

3.2 Discussion of Major Synthetic Fuels

3.2.1 Coal and Shale Derived Synthetic Crudes

3.2.1.1 Resource Availability

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

3.2.1.1.1 Coal

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

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

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

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

Table 1

Estimated Remaining Producibile Coal
Reserves of the World (1)

<u>Region and Country</u>	<u>Producibile Coal 10⁹ Metric Tons</u>	<u>Percent of Regional Total</u>	<u>Percent of World Total</u>
Asia			
U.S.S.R.	600	52.3	25.8
China	506	44.1	21.8
India	32	2.8	1.4
Japan	5	0.4	0.2
Others	4	0.4	0.2
Total	1,147	100.0	49.4
North America			
United States	753	94.4	32.5
Canada	43	5.4	1.8
Mexico	2	0.2	0.1
Total	798	100.0	34.4
Europe			
Germany	143	47.5	6.2
United Kingdom	85	28.2	3.7
Poland	40	13.3	1.7
Czechoslovakia	10	3.3	0.4
France	6	2.0	0.3
Belgium	3	1.0	0.1
Netherlands	2	0.7	0.1
Others	12	4.0	0.5
Total	301	100.0	13.0
Africa			
Union of South Africa	34	97.1	1.5
Others	1	2.9	
Total	35	100.0	1.5
Australasia			
Australia	29	99.0	1.3
Others		1.0	
Total	29	100.0	1.3
South and Central America			
Colombia	6	60.0	0.2
Venezuela	2	20.0	0.1
Others	2	20.0	0.1
Total	10	100.0	0.4
World Total	2,320		100.0

