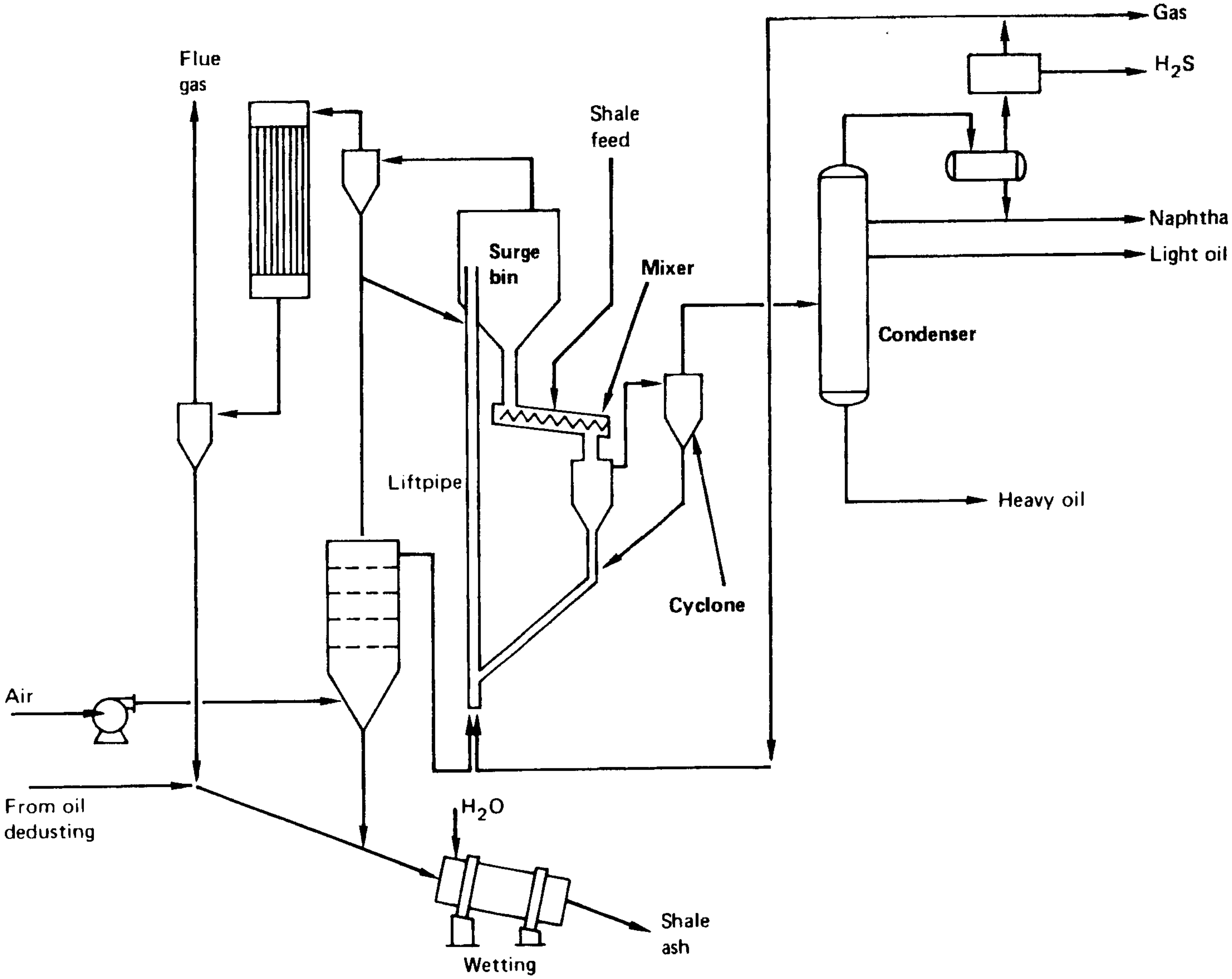

Figure 17 Lurgi-Ruhrgas process for producing hydrocarbons from oil shale (Cameron Engineers, 1975; Sladek, 1975)

in a 20-ton-per-day pilot plant at Herten, Germany; this plant has since been disassembled, but a 2- to 5-ton-per-day unit is still in operation near Essen, Germany. Two 850-ton-per-day plants for carbonizing brown coal were installed in Yugoslavia in 1963, and a large plant that uses the LR process to produce olefins by cracking light oils has been built in Japan (Rammler, 1969, 1970).

Superior's Multi-Mineral Process

The multi-mineral process is a four-step operation that produces four coproducts: nahcolite, (sodium bicarbonate, $NaHCO_3$), shale oil, alumina, and soda ash (Figure 18). The process was developed by Superior Oil for shale that contains recoverable concentrations of oil, nahcolite, and dawsonite (a sodium-aluminum salt, $Na_3Al(CO_3)_3 \cdot Al(OH)_3$). Superior has operated a pilot plant of this type in Cleveland, Ohio.

The underground shale in Superior's property is mined in panels by the room and pillar method and delivered to the surface by conveyor. After processing, the spent shale is returned to the mined-out panels to stabilize the pillars.

The nahcolite is in the form of discrete nodules that are more brittle than the shale. It is recovered by secondary crushing and screening, followed by a specialized process called "photosorting" that recovers nahcolite product of greater than 80 percent purity. After the nahcolite is removed, the shale is pyrolyzed using the McDowell-Wellman process. The unique continuous-feed, circular-moving-grate retort used in this process is a proven, reliable piece of hardware that provides accurate temperature control, separate process zones, and a water seal that eliminates environmental contamination.

The dawsonite in the shale is decomposed in the retort to aluminum oxide and soda ash. After the shale has been leached with recycled liquor and makeup water from the saline subsurface aquifer, the liquid is seeded and the pH lowered to recover the alumina. The soda ash is recovered by evaporation. The leached spent shale is then returned to the mine and the liquor is returned to the process.

Paraho Process

The Paraho retort is a stationary, vertical, cylindrical kiln of mild steel, refractory-lined, in which the shale is brought to temperature by a counterflow of combustion gases (Figure 19). As the shale (fed in at the top along a rotating "pantsleg" distributor) moves down through the retort, the rising stream of hot gas breaks down the kerogen to oil, gas, and residual carbon. The oil and gas are drawn off, and the residual carbon burns in the mixture of air and recycled gas. By injecting part of the gas-air mixture through the bottom of the kiln, much of the sensible heat in the spent shale is recovered. The temperature in the

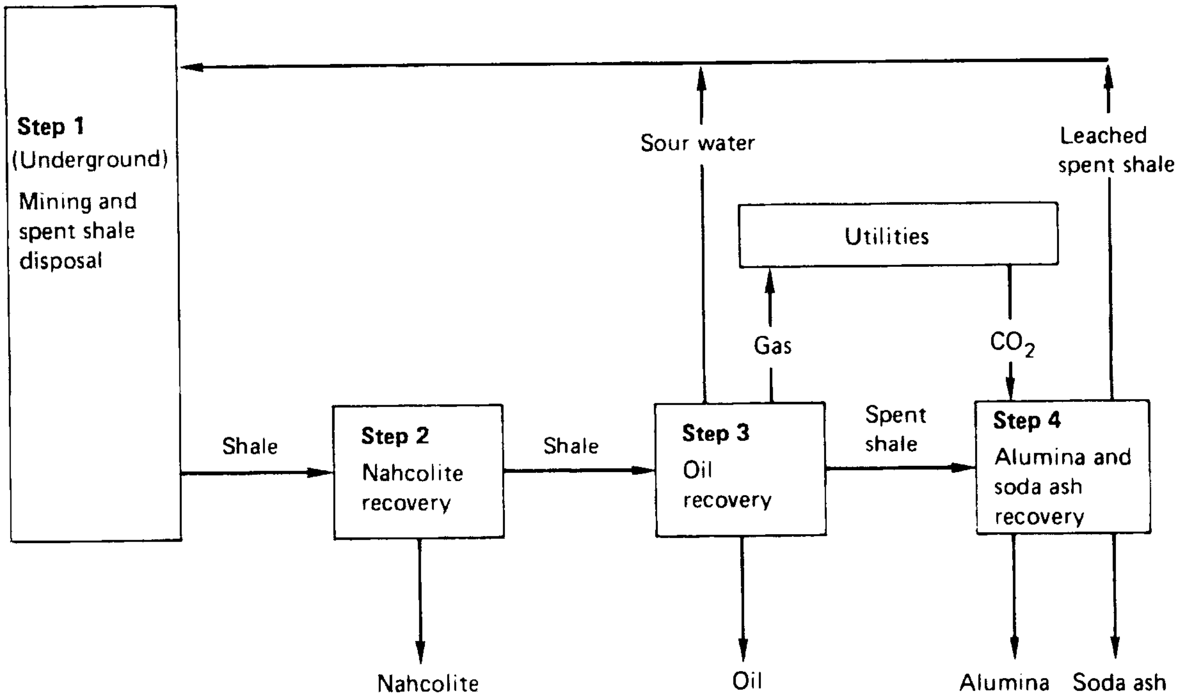

Figure 18 Superior Oil multi-mineral process (Superior Oil, 1977)

