3.3.2 Composition of Fuels

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

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

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

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

Table 19

Fuel Characteristics - Carbon Numbers

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

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

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

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

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

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

Table 20

Fuel Characteristics - Olefin and Aromatic Content

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

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

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

Table 21

Spot Analyses of Diesel Fuel Samples

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

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

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

(3) Source: W.C. Hollyday, Jr., Exxon Chemical Corp., Paramins Laboratory

(4) J. K. Appledoorn and W.G. Dukek, "Lubricity of Jet Fuels" SAE Trans. 75, 428, Paper 660712 (1967).

References Cited in Section 3.3.2

(1) F. D. Rossini, J. Institute of Petroleum, $\underline{44}$, 97 (1958).

(2) E. E. Wigg, R. J. Campion and W. L. Petersen, SAE Trans. SAE Paper 720251, 1972.

(3) Booner and Moore Associates, "U.S. Motor Gasoline Economics, Vol. I Manufacture of Unleaded Gasoline," Prepared for American Petroleum Institute, Houston, Texas, June 1967.

3.3.3 Existing Petroleum Refining Technology

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

3.3.3.1 Crude Assay

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

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

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

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

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

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

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

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

3.3.3.2 Refinery Processes

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

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

Table 22

Typical Refinery Process Combinations

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

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

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

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

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

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

Figure 11

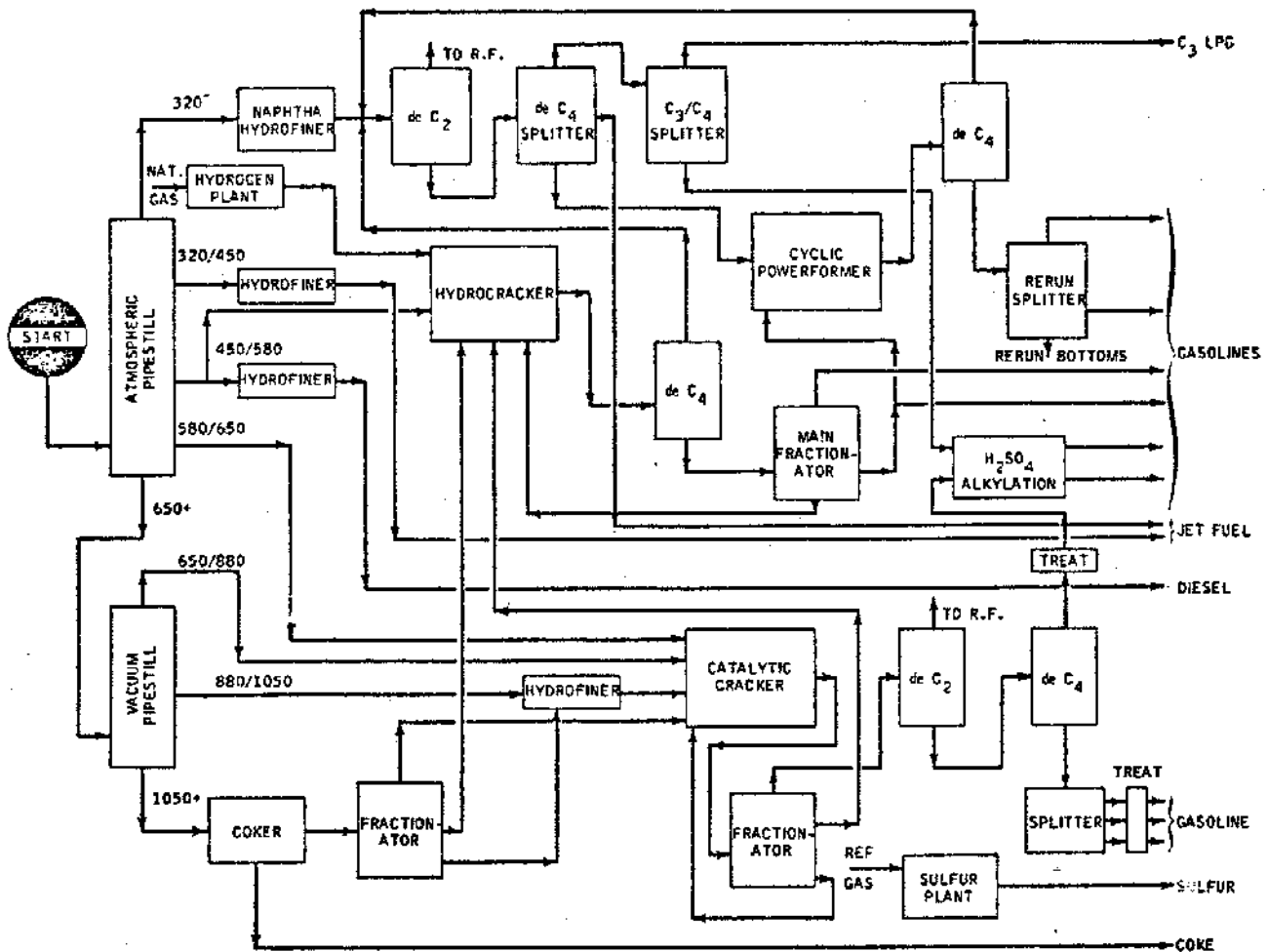### Typical Refinery Process Combinations
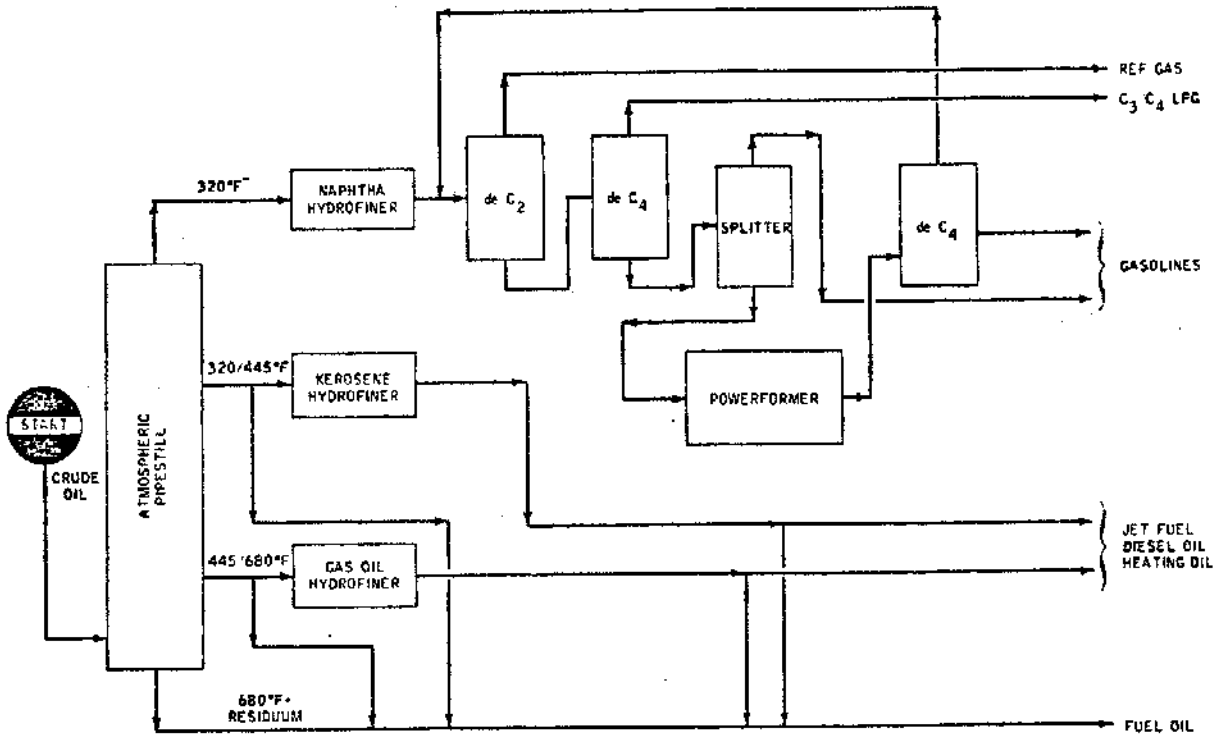
- Typical Hydroskimming Refinery
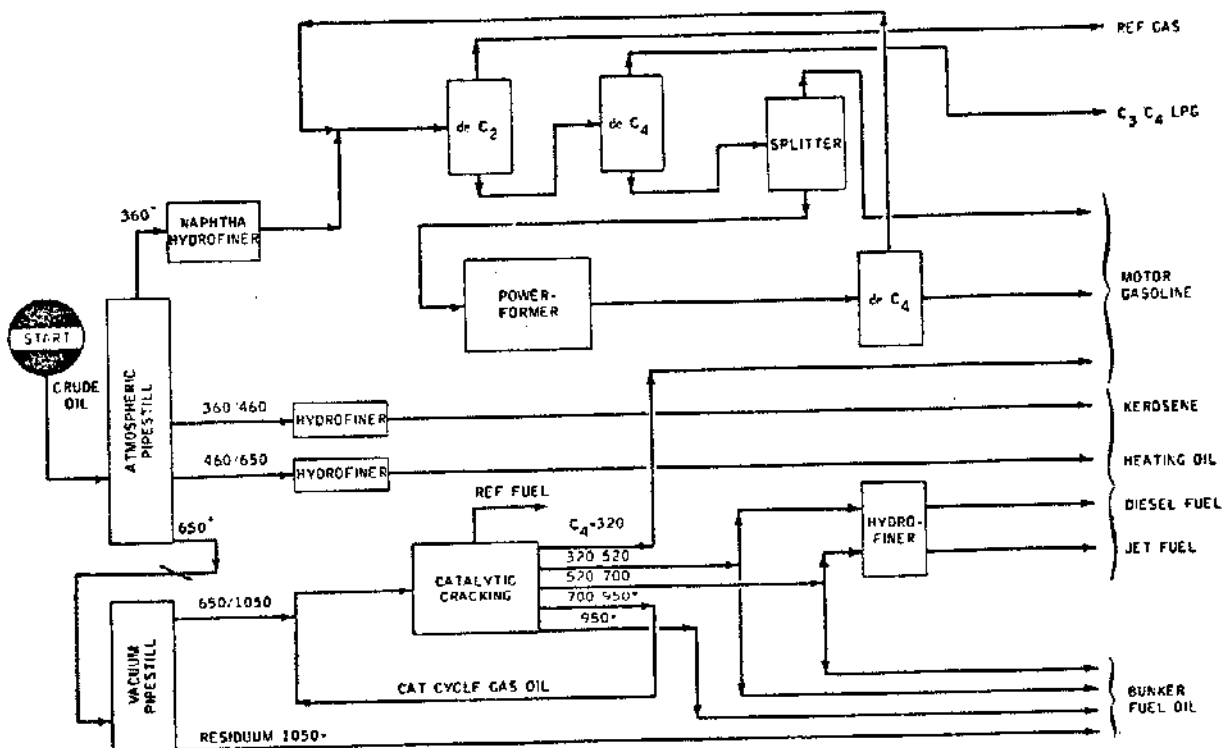
- Typical Conversion Refinery