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

Figure 1

Map Showing Location of Coal Reserves

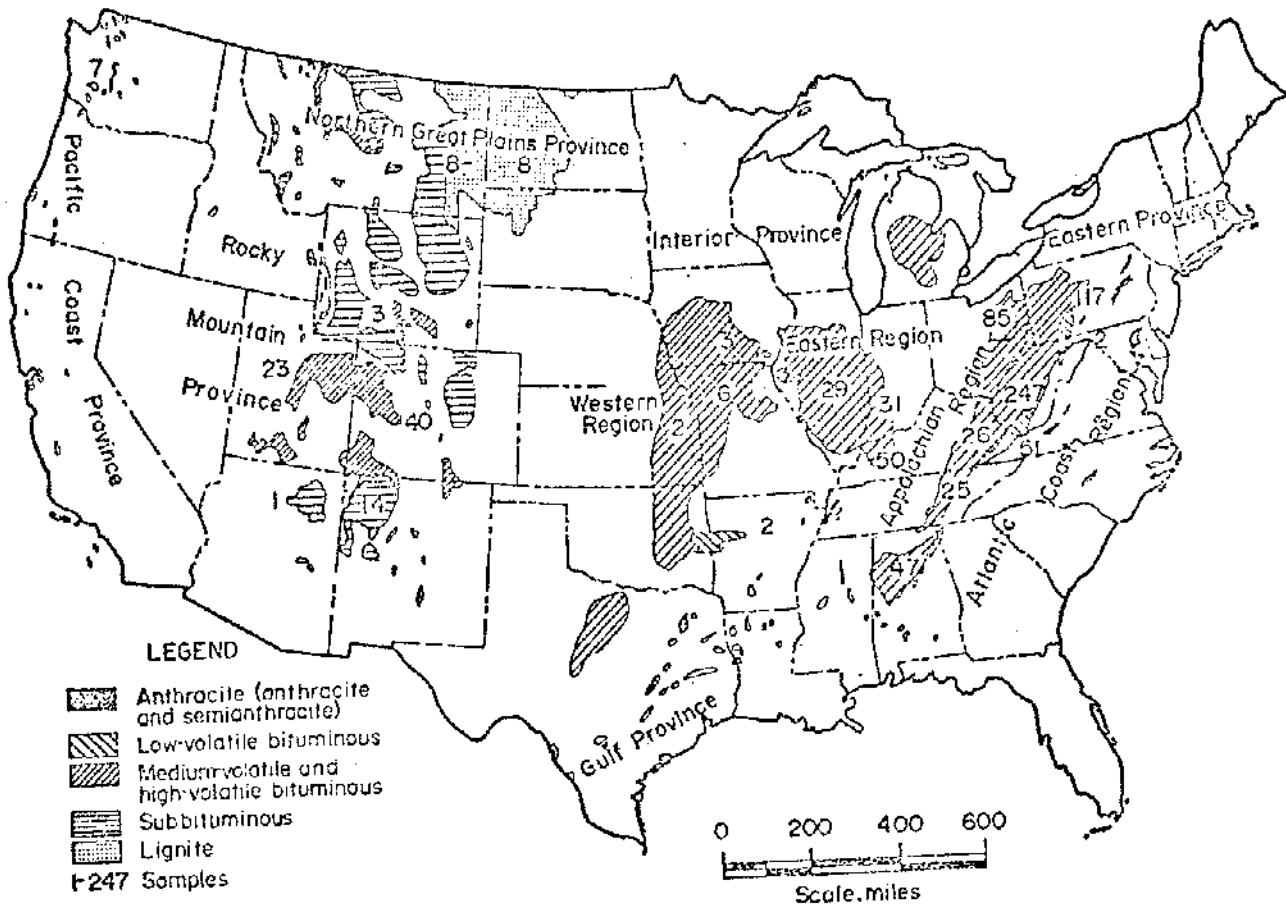


Table 2

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

Region and States	Production (2) (Million Tons)		1965	Estimated Remaining Reserves				Average for Region
	1969	1970		Bituminous	Sub-Bitum	Lignite	Anthracite	
Appalachian								
Alabama	17,456	20,560	13,597	1.5	0.5	1.3	0.5	1.5
Georgia	NA	NA	76	.9				.9
E. Kentucky	61,584	72,502	29,414	1.0				1.0
Maryland	1,356	1,615	1,180	3.1				3.1
Ohio	51,242	55,351	42,024	3.4				3.4
Pennsylvania	89,104	90,220	70,162	2.6			0.5	2.0
Tennessee	8,032	8,237	1,859	2.0				2.0
Virginia	35,555	35,016	10,155	0.9			0.5	0.9
W. Virginia	141,011	144,072	102,666	1.4				1.4
Interior Eastern								
Illinois	64,772	65,119	135,889	3.5				3.5
Indiana	20,086	22,263	34,841	2.9				2.9
W. Kentucky	47,466	52,803	36,395	3.5				3.3
Michigan	NA	NA	205	3.8				3.8
Interior Western								
Arkansas	228	268	2,396	1.5			2.1	1.5
Iowa	903	987	6,522	4.5		0.6		4.5
Kansas	1,313	1,627	20,738	3.6				3.6
Missouri	3,301	4,447	78,760	4.2				4.2
Oklahoma	1,838	2,427	3,302	2.0				2.0
Texas	NA	NA	14,860	2.3		1.3		1.8
Western								
Arizona		132						.8
Colorado		6,025	80,754	.7	.6			.7
N. Mexico	4,471	7,361	61,427	.7	.6		0.9	.6
Utah	4,657	4,733	27,808	1.4	1.3			1.4
Washington	58	37	5,885	.7	.6		0.5	.6
Wyoming	4,602	7,222	120,722	.7	.9			.8
Northern Plains								
Montana	1,020	3,447	221,702	2.6	.6			.7
N. Dakota	4,704	5,639	350,698			.7		.6
S. Dakota	NA	NA	2,031			.6		.9

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

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

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

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

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

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

3.2.1.1.2 Shale

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

Table 3

Major Shale Oil Reserves(a)

