

3.2.2 Methanol

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

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

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

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

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

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

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

References Cited in Section 3.2.2

- (1) J. A. Bolt, "Survey of Alcohol as a Motor Fuel," SAE Paper 254, June 1964.
- (2) T. B. Reed and R. M. Lerner, "Methanol: A Versatile Fuel for Immediate Use," Science, 182, No. 4119, p. 1299, December 23, 1973.
- (3) G. E. Haddeland, "Synthetic Methanol," Report No. 43, Stanford Research Institute, October 1968.
- (4) B. Dutkiewicz, "Methanol Competitive with LNG on Long Haul," Oil and Gas Journal, p. 166, April 30, 1973.
- (5) R. P. Cahn and A. L. Shrier, "Methanol Fuel," ACS Preprints, Atlantic City Meeting, September 1974.

3.2.3 Tar Sands

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

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

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

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

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

Table 13

Tar Sand Reserves (1)

<u>Location</u>	<u>In-Place Reserves, 10⁶ Barrels</u>
Canada	711,000
Venezuela	200,000
Madagascar	1,800
U.S.A.	2,100
Albania	400
Rumania	25
U.S.S.R.	25

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

References Cited in Section 3.2.3

- (1) A. B. Cambel, "Energy, R&D and National Progress," U.S. Government Printing Office, Washington, D.C., 1964.
- (2) P. H. Phizackerley and L. O. Scott, "Major Tar Sand Deposits of the World," Proc. 7th World Petroleum Congress, Amsterdam, 1967.
- (3) R. A. Baillie and T. S. Mertes, "Sixth Annual Institute on Exploration and Economics of the Petroleum Industry," Matthew Bender and Company, New York, 1968.
- (4) Proceedings of the First Athabasca Oil Sands Conference, Kings Printer, Edmonton, Canada, 1951.
- (5) J. V. D. Fear and E. O. Innes, "Canada's First Commercial Tar Sand Development," Proc. 7th World Petroleum Congress, Amsterdam, 1967.
- (6) Oil and Gas Journal, 65, 69-98, October 23, 1967.
- (7) Oilweek (Calgary, Alberta) 26 #5 pages 26, 27 and 32, March 17, 1975.
- (8) Oil and Gas Journal, page 39, April 14, 1975.
- (9) Forbes, pages 18 and 19, May 1, 1975.

3.3 Present Fuels and Petroleum Processing Technology

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

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

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

3.3.1 General Chemical Composition of Petroleum

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

Table 14

Jet Fuel Specifications Versus
Chemical and Physical Properties

<u>Specification or Desired Property</u>	<u>Needed Physical and/or Chemical Characteristics</u>
Distillation range API Gravity Vapor pressure at 100°F Freezing point Viscosity Heating value	Correct carbon number range, also influenced by n+i-paraffin, naphthene and aromatic distribution
Existant gums Total potential residue Thermal Stability Pressure drop Preheater deposit code	Level and type of olefins, level and type of trace organic sulfur, nitrogen and oxygen impurities
Total sulfur content Mercaptan sulfur content Aromatic content Olefin content	Correct chemical composition as indicated
Smoke point, smoke volatility Index (SVI), luminometer number	Chemical composition, particularly aromatic and condensed ring aromatic content, SVI influenced by percent of lower boiling fractions.
Flash point Explosiveness	Correct lowest carbon number in fuel e.g., 140°F flash point requires fuel with carbon numbers greater than C ₉ or C ₁₀
Particulate matter	Presence of insoluble impurities
Water separation index Water reaction interface rating	Level and type of organic oxygen trace impurities
Copper strip corrosion	Level and type of trace sulfur and oxygen compounds
Total acid number	Carboxylic acid level in fuel i.e., present of trace organic oxygen compounds