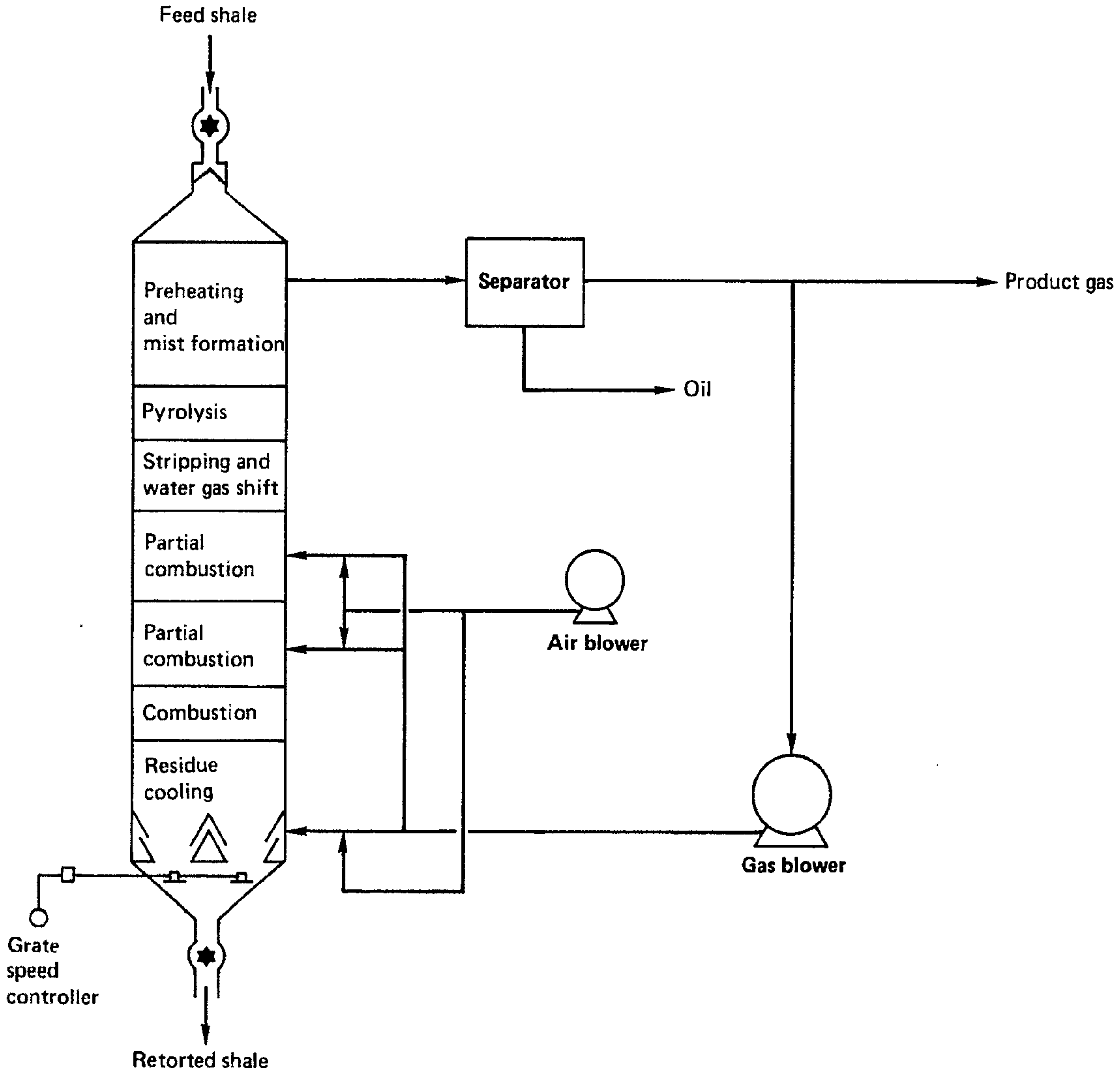

Figure 19 Paraho process for extracting shale oil (Cameron Engineers, 1975)

retort is controlled by adjusting the compositions of the gas-air mixtures to the preheat and combustion zones.

The Paraho process, developed by Development Engineering Incorporated (DEI), is conceptually similar to the internal-combustion retorting process used by the Bureau of Mines, but there are significant differences in the shale-feed mechanism, the combustion gas distributors, and the spent shale discharge grate. It is possible with this process to use either direct or indirect heating. Most of the development work so far has been carried out with the direct heating system described here.

Research and development on the Paraho retort, begun by Paraho Development Corporation (DEI's parent company) in August 1973, continued until April 1976 under the sponsorship of 17 energy and engineering companies. In 1978, Paraho delivered 100,000 barrels of raw shale oil to the U.S. Navy for defense testing purposes.

The Paraho kiln has most of the advantages common to internal-combustion retorts. It can handle shale with a feed size of at least 3 inches, keeping crushing and screening costs at a minimum. A high thermal efficiency results from burning the residual carbon and recovering sensible heat from the spent shale. The process is mechanically simple, requiring little auxiliary equipment. No water is required for product cooling. To date, more than 100 days of continuous operation have been achieved, with oil recoveries of better than 90 percent of Fischer assay.

Tosco II Process

The Tosco II process[a] uses ceramic balls to heat the oil shale. The shale, crushed to less than half an inch in size, is introduced through multiple lift pipes in which streams of hot gas elevate and preheat it to about 500°F (Figure 20). The shale is then fed to a rotating drum with half-inch ceramic balls that have been heated to about 1200°F. Inside the rotating drum, which is about 8 feet in diameter and 15 feet long, the balls turn the kerogen in the shale to oil vapor and gas and crush the shale to a fine black powder. The balls and crushed shale, now at about 950°F, are fed to a perforated rotating drum (trommel) in which the shale and the ceramic balls are separated. The spent shale drops through the holes in the drum, is cooled, and is then disposed of. The balls return to the ball heater, where they are reheated with gas from the shale, completing the cycle.

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[a] This process is a refinement of the Aspeco Process developed by the Swedish inventor Olaf Aspegren. Although Aspegren patented the concept, he did not reduce it to practice (Aspegren, 1952). The Oil Shale Corporation (Tosco) purchased the patent rights in 1952.

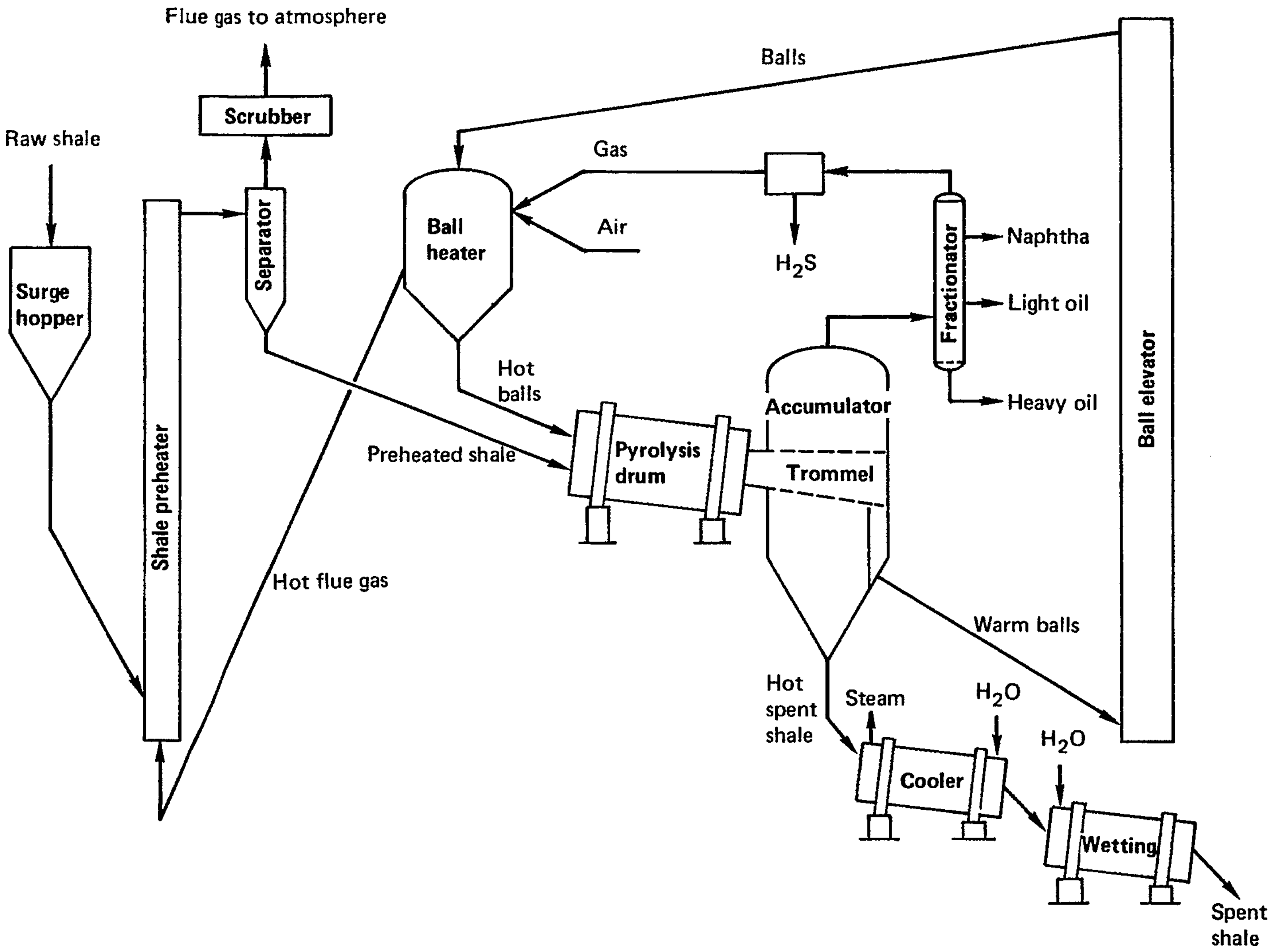

Figure 20 Tosco II process for extracting shale oil (Cameron Engineers, 1975; Sladek, 1975)

Oil yields from the Tosco II process are high. Liquid hydrocarbon recovery is about 99 percent of Fischer assay and total recovery of C_4 and heavier hydrocarbons is about 108 percent of Fischer assay (Hendrickson, 1974). The retort gas has a heating value similar to that of Fischer assay gas, since there is no combustion in the pyrolysis drum; most of the gas is used in the ball heater.

Field operations using a retort with a shale feed rate of about 1000 tons per day were carried out in Colorado during 1967-69 and 1971-72.