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

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

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

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

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

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

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

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

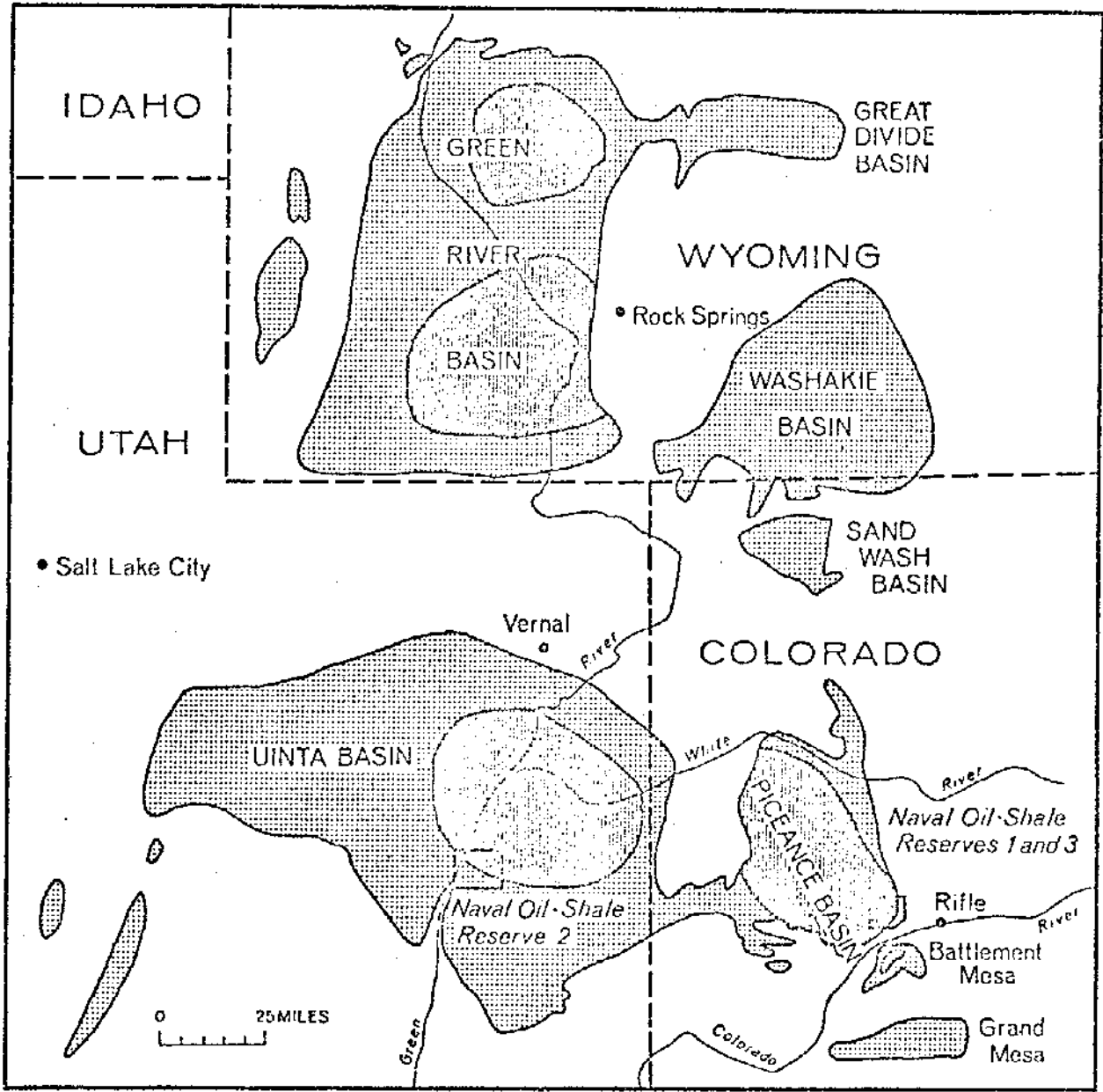
The energy potential of the Green River formation has been estimated to be approximately 1.8 trillion barrels of oil with easily recoverable reserves of 77 billion barrels (2b, 6) (See Table 4). Shale deposits vary in accessibility from those at the surface to very deeply buried shales in the Unita basin.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

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

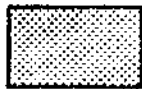
Crude shale oil derived from the Green River Formation possesses an unusually high nitrogen level. It has been found that generally the nitrogen content is higher and the sulfur level lower in the higher boiling shale oil fractions. As of this writing, no metal content data for shale oil appear to be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

Figure 2

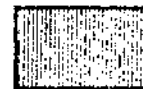
Distribution of Oil Shale in the
Green River Formation, Colorado, Utah and Wyoming



EXPLANATION



Area underlain by the Green River Formation in which the oil shale is unappraised or low grade



Area underlain by oil shale more than 10 feet thick, which yields 25 gallons or more oil per ton of shale

Table 4

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

(Billions of Barrels)

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

Table 5

Sulfur and Nitrogen Content of Crude Shale Oils**

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

* Core drilling sample.