3.3.1.1 Formation of Crude Oil

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

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

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

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

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

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

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

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

3.3.1.2 The Hydrocarbon Composition of Fuels

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

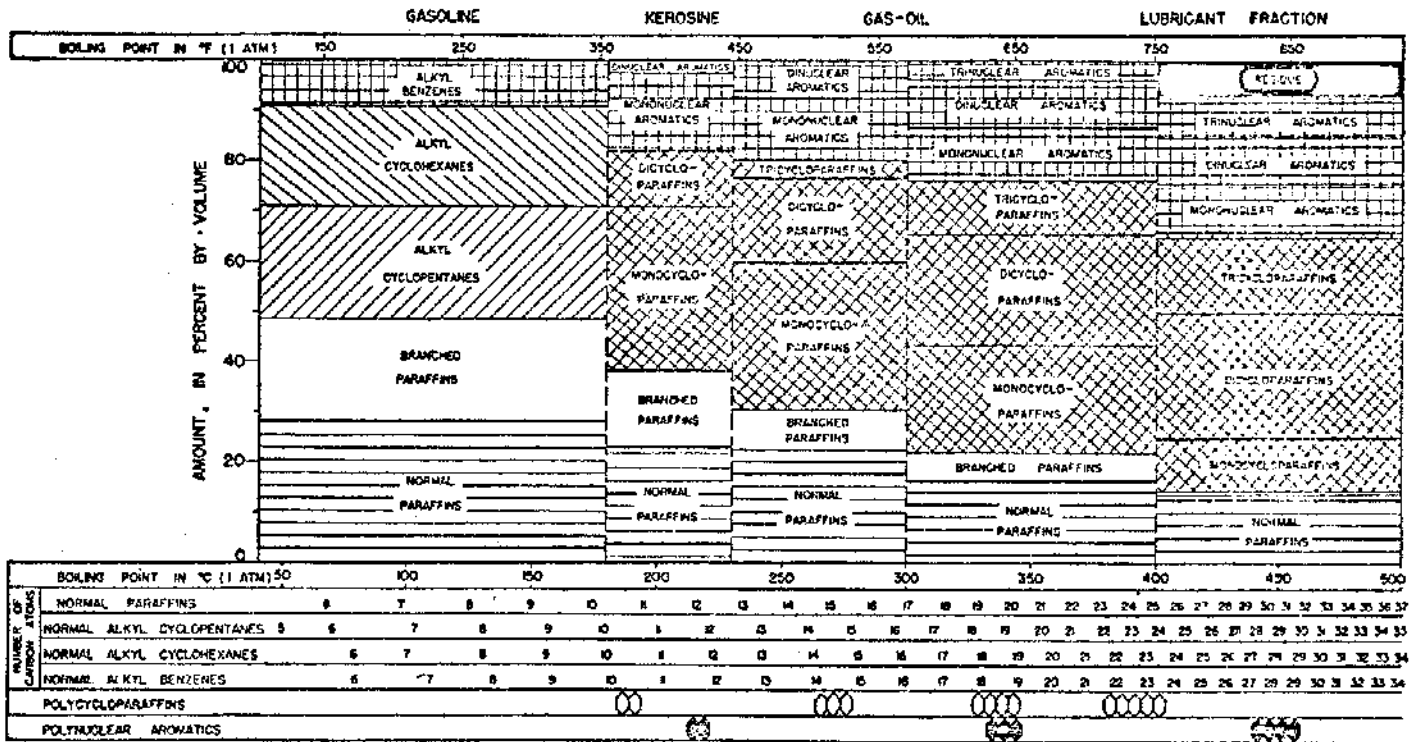
The main compound classes found in fuels are paraffins, naphthenes (cycloparaffins) and aromatics (3,4,5). As illustrated in Figures 8 and 9, the distribution of these compound classes in crude oil is both a function of crude source and carbon number (6,7). In Table 15 is shown a distribution of aromatic compound classes by carbon number in the C₉ through C₂₀ range (8).