Union Oil Retorting Processes

Union Oil, active in retort research and development since the late 1940s, has three designs: the "A" retort, in which the internal combustion of the gas and residual carbon from the shale provide the heat for the process (direct heating); the "B" design, in which the shale is heated indirectly by a recycled stream of externally heated gas (Figure 21); and the Steam-Gas Recirculation (SGR) retort, in which the heat carrier for the process is generated in a separate vessel by gasifying the residual carbon with air and steam.

Union's retorts have been characterized as "continuous, underfeed, countercurrent retorts" (Hartley, 1958). In all three, the shale is introduced at the base, travels upward through the retort, and is discharged at the top. The gaseous heat carrier (air, recycle gas, or syngas) enters at the top and exits from the bottom. The product oil flows down through the moving bed of shale to a pool at the bottom of the retort and is withdrawn from the top of that pool. Serving as a seal, the pool prevents air from leaking into the retort and also acts as a settling basin for the entrained fines.

A unique design feature of the Union retorts is the "rock pump" that pushes shale up through the retort. In an early patent (Berg, 1947), the rock pump was mechanical, providing motion to the shale bed through a series of gears and cams. The modern hydraulic rock pumps have large feed cylinders that take the crushed shale from the feed chutes and pump it into the retort.

In the "A" process, the thermal efficiency is high because sensible heat is recovered from the oil, gas, and spent shale. The oil recovery is about 84 percent of Fischer assay, but the product gas is a low-energy fuel (with a heating value of about 100 Btu per standard cubic foot) due to its dilution by combustion products. In the early tests, the high temperatures caused the agglomeration of the spent shale ash, requiring the use of hollow sodium-cooled "plows" to break up the clinkers. Better temperature control in later designs has made the plows unnecessary.

In the "B" process, the product gas exiting from the bottom of the retort is divided into two streams; one stream, burned in a heater with air, is used to preheat the second stream as the latter is recycled to

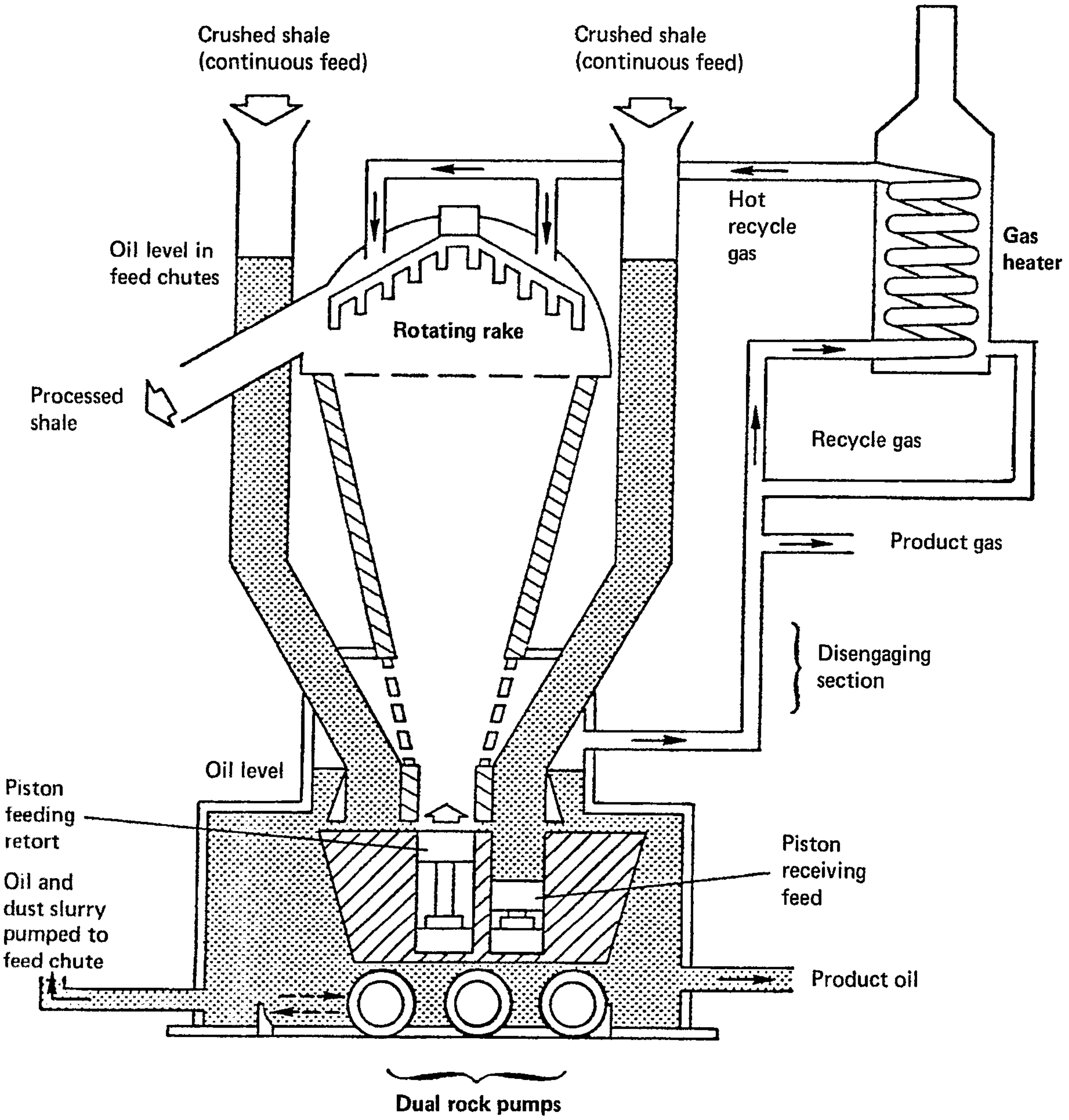

Figure 21 Union B process, showing indirect heating of shale (Duir, 1977; Hopkins, 1976)

the retort. The recycle stream and the product stream are not diluted by combustion products, as they are in the "A" process. The absence of combustion inside the retort offers other advantages. Temperature control is better and, as a result, there is no clinkering problem. In addition, the oil yields are higher than in the "A" process, reaching 100 percent of Fischer assay (Hartley, 1974).

Union's latest retort, the SGR, is basically a "B" retort with auxiliary equipment for recovering energy from the residual carbon by gasification.

Union's experience with the three processes has been as follows:

- The early development work on the "A" retort included the operation of a 2-ton-per-day prototype and a 50-ton-per-day pilot plant at Wilmington, California. Additional operating experience has been obtained from a semiworks unit near Grand Valley, Colorado, with a design capacity of about 350 tons per day. Production rates higher than this were achieved soon after startup in March 1957. By the time the field tests on the latter unit were completed in August 1958 the capacity had been increased, allowing continuous operation at rates of up to 1200 tons per day (Hartley and Hemmen, 1957; Hartley, 1958).

- Since 1971, a nominal 6-ton-per-day pilot retort has been operated in the "B" mode and the SGR mode at the Union Research Center in Brea, California.

IN SITU RETORTING PROCESSES

During the past 10 years, an increasing amount of research has been directed toward the production of oil from shale in situ, or underground.

Most oil shales have very little if any natural permeability,[a] and this makes it nearly impossible to recover oil from them in situ. Two techniques have been proposed for producing some permeability in such formations. With the modified in situ technique, part of the shale bed is removed to create a void that will allow fracturing the rest of the bed with explosives. With the true in situ technique, no mining or other void-producing preparation is required; the permeability is produced with well bores from the surface.

Occidental Petroleum Process

Occidental Petroleum Corporation is developing a vertical modified in situ process in which conventional explosives are used to expand solid

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[a] The main exception is a leached zone in the Piceance Creek Basin in Colorado.

blocks of shale into a vertical mined-out cavity, creating underground chimneys of fractured shale (Figure 22). After 10 to 25 percent of the shale in the chimney is removed, air is blown down through the remaining crushed shale and the top is ignited with a burner that can be fueled with shale oil or off-gas from other retorts. On ignition, the burner is withdrawn and steam is mixed with the inlet air to control the process. The liquid and gaseous products flow to the bottom of the chimney, leaving the carbon in the shale behind as the main source of fuel for the slowly advancing flame front.

Occidental Petroleum began a series of field tests on its modified in situ process at Logan's Wash in Debeque, Colorado, in 1972. Three retorts, 30 feet across and 72 feet deep, each containing 6,000 to 10,000 tons of oil shale, were created. The subsequent series of tests are being used as the basis for three commercial-scale retorts that are 30 to 40 times larger. Occidental Petroleum has also leased Colorado federal oil shale tract C-b for shale oil recovery with modified in situ technology on a commercial scale. Full-scale production of 57,000 barrels per day was originally planned for 1983, but plans now call for full-scale production in 1987.

LETC Process

The Department of Energy at its Laramie Energy Technology Center (LETC) is sponsoring several field projects to demonstrate the technical and economic feasibility of shale oil recovery by in situ methods. The projects include in-house research and joint government-industry efforts (Table 19).

LETC began its study of true in situ processes in the early 1960s with laboratory tests, simulated pilot-plant tests on 10-ton and 150-ton retorts, and field tests at Rock Springs, Wyoming. The results of the tests were encouraging, demonstrating that it was possible to move a self-sustaining combustion zone through an oil shale formation and produce oil. The technique appears, at this stage, to be more suitable than the other processes described so far for thin oil shale formations.

The underground shale is prepared for the LETC process by first boring injection and production wells into the shale (Figure 23) and then increasing the permeability of the formation by conventional fracturing techniques. (LETC tried electrolinking, well-bore shooting, and hydraulic fracturing, and found that the sequential use of hydraulic fracturing and explosives succeeded best.) Once the formation has been fractured, hot gases are forced into it to heat the area around the injection point. As the desired temperature is reached and air is substituted for the hot gas, combustion begins and becomes self-sustaining across a front that gradually moves through the bed. As retorting progresses, oil and gas products are pumped out through the production well.