** From Ref. 4.

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

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

3.2.1.2 Present Status of Conversion Processes

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

3.2.1.2.1 Coal Liquefaction Processes

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

3.2.1.2.1.1 Direct Hydrogenation Processes

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

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

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

3.2.1.2.1.2 Donor-Solvent Extraction Processes

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

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

3.2.1.2.1.3 Fischer-Tropsch Synthesis

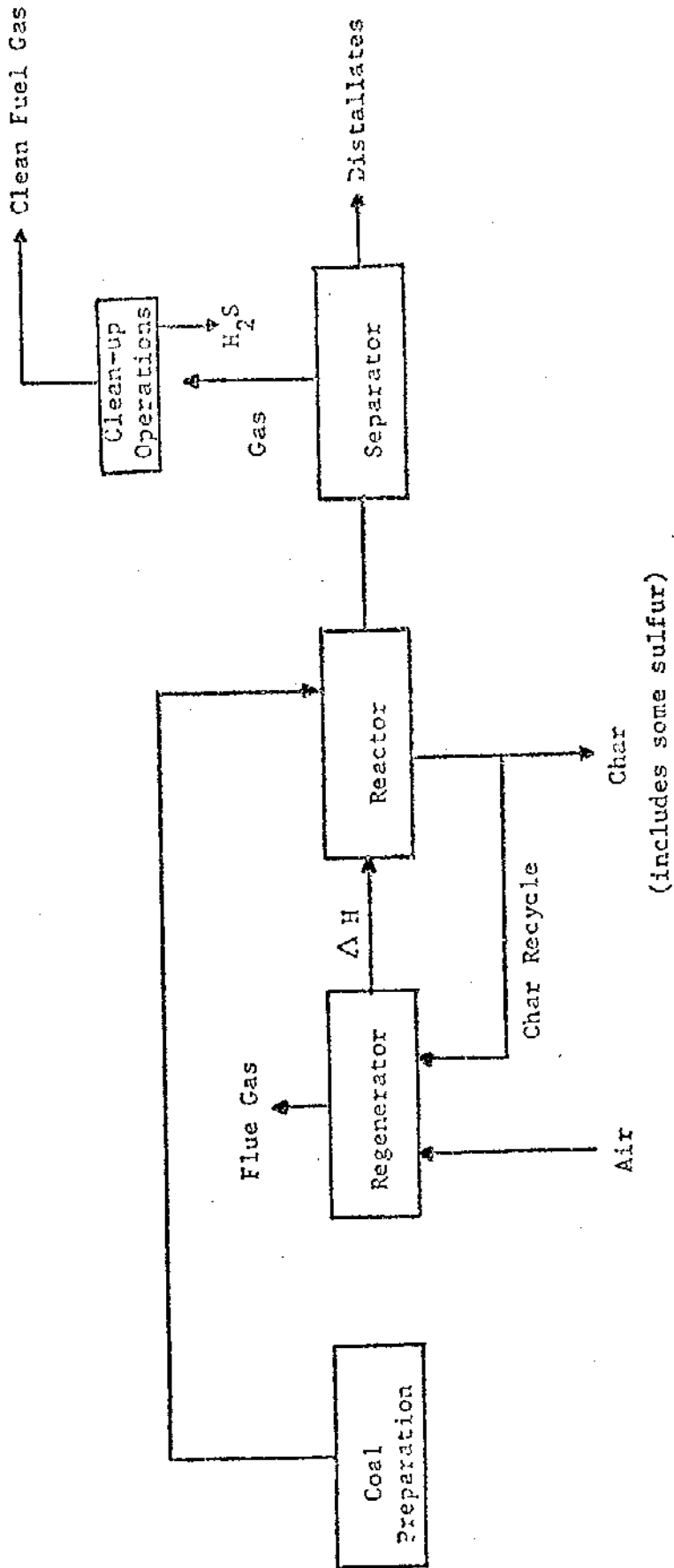
The Fischer Tropsch process for hydrocarbon synthesis is based on gasifying coal to CO and H₂ (synthesis gas) and then reacting these to form hydrocarbons and oxygenated organic compounds. The first commercial plants went into operation in Germany in the period 1936-1939. Others were built during World War II. More recently, the South African State Oil Company started up a facility in 1955 which processes about 1000 tons per day of soft coal to produce both chemicals and fuels. The economics of Fischer-Tropsch synthesis for fuel products are generally considered unfavorable.