3.3.1.3 Trace Impurities Potentially Present in Fuels

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

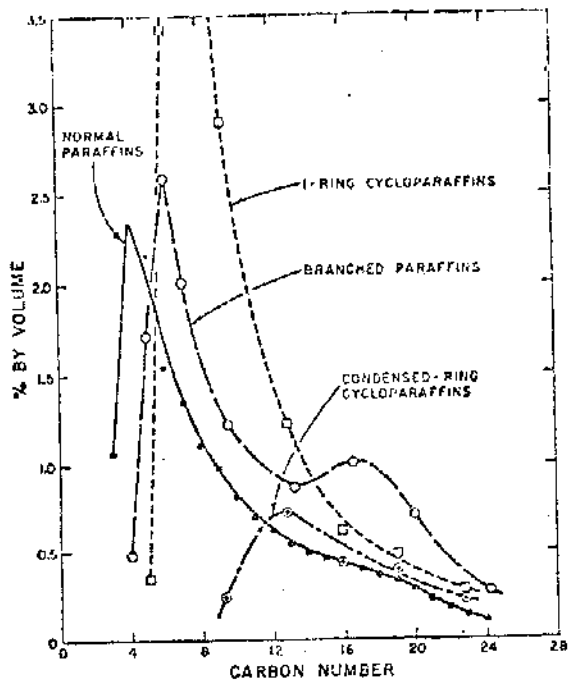
Figure 7

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

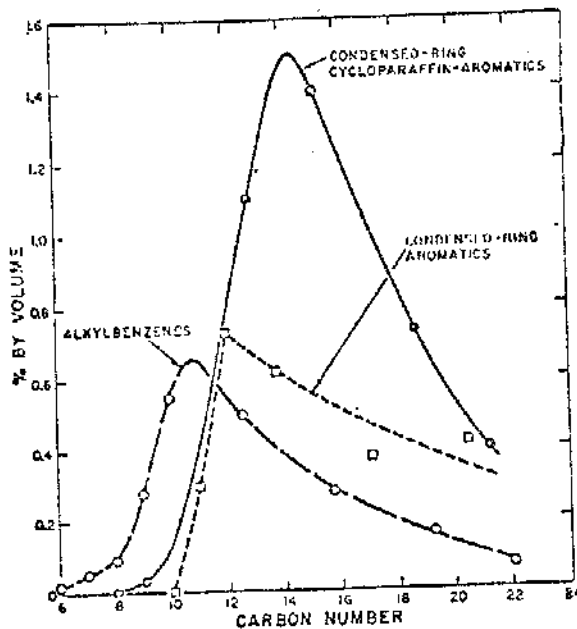


Source: F. D. Rossini, J. Petroleum Institute 44, 97 (1958).