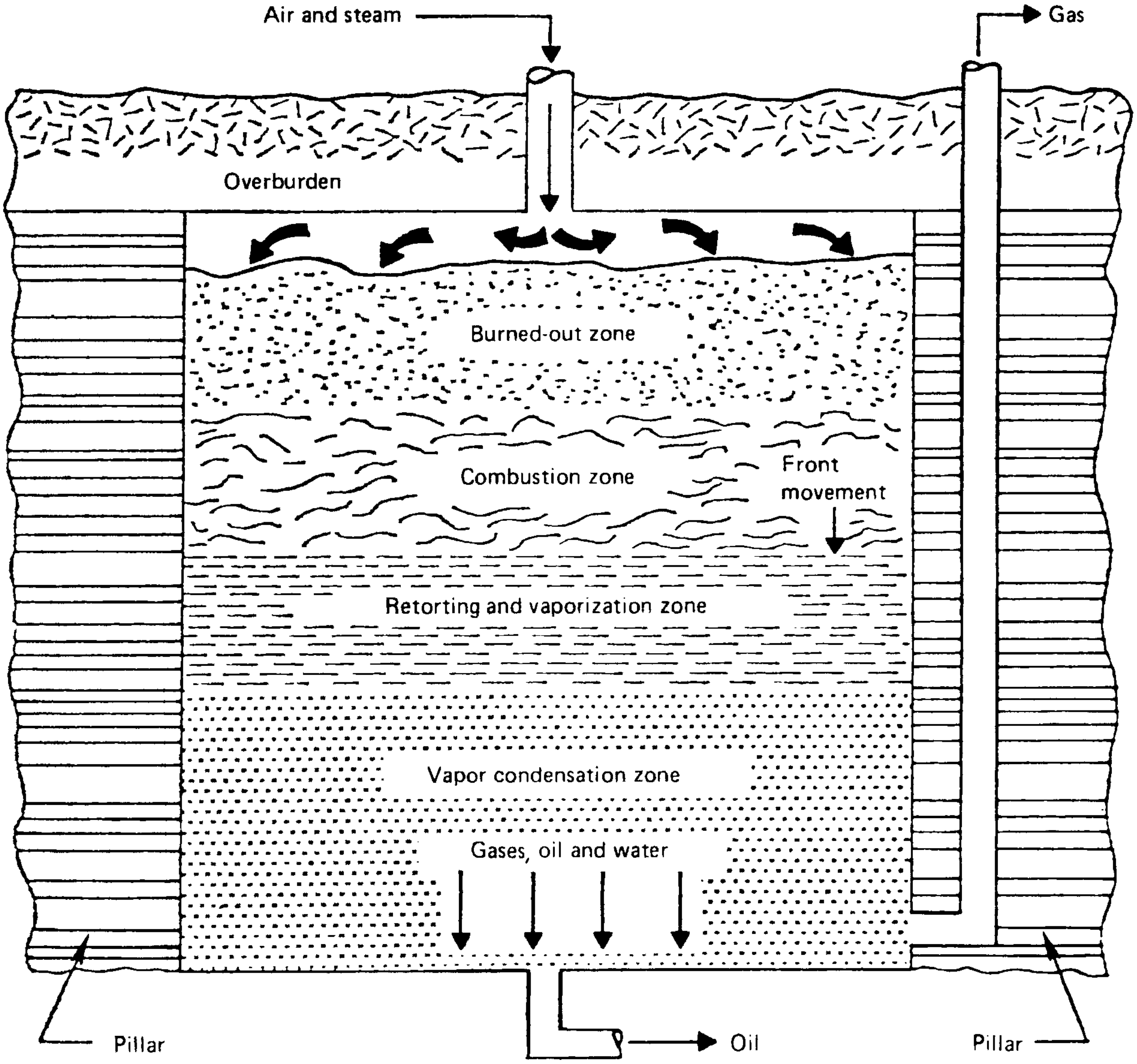

Figure 22 Modified <u>in situ</u> retort of Occidental Petroleum (McCarthy and Cha, 1976; Sass and Lumpkin, 1977)

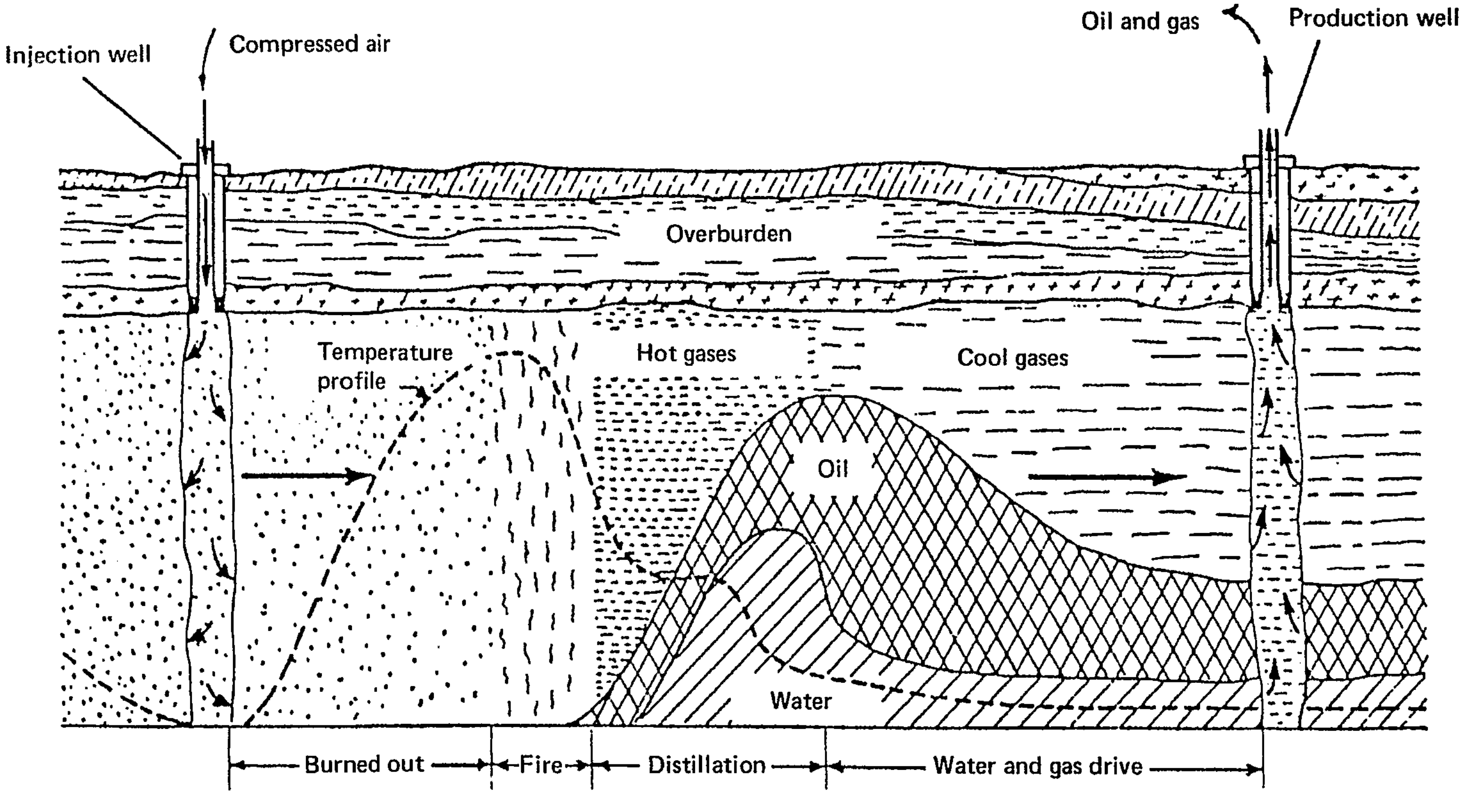

Figure 23 Laramie Energy Technical Center (LETC) in situ retorting process (Sladek, 1975)

Table 19 U.S. Department of Energy-industry cooperative oil shale projects

	Dow Chemical Company	Talley Energy Systems, Inc.
Resource site		
Location	75 miles NE of Detroit, Mich.	11 miles west of Rock Springs, Wyo.
Anticipated size, in acres	1	163
Status	Owned	Leased from Rocky Mountain Energy
Geological formation	Antrim oil shale	Green River Oil Shale
Member	Not applicable	Tipton
Zone	Not applicable	Upper
Age, years	260 million	50 million
Structural basin	Michigan	Green River
Target zone thickness, feet	200	40
Overburden above zone, feet	1200	360
Average oil content, gallons per ton	10	23
Average sulfur content, percent	3.5	0.7
Process		
Technology		
Category	True *in situ*	True *in situ*
Method	Explosive fracturing; additional hydraulic fracturing; no mining	Explosive fracturing; additional hydraulic fracturing; no mining
Special problems	Project depth; low hydrogen organics; sulfur content	Creating permeability in fissile shale
Special potentials	Shale gasification; very extensive resource	Shallow thin-seam recovery

Source: Dockter (1978).

(as of May 1, 1978)

Equity Oil Company	Geokinetics Inc.	Occidental Oil Company
53 miles north of Grand Junction, Colo.	61 miles NW of Grand Junction, Colo.	31 miles NE of Grand Junction, Colo.
4	640	3
Owned	Leased from Utah	Owned
Green River Oil Shale Parachute Creek Leached 50 million Piceance Creek	Green River Oil Shale Parachute Creek Mahogany 48 million Uinta	Green River Oil Shale Parachute Creek Mahogany 48 million Piceance Creek
550 800	30 0-100	300 400
28	25	16
0.7	0.7	0.7
Solution injection	Modified horizontal	Modified vertical
No explosives; no mining	Explosive fracturing; no mining	Explosive fracturing; limited mining
Saline aquifer; waste water disposal	Surface disturbance	Mined shale disposal
Utilizing natural porosity	Shallow thin-seam recovery	Deep thick-seam recovery

Lawrence Livermore Laboratory's RISE Process

The Lawrence Livermore Laboratory, administered by the University of California is working on a Rubble *In Situ* Extraction (RISE) process, a modified *in situ* process that has not yet been field-tested.