Figure 12

Maximum Conversion Type Refinery

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

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

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

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

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

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

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

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

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

3.3.4 Anticipated Synthetic Crude Processing

3.3.4.1 General Problems

The organic matter present in shale and coal is different from that found in petroleum. Shale organic matter appears to contain a molecular complex of saturated, condensed polycyclic ring systems loosely interconnected with alkyl and heteroatom side chains. Pyrolysis of this matter produces

a shale oil containing a large proportion of heterohydrocarbon compounds containing nitrogen, oxygen and sulfur and a large proportion of olefins. Nitrogen compounds found in shale oil include pyrroles, indoles, carbazoles, pyridines, quinolines, amines and amides, while oxygen compounds are rich in phenols and carboxylic acids. Typical coal contains a molecular complex of condensed ring aromatics ranging from single rings up to several condensed rings per cluster. The clusters are joined together by connecting bridges principally short aliphalic groups and ether, sulfide and disulfide linkages. Organic sulfur structures in coal include condensed thiophenes, sulfides, disulfides and thiols. Oxygen structures include phenols, naphthols, ethers, ketones, quinones, furans and carboxylic acids. Nitrogen structures include pyridines, quinolines, amines, pyrroles and carbazoles. Upon pyrolysis coal produces a liquid high in aromatics and containing appreciable nitrogen, oxygen and sulfur.

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

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

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

Direct

● Direct processing of synthetic crude to a single product.

● Direct processing of synthetic crude to a variety of products.

Combined

● Combined processing of both synthetic crude and petroleum crude in an existing refinery.

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

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

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

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

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

Hydroconversion (Hydrocracking) processes came into wide use during the 1960's. A major reason for its rapid growth is the increasing demand for kerosene type jet fuel relative to motor gasoline. The hydrocracking process is basically a combination of catalytic cracking and hydrogenation. A wide variety of feed stocks can be processed. Light and heavy gas oils, often undersulfurized, account for a large percentage of the feed stocks. Operating

conditions are more severe than with hydrotreating, i.e., temperature from 600 to 800°F, pressures from 800 to 3000 psig and hydrogen consumption rates from 200 to 1000 SCF of H_2 per barrel. Because of the high pressure hydrogen treatment employed, products from Hydrocracking processes have negligible sulfur, nitrogen and olefin content. Unless operating conditions are severe, aromatic rings are not hydrogenated, but side chains are often removed.

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

3.3.4.2 Processing Synthetic Crude from Coal

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

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

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

Table 23

Analysis of COED Oil from Pittsburgh Coal

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

Table 24

Material Balance - Hydrotreating

Oil Source   Illinois No. 6-Seam Coal

Run Duration, hr.   168

Summary Operating Conditions

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

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

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

Table 25

Full Range COED Syncrude
from Illinois No. 6 Coal

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

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

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

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

3.3.4.3 Processing Synthetic Crude from Shale

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

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

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

3.3.4.4 Hydrogen Production

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

Table 26

Properties of Crude Shale Oil and Syncrude(a)

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

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

Table 27

Hydrogen Required in Production of Fuel

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

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

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

(3) Reference 23.

(4) Reference 25.

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

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

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

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

3.3.4.5 Consideration of Refinery Integration

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

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

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

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

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

References Cited in Section 3.3.4

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

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

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

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

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

4. AREAS FOR FRUITFUL R&D EFFORT

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

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

1. Analytical Studies and Forecasts

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

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

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

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

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

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

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

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

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

2. Product Quality Studies

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

3. Storage Stability

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

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

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

4. Deterioration, Corrosion and
   Material Compatibility

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

5. Toxicity, Emission
   and Odor Problems

Potential toxicity problems associated either with handling synthetic fuels or with emissions and/or odors from engines burning synthetic fuels should be considered. For example, Russian workers associated with

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

6. Combustion

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

7. Water Reactivity

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

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

8. Fire Safety

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

9. Other Areas

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

- **New Opportunities**

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

  - A high density fuel for increased range of volumetrically limited systems.

  - Should the phenols present in synthetics such as shale liquids be left in the fuel to function as a natural antioxidant for enhanced storage stability.

  - Should condensed thiophene type sulfur compounds such as alkyl benzothiophenes or dibenzothiophenes which are the most stable of all classes of sulfur compounds (in terms of storage stability) be left in the fuel to insure good lubricity properties.

- **Additives**

  What new additives will be necessary or desirable.

  - New storage stability additives.

  - New additives for improved cold flow properties of middle distillate fuels.

  - Additive packages for emergency fuels to insure operability.

  - Additives to improve phase separation properties of methanol-fuel blends.

- **Emergency Fuel Operability**

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