3.2.1.2.1.4 Pyrolysis of Coal

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

Figure 3

Pyrolysis Processing Sequence



Pyrolysis is presently used commercially in the U.S. to produce coke and coal tar derivatives. Processes involved in this category involve the supply of heat to the coal in order to volatilize and thermally rearrange the hydrocarbon constituents into a fraction relatively rich in hydrogen and a high carbon solid fuel residue. Sulfur is removed either as H₂S from the gas clean-up stage or as a contaminant in the char.

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

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

3.2.1.2.1.5 Solvent Refined Coal

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

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

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

3.2.1.2.2 Shale Oil Processes

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

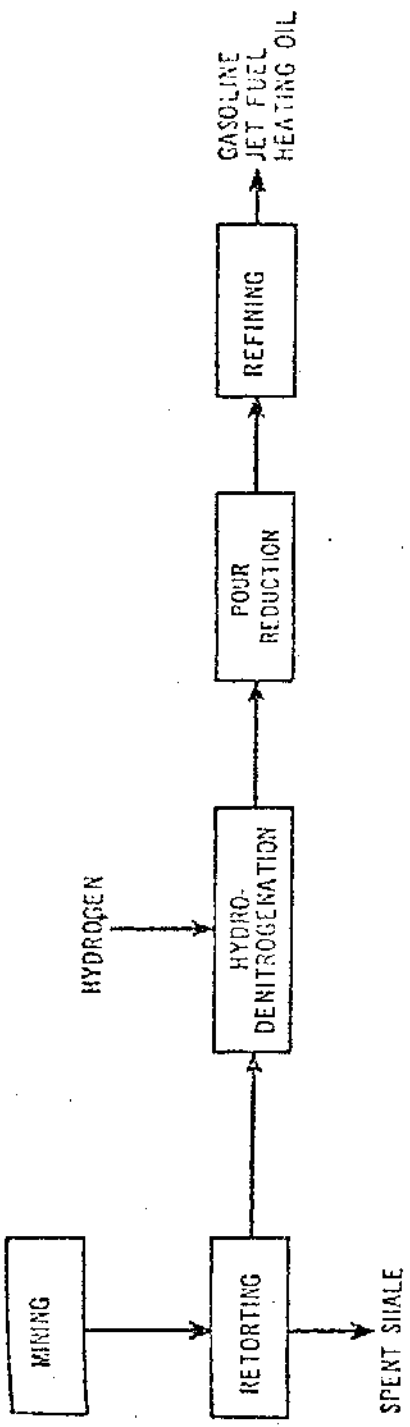
Currently there is a USN-DOI program to determine the performance capabilities of "military operational fuels" produced from shale liquids obtained from the Parahoe facility at Anvil Points.