The process, shown in Figure 24, is conceived as essentially continuous; as one part of a formation (approximately 100 feet across and 1000 feet deep) is being retorted, adjacent sections are in various stages of preparation. To prepare a section for retorting, it would be blasted to loosen and break up the shale, and part of the rubble would be removed to the surface.

No field testing has yet been done, but large-scale tests to simulate below-ground processing, along with a variety of small-scale tests and mathematical modeling programs, have been carried out.

According to the Livermore Laboratory, the process could be used on much leaner deposits than those now being considered for above-ground retorting (e.g., deposits with an oil content of 20 gallons per ton, but rather deep shale formations would be required.

PHYSICAL AND CHEMICAL DATA ON RAW SHALE OIL FROM VARIOUS RETORTING PROCESSES

Table 20 lists the available physical and chemical properties of whole raw shale oil from different retorting processes, and Tables 21-23 present some fractional analyses that are helpful in understanding the concentrations of the types of compounds in these shale oils as a function of boiling range.

On examining the physical properties of raw shale oils, it can be seen that the principal variations are those in boiling range, pour point, and viscosity. In general, shale oils have a somewhat narrower boiling range than most petroleum crudes because they tend to contain less naphtha material (having boiling points below 400 °F) and less high-boiling-range material (having boiling points above 1000°F). As can be seen from Figure 25, the shale oil from the *in situ* retorting process of Occidental Petroleum tends to have a flatter distillation curve than the shale oils from the Paraho, Tosco, and Union surface retorting processes since it contains less naphtha and less heavy ends. According to Occidental, this is due to the mild coking the oil undergoes during retorting (McCarthy and Cha, 1976). The lower concentrations of naphtha and heavy ends in the *in situ* retorted oils also result in somewhat lower pour points, viscosities, and nitrogen contents.

The distillation curves of Figure 25 have been shown as bands, rather than lines, because slight changes in retorting conditions will produce variations in the boiling range. (The Lurgi curve is shown as a broken

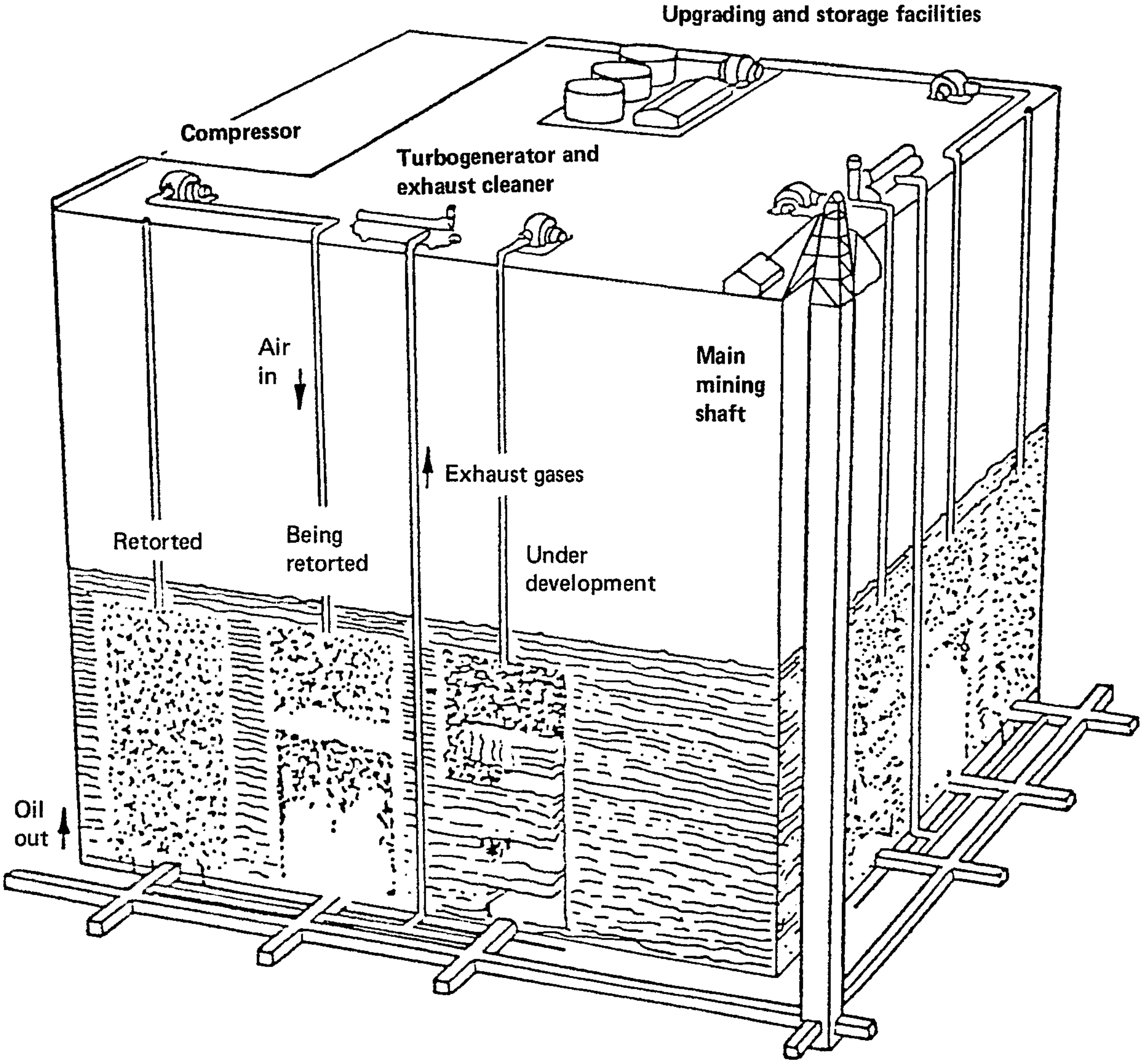

Figure 24 Lawrence Livermore Laboratory Rubble In Situ Extraction (RISE) process (Sladek, 1975)

Table 20 Physical and chemical properties of whole raw shale oils

	Union Oil A	Union Oil B							
							SGR-3[a]	SGR-3[a]	SGR-3[a]
Shale source	Colo	Colo	Colo	Colo	Utah	Utah	Colo	Colo	Utah
Grade, gallons per ton	--	--	28	28	32	32	--	36	33
Gravity, °API	18.6	22.7	22.8	21.2	21.4	20.2	21.5	22.2	22.8
Carbon, wt %	84.0	84.8	84.45	85.3	84.2	84.27	--	--	84.2
Hydrogen, wt %	12.0	11.61	11.55	11.15	11.7	11.68	--	--	11.4
Oxygen, wt %	0.9	0.9	0.94	1.12	1.51	1.23	--	0.9	--
Nitrogen, wt %									
Basic	--	--	--	1.04	--	1.26	--	--	--
Total	2.0	1.74	1.76	1.77	2.09	1.93	1.8	1.8	1.91
Sulfur, wt %	0.9	0.81	0.79	0.61	0.66	0.55	0.7	0.8	0.60
Hydrogen/carbon ratio	1.79	1.64	1.64	1.56	1.67	1.67	--	--	1.64
Ash, ppmw	--	50	600	300	4,400	3,000	--	--	1,400
Carbon residue, wt %	5.6[b]	--	1.7[b]	--	2.7	4.3[b]	1.8	2.1	2.0
Flash point, °F[c]	192[d]	79[d]	--	118	--	128	--	--	--
Pour point, °F	80	60	60	60	--	40	70	60	50
Visbreaking, ssu[e]									
100°F	210	98.2	--	136	150	165	--	--	190
210°F	--	--	--	--	--	42	--	--	--
Acid number, mg/g	--	--	--	2.6	--	4.0	--	--	--
Base number, mg/g	--	--	--	--	--	12.1	--	--	--
Nickel, ppmw	4	--	--	2.5	--	<2	--	--	--
Vanadium, ppmw	1.5	--	--	0.56	--	<20	--	--	--
Iron, ppmw	55	--	40	60	142	56	--	--	40
Copper, ppmw	--	--	--	11	--	<2	--	--	--
Arsenic, ppmw	--	--	50	52	45	49	--	50	37
Chloride, ppmw	--	--	5	--	--	15	--	--	--
Paraffins, ppmw	--	--	--	9	--	9	--	--	--
Olefins, ppmw	--	--	--	7	--	7	--	--	--
Naphthenes, ppmw	--	--	--	8	--	10	--	--	--
Aromatics, ppmw	--	--	--	48	--	45	--	--	--
Polar aromatics, ppmw	--	--	--	24	--	24	--	--	--
Carbon insolubles, ppmw	--	--	--	4	--	5	--	--	--
Distillation temperatures, °F									
IBP		139	120	145		152			176
10%	465	400	330	397		345			443
30%	640		551	660		633			666
50%	775	731	711	797		799			791
70%	980		848	903		919			891
90%		960	984	1037		1078			949
End point		1077	1100	1100		1100			1092

[a] Steam Gas Recirculation retort.

[b] Conradson carbon.

[c] Pensky-Martens, unless otherwise noted.

[d] Cleveland Open Cup.