Figure 8
Crude Analyses



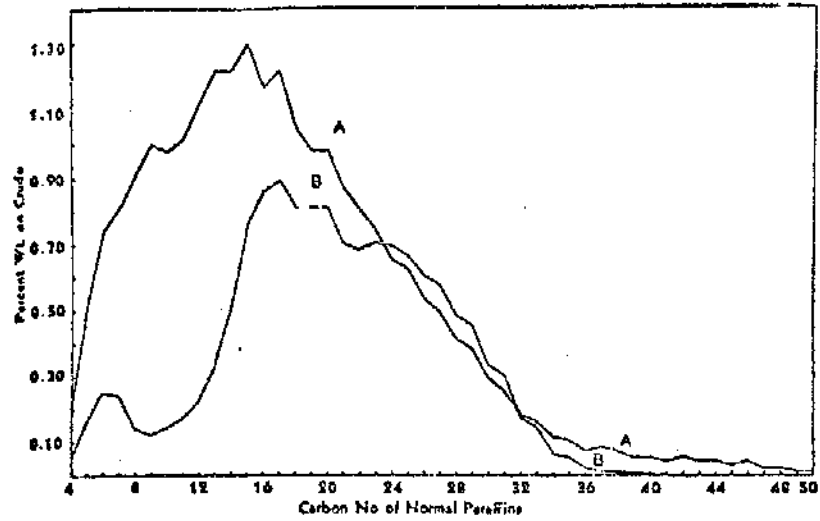
*SATURATED HYDROCARBONS BY CARBON NUMBER
IN NORTH SMYER CRUDE OIL*



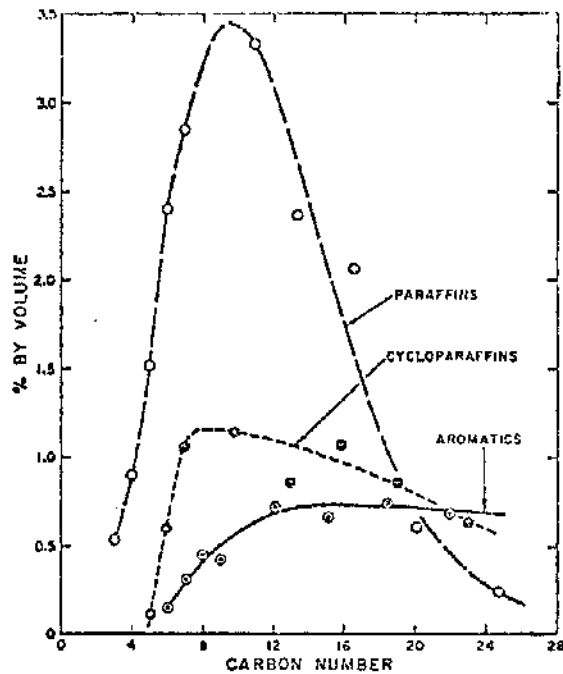
*AROMATIC TYPES BY CARBON NUMBER
IN SOUTH HOUSTON CRUDE OIL*

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

Figure 9
Crude Analyses



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



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

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

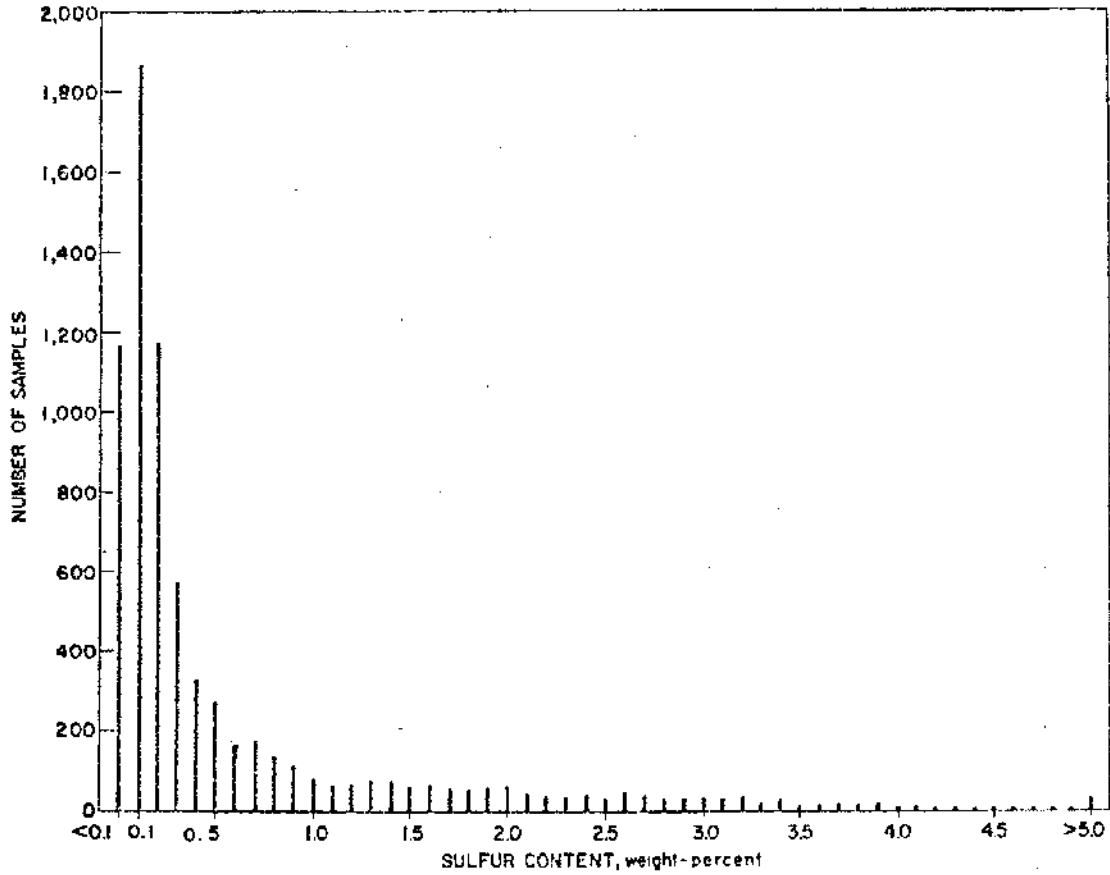
Table 15
Distribution of Aromatics (Volume Percent)