3.2.1.2.2.1 TOSCO II Process

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

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

Figure 4
Shale Oil Processing Sequence



3.2.1.2.2.2 Bureau of Mines Process

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

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

3.2.1.2.2.3 Union Oil Company Process

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

3.2.1.2.3 Composition of Raw Products

3.2.1.2.3.1 Synthetic Crude Oils
from Shale

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

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

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

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

Table 6

Physical Properties of Synthetic
Crude Oils Produced from Shale

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

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

Table 7

Sulfur and Nitrogen Levels of Synthetic
Crude Oils Produced from Shale

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

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

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

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

Table 8

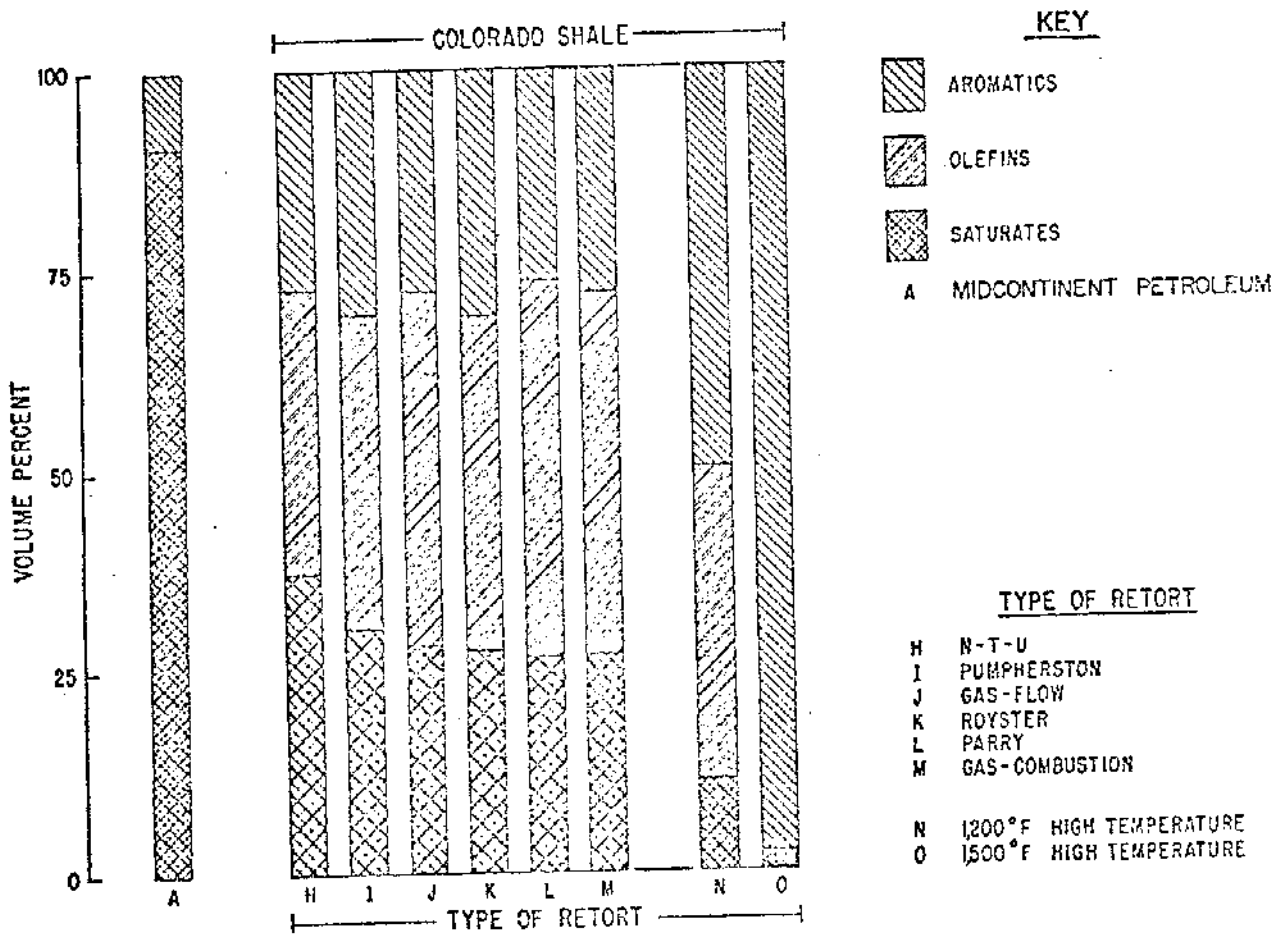
Distillation of Synthetic
Crude Oils Produced from Shale

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

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

Figure 5

Composition of Shale Oil Distillates Below 600°F



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

Table 9

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

	<u>Treated Crude*</u>	
Gravity °API	46.2	
Pour Point, °F	50	
Sulfur, Wt. %	0.005	
Nitrogen, Wt. %	0.035	
Reid Vapor Pressure Psi	8	
Viscosity, SUS at 100°F	40	
Analysis of Fractions	<u>C5-350°F</u>	<u>350-550°F</u>
Volume %	27.5	41.0
Gravity °API	54.5	38.3
Sulfur, Wt. %	<0.0001	0.0008
Nitrogen, Wt. %	<0.0001	0.0075
Aromatics	12	34
Saturates	82	66
Olefins	0	0

* Based properties of "Syn crude".