Paraho			Tosco	Lurgi		Laramie	Occidental[f]		
DH	DH	IH	II	C_4+		(in situ)	E	U	O
Colo	Utah	Colo	Colo	Colo	Colo	Colo	Colo	Colo	Colo
28	19	--	35	--	--	--	--	--	--
21.4	19.6	20.2	20.6	27.0	23.8	28.4	25.0	24.8	24.3
84.5	84.21	83.13	85.1	85.2	85.9	--	--	--	84.86
11.2	11.82	11.43	11.1	11.34	11.1	--	--	--	11.80
1.6	1.89	1.16	1.2	1.15	1.17	--	--	1.03	--
1.27	1.19	--	1.1	--	--	--	--	--	--
1.96	2.09	2.18	1.9	1.65	1.72	1.41	1.3	1.58	1.50
0.64	0.5	0.66	0.7	0.66	0.75	0.72	0.64	0.74	0.71
1.59	1.69	1.64	1.56	1.59	1.50	--	--	--	1.67
800	500	3000	1000	--	--	0.06	--	--	--
1.4	3.1[b]	--	4.0[b]	--	3.86	1.7	--	--	--
186	198	--	--	--	115	--	--	--	--
75	75	90	80	--	65	40	50	--	65
177	285	--	110	39	53	78	80	--	116
--	45	44	38	--	--	--	--	--	--
2.1	2.9	2.3	--	--	--	--	1.53	1.63	--
--	13.6	38	--	--	--	--	--	--	--
3.5	20	--	1.6[g]	--	4	--	--	--	--
0.22	<20	--	0.4[g]	--	5	--	--	--	--
100	140	70	40	--	--	--	--	--	--
0.3	<2	--	0.15[g]	--	--	--	--	--	--
28	19	28	21	--	10	--	--	--	--
--	6	<0.2	10	--	--	--	--	--	--
10.7	7	10	--	--	--	--	--	--	--
5.8	5	6	--	--	--	--	--	--	--
7.1	10	8	--	--	--	--	--	--	--
46.3	44	46	--	--	--	--	--	--	--
25.9	29	23	--	--	--	--	--	--	--
4.1	5	6	--	--	--	--	--	--	--
145	220	886	80	--	158	--	250	204	--
442	503	608	340	230	320	--	465	450	475
660	690	659	525	420	457	--	575	540	600
794	827	776	720	605	619	--	670	616	685
912	952	871	885	770	777	--	765	684	775
1050	--	995	1035	950	842[h]	--	900	742	915
1100	1100	1022	1125	--	--	--	1050[i]	--	--

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[e] Saybolt seconds, universal.

[f] E, analyzed by Exxon; U, by Universal Oil Products, and O, by Occidental.

[g] Fischer assay oil data.

[h] At 80 percent.

[i] At 95.5 percent.

Table 21 Fractional analyses of shale oil from Union B process

	Whole oil[a]	IBP- 375[c]F	375- 425°F	425- 500°F	500- 650°F	650- 850°F	850- 1050°F	1050°F+
Composition, wt %								
Carbon	84.27	84.54	83.20	83.82	84.31	84.81	85.20	84.21
Hydrogen	11.68	13.07	12.78	12.41	12.75	11.51	11.24	10.37
Oxygen	1.23	1.33	1.99	1.88	1.38	1.27	1.07	1.28
Nitrogen, basic	1.26	0.56[b]	1.06[b]	0.97	1.10	1.17	1.33	1.52
Nitrogen, total	1.93	0.23	0.85	1.34	1.39	2.04	2.15	3.25
Sulfur	0.55	0.62	0.54	0.71	0.76	0.52	0.46	0.42
Hydrogen/carbon ratio	1.66	1.86	1.84	1.78	1.81	1.63	1.58	1.48
PNOA by mass spectroscopy, vol %								
Paraffins		24.6	21.0					
Naphthenes		7.4	4.8					
Aliphatic monoolefins		31.0	33.1					
Cyclic monoolefins		13.7	11.1					
Alkylbenzenes		22.0	20.8					
Alkylindans + Tetralins		1.3	8.3					
Alkylnaphthalenes		0.0	0.9					
Structure by ASTM D-2007, wt %								
Paraffins	--	22.9[c]	19.3[c]	15.3	18.5	9.4	3.0	2.6
Naphthenes	--	7.5[c]	4.9[c]	12.7	16.1	12.8	8.7	
Monoolefins	--	43.5[c]	42.5[c]	10.4	2.2	2.3	3.5	
Aromatics	--	26.1[c]	33.3[c]	52.5	41.2	52.9	52.8	31.7
Polar aromatics	--	--	--	8.7	21.3	21.8	32.0	38.7
Pentane insolubles	1.5	--	--	0.4	0.7	0.8	0.0	27.0
CHONS, within a boiling fraction, wt %								
Pentane insolubles	79.05							
Carbon	79.05							
Hydrogen	7.80							
Oxygen	6.78[d]							
Nitrogen, total	5.71							
Sulfur	0.66							
Polar aromatics								
Carbon				78.90	82.21	81.96	82.94	
Hydrogen				10.05	9.86	10.14	10.34	
Oxygen				5.50	3.61	2.52	2.27	
Nitrogen, total				5.25	4.13	4.50	3.83	
Sulfur				0.30	0.22	0.32	0.26	
Total acid number, mg/g	4.0	4.0	7.9	6.5	2.8	--	--	--
Total base number, mg/g	12.1	15.8	24.2	26.0	37.1	--	--	--
Chloride, ppm	15	18	--	--	6	--	--	--

---

[a] Whole oil structure (percent by weight): 9 paraffins, 10 naphthenes, 7 monoolefins, 45 aromatics, 24 polar aromatics, 5 pentane insolubles.

[b] Problems with the test.

[c] Estimated wt % by PNOA-MS, not ASTM D-2007.

[d] By difference.

Source: McCarthy and Cha (1976).

Table 22 Fractional analyses of shale oil from Paraho process

	Whole oil[a]	IBP-375°F	375-425°F	425-500°F	500-650°F	650-850°F	850-1050°F	1050°F+
Composition, wt %								
Carbon	84.21	83.89	83.88	84.34	83.29	84.12	84.40	84.41
Hydrogen	11.82	12.98	12.25	12.41	11.83	11.43	11.16	10.13
Oxygen	1.89	1.67	2.20	2.05	1.92	1.52	1.43	2.06
Nitrogen, basic	1.19	1.03[b]	1.20[b]	0.99	1.14	1.25	1.58	
Nitrogen, total	2.09	0.94	0.94	1.06	1.74	1.99	2.35	2.73
Sulfur	0.50	0.37	0.46	0.51	0.47	0.58	0.37	0.30
Hydrogen/carbon ratio	1.68	1.86	1.75	1.77	1.70	1.63	1.59	1.44
PNOA by mass spectroscopy, vol %								
Paraffins		19.5	19.8					
Naphthenes		6.2	6.2					
Aliphatic monoolefins		31.0	24.2					
Cyclic monoolefins		14.9	11.0					
Alkylbenzenes		26.1	28.4					
Alkylindans + Tetralins		2.2	8.5					
Alkylnaphthalenes		0.1	1.9					
Structure by ASTM D-2007, wt %								
Paraffins	--	18.0[c]	17.9[c]	15.9	14.8	9.5	3.3	
Naphthenes	--	6.2[c]	6.2[c]	11.4	10.0	16.4	11.2	2.1
Monoolefins	--	44.3[c]	33.4[c]	11.2	6.4	1.6	2.7	
Aromatics	--	31.5[c]	42.5[c]	49.3	50.4	49.7	50.2	26.8
Polar aromatics	--	--	--	11.9	17.7	22.3	31.8	52.3
Pentane insolubles	0.7	--	--	0.3	0.7	0.5	0.8	18.8
CHONS, within a boiling fraction, wt %								
Pentane insolubles								
Carbon	76.65							
Hydrogen	7.13							
Oxygen	10.42[d]							
Nitrogen, total	5.29							
Sulfur	0.51							
Polar aromatics								
Carbon				78.23	81.08	82.30	83.56	
Hydrogen				9.81	10.28	9.98	10.24	
Oxygen				5.83	3.16	2.42	1.45	
Nitrogen, total				5.61	5.01	4.57	3.96	
Sulfur				0.21	0.22	0.36	0.35	
Total acid number, mg/g	2.9	3.1	4.3	4.7	3.3	--	--	--
Total base number, mg/g	13.6	24.7	30.0	31.0	37.4	--	--	--
Arsenic, ppm	19	12	6	6	14	16	19	27
Chloride, ppm	6	14	--	--	--	--	--	--

[a] Whole oil structure (weight percent): 7 paraffins, 10 naphthenes, 5 monoolefins, 44 aromatics, 29 polar aromatics, 5 pentane insolubles.

[b] Problems with the test.

[c] Estimated wt % by PNOA-MS, not ASTM D-2007.

[d] By difference.

Source: McCarthy and Cha (1976).

Table 23 Fractional analyses of shale oils from Tosco and Occidental petroleum processes, in percent by volume

Process/ composition	Boiling range			
Tosco[a]	IBP-170°F	170-310°F	310-375°F	375-640°F
Aromatics	4.0	15.0	23.5	47.5
Olefins	63.0	55.5	49.0	37.0
Saturates	33.0	29.5	27.5	15.5
Paraffins	28.0	22.2	20.2	-
Cyclo paraffins	4.8	7.2	7.3	-
Di-cyclo paraffins	0.2	0.1	0.0	-
Occidental[b]		IBP-375°F		375-500°F
Position in shale oil		0.2-2.4		2.4-14.2
Paraffins		26		
Olefins		21		
Naphthenes		4		
Aromatics[c]		49		
FIA analysis[d]				
Paraffins and naphthenes				43.8
Olefins				22.7
Aromatics				33.5

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[a] C. W. Waitman of Tosco Corp., personal communication to J. O. Berga, November 16, 1977.

[b] R. D. Ridley of Occidental Oil Shale, Inc., personal communication to J. O. Berga, November 21, 1977.

[c] Oxygen, nitrogen, and sulfur compounds included with aromatics.