Aromatic Class	H-4	H-5	Lm,MA	EUS,MA	Cat. Cracked	Cat. Cracked
					Gas Oil (Fuel Oil)	Gas Oil (Fuel Oil)
Benzenes						
C6	13.1	1.7	-	0.3	0.2	0.3
C6H	4.1	4.4	-	1.4	0.5	1.7
C6I	1.3	2.5	0.4	1.6	1.0	3.5
C6J	6.5	1.0	0.7	1.0	1.4	5.3
C6K	8.3	0.7	0.4	0.8	1.8	4.8
C6L	-	0.2	0.7	0.3	1.4	3.7
C6M	-	0.1	0.7	0.3	1.0	1.4
C6N	-	-	0.7	0.3	0.7	0.7
C6O	-	-	0.4	-	1.4	0.3
C6P	-	-	0.6	-	0.4	0.1
C6Q	-	-	0.3	-	0.2	-
C6R	-	-	-	-	0.1	-
Indenes						
C7	-	-	-	-	0.1	-
C7H	0.1	0.3	-	0.2	0.3	0.3
C7I	0.1	1.0	-	1.0	1.5	2.5
C7J	0.2	1.0	-	1.3	3.8	2.5
C7K	-	0.4	-	1.2	2.3	1.8
C7L	-	0.1	0.1	0.7	1.5	0.9
C7M	-	-	0.2	0.3	0.8	0.4
C7N	-	-	0.1	0.1	0.3	0.7
C7O	-	-	0.1	-	0.2	-
C7P	-	-	-	-	0.2	-
C7Q	-	-	-	-	0.1	-
Benzenes						
C8	-	-	-	-	0.1	-
C8H	-	-	-	-	0.1	-
C8I	-	0.1	-	-	0.3	0.3
C8J	-	0.1	-	0.1	0.5	0.3
C8K	-	0.1	-	0.2	0.8	0.5
C8L	-	-	-	0.3	0.4	0.5
C8M	-	-	-	0.1	0.4	0.1
C8N	-	-	-	-	0.2	0.1
C8O	-	-	-	-	0.1	-
C8P	-	-	-	-	0.1	-
C8Q	-	-	-	-	0.1	-
Naphthalenes						
C10	0.1	0.4	-	0.1	0.2	0.1
C10H	0.1	1.5	-	0.4	1.8	2.3
C10I	0.2	1.7	-	1.0	4.8	8.7
C10J	-	0.4	-	1.0	3.5	4.8
C10K	-	0.1	-	0.3	1.5	3.4
C10L	-	-	-	0.1	1.2	2.3
C10M	-	-	-	-	0.4	0.4
C10N	-	-	-	-	0.3	0.1
C10O	-	-	-	-	0.2	-
C10P	-	-	-	-	0.1	-
Acenaphthenes						
C12	-	-	-	-	0.1	0.1
C12H	-	-	-	-	0.9	0.8
C12I	-	-	-	0.1	2.2	1.4
C12J	-	-	-	-	2.7	3.0
C12K	-	-	-	-	1.4	0.4
C12L	-	-	-	-	0.4	0.8
C12M	-	-	-	-	0.2	-
C12N	-	-	-	-	0.1	-
Acenaphthylenes						
C13	-	-	-	-	0.1	-
C13H	-	-	-	-	0.3	0.2
C13I	-	-	-	-	0.7	0.3
C13J	-	-	-	-	0.8	0.2
C13K	-	-	-	-	0.5	0.1
C13L	-	-	-	-	0.3	-
C13M	-	-	-	-	0.1	-
Anthracenes						
C14	-	-	-	-	0.3	0.1
C14H	-	-	-	-	0.3	0.1
C14I	-	-	-	-	0.4	0.1
C14J	-	-	-	-	0.3	-
C14K	-	-	-	-	0.1	-
Other						
Alkyls	30.7	30.8	2.7	41.7	31.4	22.8
Nonaromatic Cycloalkanes	27.5	24.4	44.6	27.7	33.0	30.3
Condensed Cycloalkanes	3.4	14.8	44.0	12.9	4.8	3.7
Dialkyls	1.4	0.0	2.3	3.8	4.4	9.7
Aromaticity	19.9	14.0	0.2	13.4	34.7	33.0
Average Substitution per Benzene Ring	1.0	1.2	1.0	2.3	see table	see table