3.2.1.2.3.2 Synthetic Crude Oils from Coal

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

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

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

Figure 6

Molecular Structure of Coal

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

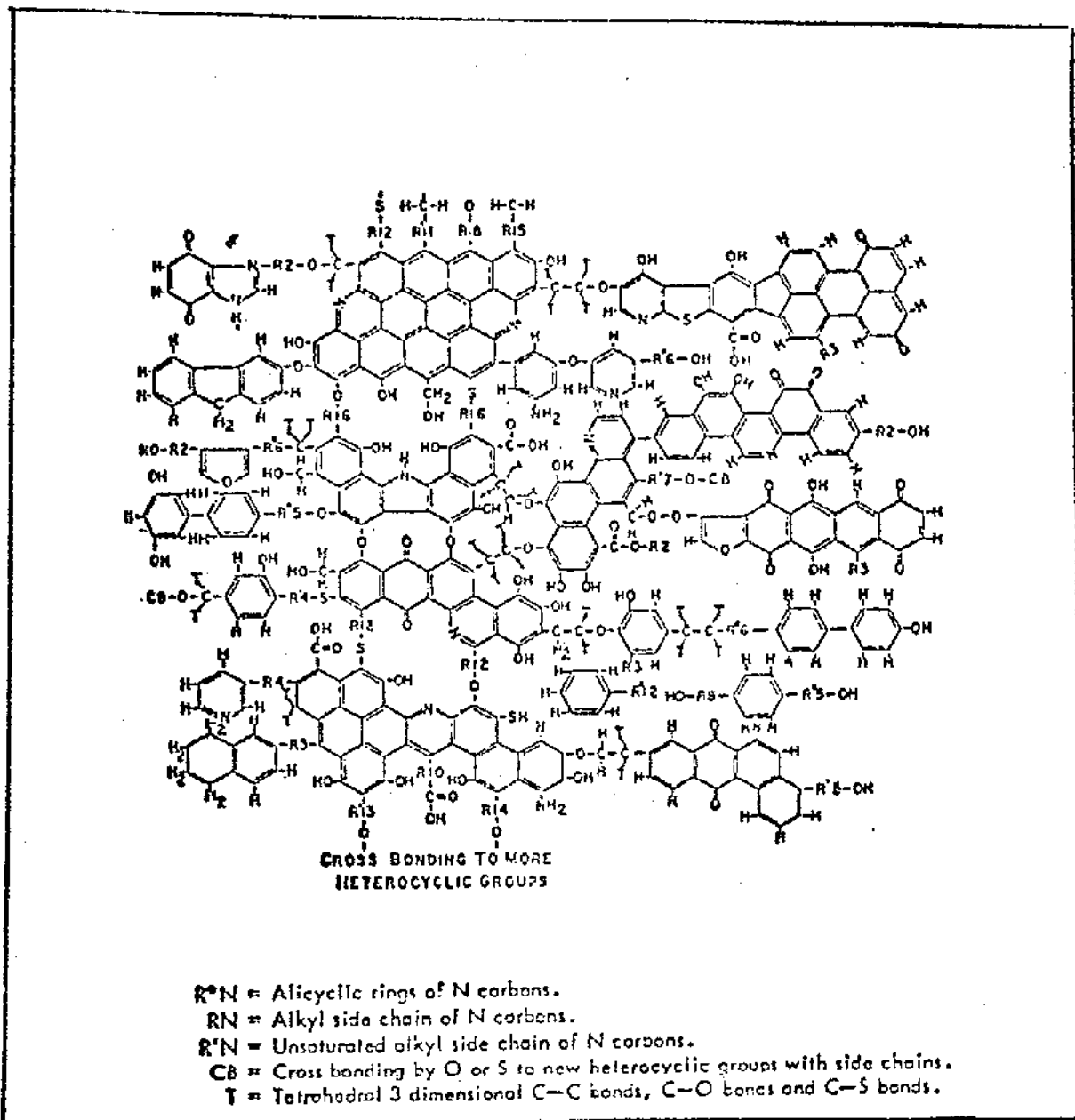


Table 10

Composition of Synthetic Crude Oil
Produced by the Pyrolysis of Coal

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

Table 11

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

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

* Illinois No. 6 coal.

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

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

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

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

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

Table 12

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

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

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

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