[d] Fluorescent indicator adsorption.

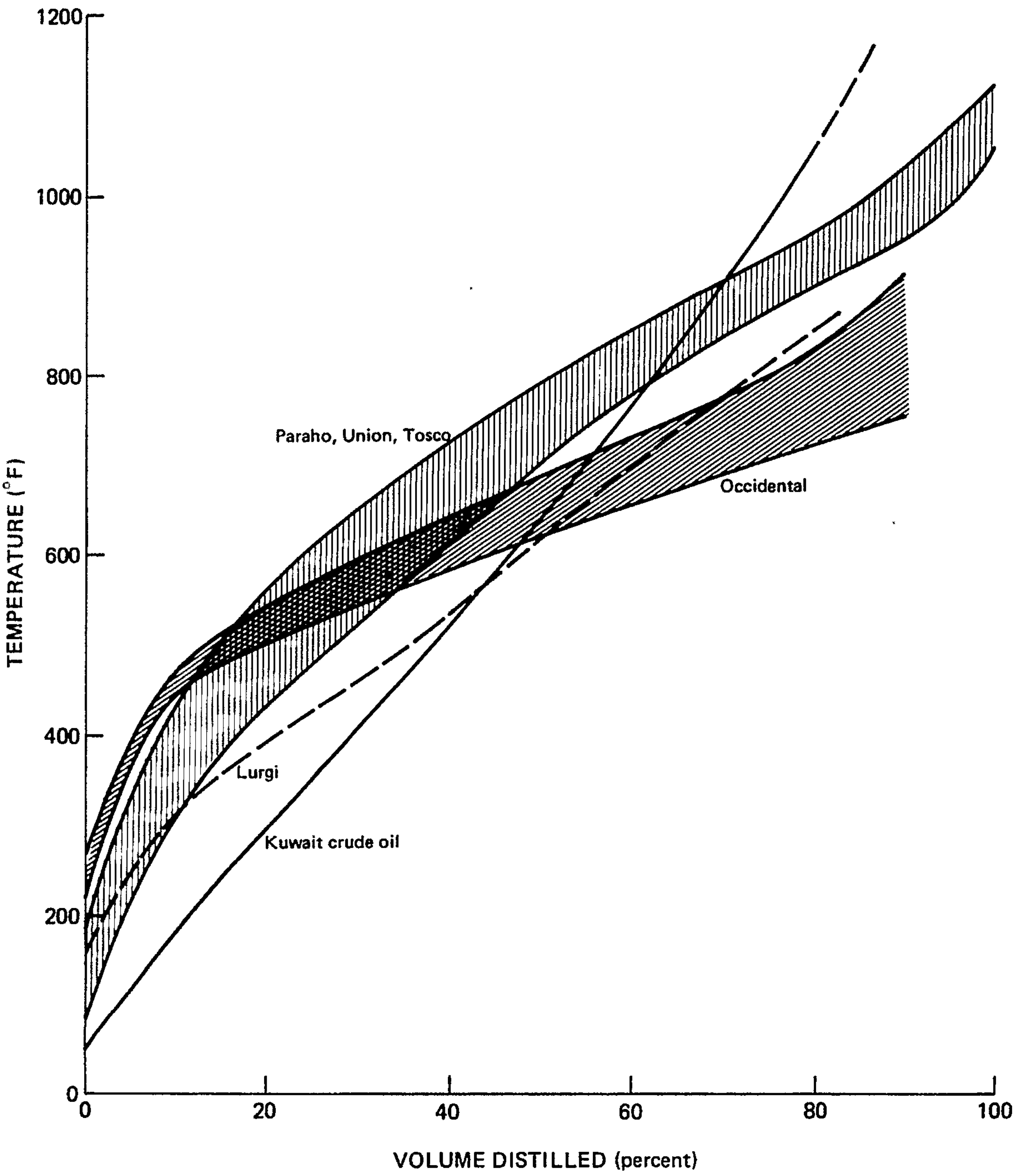

Figure 25 Distillation curves of shale oils

line because only one source of data was available for the United States and there is some question as to whether these data are typical.)

One of the most significant characteristics of raw shale oil is the high nitrogen content. The distribution of nitrogen and sulfur over the boiling range is shown in Figure 26. The nitrogen content of raw shale oil increases as distillation progresses, as does that of petroleum crude oil, but this is not true of the sulfur content. The concentration of sulfur in the raw shale oil reaches a peak at the 10 percent point and then decreases as distillation continues.

Although the metal concentrations in raw shale oil are lower than those in petroleum crude, there are a number of other trace elements that present difficulties. The most significant of these is arsenic, which, along with nitrogen, is discussed in greater detail below. In fixed bed hydrotreating, the fine shale rock particles in the raw shale oil (known as "fines" or "ash") present additional problems, plugging the catalyst beds and increasing the pressure drops in the system; to deal with this particular problem, de-ashing will be necessary, either as a separate step or as part of the de-arseniting process.

The limited data available show that raw shale oils from all retorting processes studied have similar chemical structures, which are significantly different from those of petroleum crudes. In general, the shale oils are lower in paraffins, higher in olefins, and higher in aromatics and polar aromatics.

In raw shale oils, the lower boiling fractions tend to have higher concentrations of paraffins and olefins and lower concentrations of aromatics than the higher boiling fractions (Figure 27). The naphthene content tends to remain fairly constant across the boiling range.

The high percentage of polar aromatics in the higher boiling range fractions indicates the presence of nitrogen, oxygen, and sulfur in the ring structure of the higher molecular weight aromatics, and the data bear this out. This characteristic increases the difficulty of denitrifying shale oil to levels that are acceptable for processing into transport fuels.

The significance of the nitrogen, arsenic, sulfur, and oxygen contents in the refining of raw shale oil are discussed below.

Nitrogen

The predominant nitrogen compounds in raw shale oils are pyridines, pyrroles, quinolines, and nitriles (Burger et al., 1975). The basicity of these and other nitrogen compounds found in raw shale oils has been reported previously (Poulson et al., 1976).

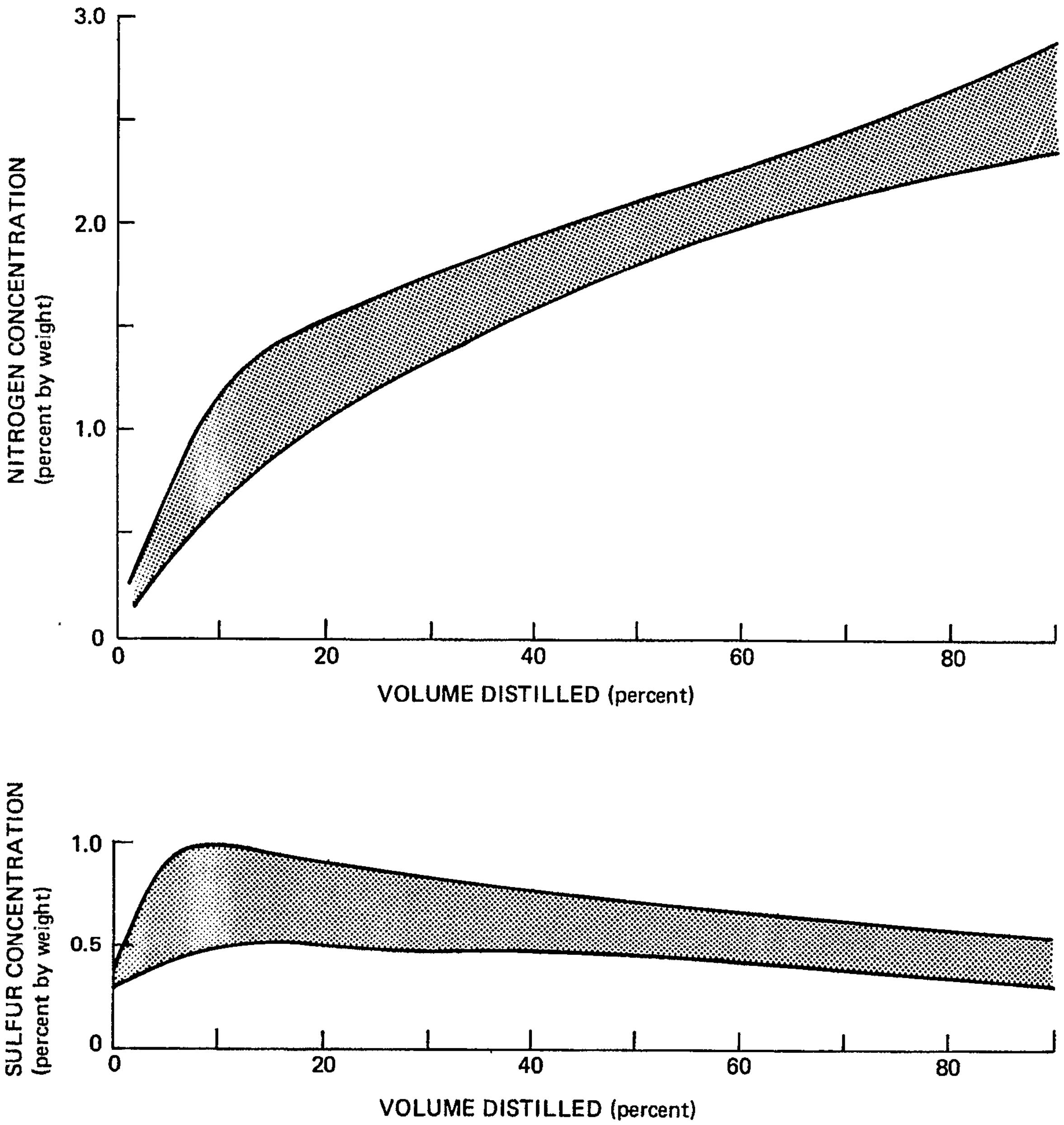

Figure 26 Nitrogen and sulfur concentrations in raw shale oil, as a function of distillation range (Lovell, 1978)