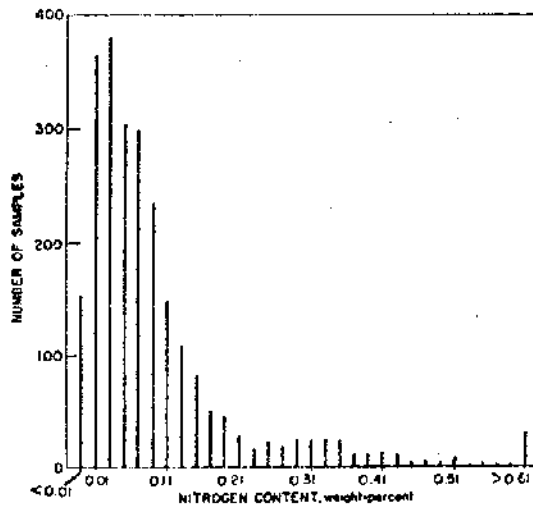
Source: C. L. Kearns et al, ACS Pet. Div. Preprints 3 No. 3, 73 (1958).

Figure 10

Sulfur and Nitrogen Distribution



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



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

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

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

3.3.1.3.1 Sulfur Compounds

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

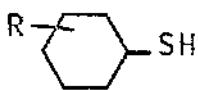
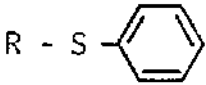
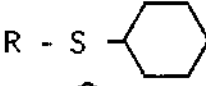
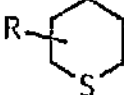
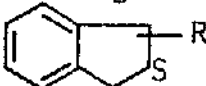
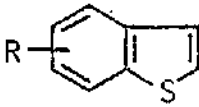
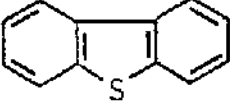
3.3.1.3.2 Nitrogen Compounds

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

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

Table 16

Sulfur Compounds Identified in Crude Oil(a)