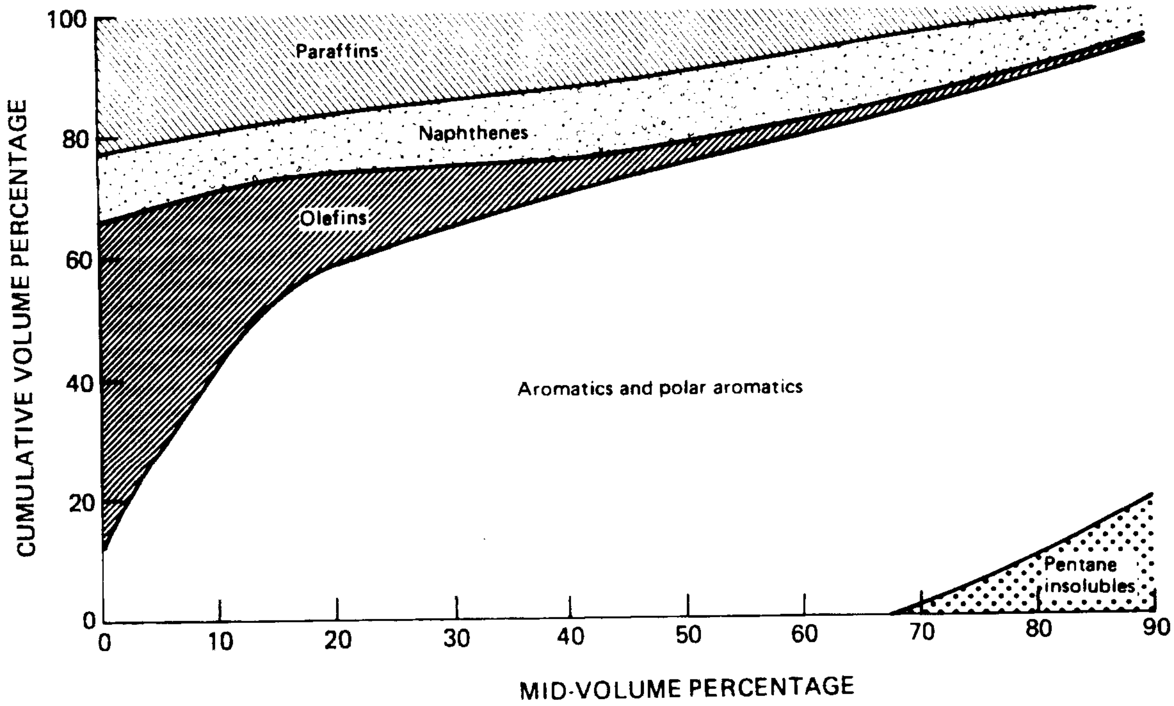

Figure 27 Chemical structure of raw shale oil (Lovell, 1978)

Table 24 gives a qualitative breakdown of the polar compounds in two Utah shale oils that were produced by direct-heated and indirect-heated surface retorting processes (Lovell, 1978).

Some evidence indicates that shale oils retorted in situ may generally contain somewhat lower concentrations of heteroatom and polar compounds than surface-retorted oils (Poulson et al., 1976) but the concentrations are still much higher than those in conventional crude oils. A significant degree of upgrading (denitrification) will be necessary with all raw shale oils before they can be refined to useful end products by conventional processes.

Removing the nitrogen from raw shale oil is critical because of its effect on downstream processing. Direct fixed-bed hydrogenation of both whole and fractionated raw shale oil has been used for nitrogen reduction (Sullivan and Stangeland, 1978), and results to date support the conclusion that hydrodenitrification of whole shale oil to the ppm range is feasible. The process conditions required would be more severe than those of present refining operations, however; high pressures ($\gtrsim$2000 psi) and high hydrogen consumptions ($\gtrsim$2000 standard cubic feet per barrel) would be necessary to reach the desired nitrogen levels. Although this is technically feasible, the costs would be high.

Another possible approach to nitrogen removal is to combine hydroprocessing of the raw shale oil with an acid extraction step to reduce the nitrogen compounds by precipitation.[a] Relatively mild hydroprocessing conditions can bring about a substantial conversion of neutral and acidic nitrogen compounds to basic amines that can then be converted into insoluble amine salts with a strong acid (e.g., HCl).

There is a need for more research on such mechanisms together with process research and development on nitrogen removal using catalyst selectivity, solvent extraction (acid treating), and hydroprocessing.

Arsenic

The concentration of arsenic in raw shale oil is on the order of 1000 times higher than the concentration of arsenic in conventional crude oil. Green River oil shale has an arsenic content of about 50 ppm (Burger et al., 1975), and comparable levels have been found in shale oils recovered elsewhere by various retorting processes. Since arsenic poisons certain catalysts currently used for refining oil, most of the arsenic in shale oil must be removed before it is piped into a conventional refinery. Generally speaking, it is desirable to reduce the level of arsenic in the naphtha fraction charge to 5 ppb or less before catalytic reforming. The distribution of arsenic throughout the boiling range of raw shale oils is most likely due to the presence of various species of molecular arsenic.

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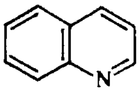
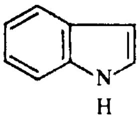
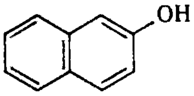
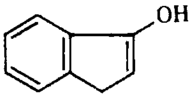
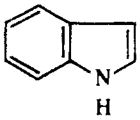
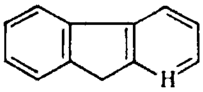
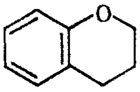
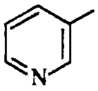
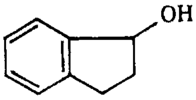
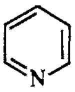
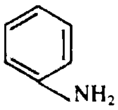
[a] A. Schneider, Suntech, Inc., personal communication.

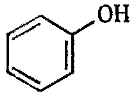
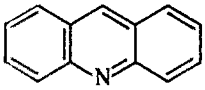
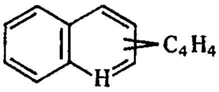
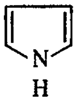
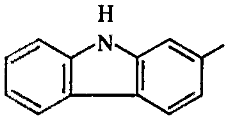
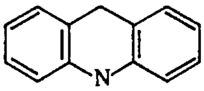
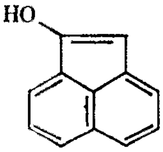
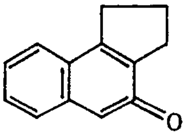
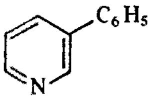
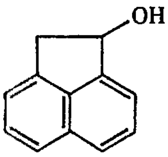
Table 24 MS characterization of polar fractions of Utah shale oils

		Union B			Paraho DH		
		425-500°F	500-650°F	650-850°F	425-500°F	500-650°F	650-850°F
QUINOLINES 	CYCLOALKYLINDOLES 	M	M	M	M	L	M
NAPHTHOLS 	INDENOLS 	T	M	M	T	M	S
INDOLES 	INDENO-PYRIDINES 	M	L	M	M	L	S
CHROMANS 		S	M	S	S	S	S
CYCLOALKYLPYRIDINES 		M	M	M	M	M	M
INDANOLES 		M	M	M	S	M	M
PYRIDINES 	ANILINES 	M	M	M	M	S	M

L: large; M: medium; S: small; T: trace.

Source: Lovell (1978).

Table 24, continued

			Union B			Paraho DH		
			425-500°F	500-650°F	650-850°F	425-500°F	500-650°F	650-850°F
PHENOLS 			L	S	M	L	S	S
ACRIDINES 	BENZOQUINOLINES 		M	S	M	S	S	M
DIHYDROXYPHENOLS CATECHOL RESORCINAL QUINOL	FURANS 	PYROLES 	S	S	S	S	S	S
ALKYLCARBAZOLES 	ACRIDANS 		S	S	L	S	S	L
ACENAPHTHYLENOLS 	BENZINDANONES 		S	S	M	T	T	M
PHENYL-PYRIDINES 			S	M	M	T	M	M
ACENAPHTHENOLS 			T	S	S	T	S	S

Arsenic is a very difficult element to identify analytically, and the imbalances that frequently occur in fractional versus whole oil determinations are difficult to explain. Some arsenic compounds may be thermally unstable and volatilize overhead. All in all, very little is known about the nature of arsenic compounds in raw shale oil. More research needs to be done in this area.

As has already been noted, part of the arsenic in raw shale oil is contained in the fines, or ash. Care should be used in drawing inferences from the ash content figures reported in Table 20, however, since it is not known if they were obtained from the different retorting processes in comparable ways. It is highly probable, in any event, that de-ashing to about 10 ppm (maximum) will be required where fixed-bed catalytic processing (e.g., hydrotreating) is to be used as the initial upgrading step. In some instances, de-ashing may take place during the de-arseniting step. Several de-arseniting processes are currently available for licensing from Union Oil, Arco, and others (Burger *et al*., 1975), but the removal of arsenic requires additional research.

Sulfur

Sulfur concentrations in raw shale oils are in the range of 0.6-0.7 percent by weight, the distribution being fairly flat across the boiling range, as seen in Figure 26. (The sulfur concentrations in the lighter fractions of raw shale oil are slightly higher than those in the lighter fractions of petroleum crude oils.) Since sulfur is removed by hydroprocessing more easily than nitrogen, the denitrification of raw shale oil to a satisfactorily low level will also reduce the sulfur content to an acceptable level.

Oxygen

The oxygen content of raw shale oil is about 1.0-1.5 percent by weight, higher than the oxygen content of most petroleum crudes, although some California crudes have oxygen concentrations close to this level. The oxygen content is not expected to cause any unusual problems during the processing of shale oils into transportation fuels.

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