Class	Structure
<p>Thiols</p> <p>Alkyl</p> <p>Cyclic</p>	<p>R - SH</p> 
<p>Sulfides</p> <p>Dialkyl</p> <p>Alkyl-Aryl</p> <p>Alkyl-Cycloalkyl</p> <p>Cyclic</p> <p>Thianindans</p>	<p>R - S - R</p>    
<p>Thiophenes</p> <p>Alkyl Benzothiophene</p> <p>Dibenzothiophene</p>	 

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

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

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

Table 17

Classes of Nitrogen Compounds


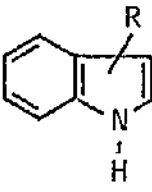
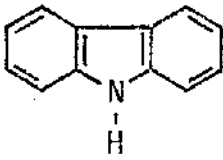
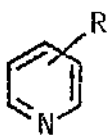
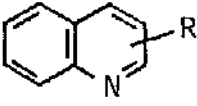
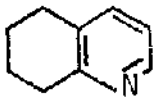
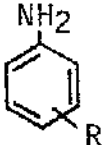
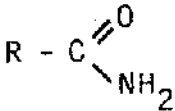
Type	Structure	Petroleum Material Found In	Reference
Pyrrole		374-635°F catalytically cracked product 305-620°F virgin Kuwait 480-540°F Cat. cracked cut from California crude 410-538°F Cat. cracked cut from California crude	Sauer et al, I&EC, <u>44</u> 2606 (1952) Sauer et al Nixon & Thorpe, J. Chem.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

Table 17 (Cont'd.)

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

3.3.1.3.3 Oxygen Compounds

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

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

Table 18

Classes of Oxygen Compounds

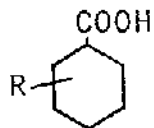
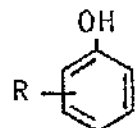
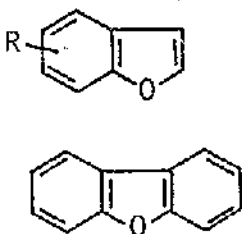
Type	Structure	Petroleum Material Found In	Reference
Aliphatic Carboxylic Acids (Fatty Acids)	$\text{CH}_3(\text{CH}_2)_n\text{COOH}$	Crude oil Catalytic cracked product 260-426°F	Lochte & Littmann "Petroleum Acids and Bases", Chem. Pub. Co. 1955 Gallo et al I&EC <u>44</u> 2610 (1952)
Naphthenic Carboxylic Acids		Crude oil kerosene fractions	Lochte & Littmann
Phenols		Crude oil Cat. cracked product 260-426°F Thermally cracked naphtha Cat. cracked product 340-430°F 400-700°F crude oil cut	Lochte & Littmann Gallo et al Field et al I&EC, <u>32</u> 489 (1940) Nixon & Thorpe, J. Chem. Eng. Data <u>7</u> , 429 (1962) Snyder, Acc. Chem. Res. <u>3</u> 290 (1970)
Furans		400-700°F crude oil cut	Snyder
Ketones	$\begin{array}{c} \text{O} \\ \\ \text{R} - \text{C} - \text{R}' \end{array}$	Crude oil 400-700°F crude oil cut	Lochte & Littmann Snyder
Alcohols	$\text{R} - \text{OH}$	Cat. cracked product 410-538°F	Hendrickson, ACS Pet. Div. Preprints <u>4</u> No. 1 55 (1959)

Table 18 (Cont'd.)

Type	Structure	Petroleum Material Found In	Reference
Esters	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R} - \text{C} \\ \backslash \\ \text{OR}' \end{array}$	Cat. cracked product 410-538°F 400-700°F crude oil cut	Hendrickson Snyder
Amides	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R} - \text{C} \\ \backslash \\ \text{NH}_2 \end{array}$	Cat. cracked product 410-538°F 400-700°F crude oil cut	Hendrickson Snyder
Hydroperoxides and Peroxides	$\begin{array}{c} \text{ROOH} \\ \text{ROOR} \end{array}$	Reaction product of autoxidation	

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