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COMPARISON OF THE PROPERTIES OF SOME SYNTHETIC CRUDES WITH PETROLEUM CRUDES

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SUMMARY

Physical properties and chemical compositions of six (6) synthetic crude oils were determined. Two were crudes prepared from oil shale, two were coal syncrudes, and two were solid materials from the solvent refined coal process. The results were compared to those of typical petroleum crudes, with the interest being the feasibility of making jet fuels from oil shale and coal syncrudes. The specific gravity, viscosity, and pour point of three (3) fluid crudes were measured. The results show that these crudes would be described as "heavier" rather than "lighter" crudes. The boiling range distribution of the crudes was determined by distillation and by gas chromatography. In addition, gel permeation chromatograms were obtained, giving a unique molecular weight distribution profile for each crude.

Elemental analyses for carbon, hydrogen, nitrogen, and sulfur were performed. The shale crudes had hydrogen contents at about the lower limit for typical petroleum crudes. The coal-derived crudes had hydrogen contents below that limit. The nitrogen contents of all of the crudes were higher than those of petroleum crudes, while the sulfur contents were all within the range found in petroleum. Hydrocarbon group type analyses were performed to determine the percentages of saturates, aromatics, polar compounds, and (hexane) insolubles. Finally, trace element concentrations were determined. It was found that the range in concentration of vanadium, an element whose presence in turbine fuels is of major concern, was lower than that of petroleum crudes. Sodium and potassium, other elements of concern, were present in comparatively high concentrations.

E-115

INTRODUCTION

Consideration is being given to the feasibility of making jet fuels from oil shale and coal syncrudes. The need arises because of the uncertainties in the availability of petroleum-based aviation turbine fuels. The characteristics of synthetic crudes have been generally defined, and in some instances the operations needed to make fuels have been suggested. The purpose of this work was to analyze some synthetic crudes which may become available in commercial quantities and compare the results to known petroleum crude properties. The results of the comparison should indicate possible processing problems, or suggest particular processing needs in the preparation of jet fuels. In this work, six (6) synthetic crude oils that were readily available were examined. Two were shale oils, prepared by the TOSCO and Paraho processes, respectively. Two were coal syncrudes prepared by the Synthoil and H-coal processes. Two were solid materials prepared from coal by the Solvent Refined Coal process.

A typical examination of petroleum crude oils determines physical properties such as specific gravity, viscosity, pour point and distillation range. In addition, elemental analyses for carbon and hydrogen are often performed. Less frequently, but when needed, the percentages of nitrogen and sulfur are determined. All of these properties were determined for the synthetic crudes in this work, since it is known that some nitrogen compounds are effective poisons for hydroprocessing catalysts, and the corrosive effects of sulfur compounds are recognized in petroleum processing.

In addition to these tests, hydrocarbon group type analyses and trace element analyses were performed. The group type analyses were done to determine the chemical makeup of the synthetic crudes. This would aid in determining the type of refining that would be needed in order to increase the availability of specification jet fuel. It has been suggested that shale oil could contribute directly by being fully integrated into refinery feed streams. Coal, on the other hand, may not be integrated directly into the jet fuel refining process. However, some hydroprocessed coal liquids could be used in jet fuel manufacturing to increase the supply by increasing the levels of naphthenes and aromatics, without exceeding current aviation specifications.

The trace element analyses were performed to determine if significant differences from petroleum crudes were evident. Of particular interest and concern would be the presence of vanadium and the alkali metals because of their effect on corrosion of turbine blades. Other elements are of concern, some because of environmental effects and others because of hydroprocessing catalyst deterioration effects. Thus, two methods, spark source mass spectrometry and optical emission spectrometry, that give multielement results, were used for the analyses. Several methods are being used for determining trace elements in various kinds of fuels, including oils of comparable viscosity and volatility as the crudes in this study. The results from inter-laboratory studies are being evaluated to assess the comparability of these various methods (ref. 1). The results to date indicate that different sample preparation and analytical techniques can lead to different results. Further, they also show that different laboratories using the same method report concentrations that vary in some cases by more than an order of magnitude. In this study, results were obtained by spark source mass spectrometry from two different laboratories, and by optical emission spectrometry from a third laboratory.

The boiling range of a crude oil is traditionally obtained by standard atmospheric and vacuum distillation techniques applicable to petroleum products which can be vaporized at a maximum liquid temperature of 672 K at pressures down to 1.33×10^2 newtons/meter^2 (1 torr). Recently two other techniques have been used to obtain an estimation of the distillation range of crude oils. The first employs a temperature programmed gas chromatographic system and gives a boiling point distribution as determined by gas chromatography. The second, a liquid chromatographic technique, gel permeation chromatography, has been applied to petroleum residua and can provide some molecular weight discrimination in the high molecular weight region where distillation is impractical. For a highly complex mixture such as a crude oil, a gross separation is expected. However, a molecular weight distribution profile can be obtained in a short time and the profiles have been shown to be unique for each of the crude oils examined. In this work, the gas chromatographic technique was applied to three of the crude oils, while the gel permeation technique was applied to all six crude oils to obtain the distillation data.

PROCESSES FOR PRODUCING SYNTHETIC CRUDE OILS

Detailed descriptions for producing synthetic crude oils from oil shale and coal are given in reference 2. Brief descriptions of the methods used to obtain the crudes used in this work are given here.

The methods for obtaining oil from oil shale involve thermal decomposition. Many kinds of retorts have been designed to apply heat to shale. In the TOSCO II process, raw shale is preheated by dilute phase fluid bed techniques. The preheated feed is then contacted with heated ceramic pellets in a pyrolysis drum and pyrolysis vapors are condensed in a fractionator. The Paraho process uses a cylindrical, vertical-shaft vessel for its retort. Shale rock is fed in at the top of the retort. Gas-air mixtures are entered through a series of burner bars below and the amount of gas-air mixture is controlled to maintain a desired temperature. Retorted oil and gas from the shale rise with the products of combustion through the descending fresh shale, preheating it and condensed droplets of oil are collected as a vapor mist near the top of the shale bed.

Catalytic coal hydrogenation processes have been investigated for some time and have many variants. One of these variants involved the hydrogenation of coal/oil pastes mixed with a catalyst in tubular reactors at high pressure and low residence times to give high yields of liquid products. The Synthoil process is an outgrowth of an effort to hydrodesulfurize coal in a similar system using highly turbulent flow over a fixed catalyst bed. The reactor is packed with catalyst to about 50 percent of the volume and the ground coal to be fed is kept suspended in tar or in recycled product oil in a stirred feed system. Compressed hydrogen is mixed with the feed coal slurry ahead of a preheater which serves to bring the combined stream to reaction temperature. The product from the reactor is cooled and separated into gaseous, liquid and solid phases.

In the H-Coal process, coal is dried, pulverized and slurried with coal-derived oil for charging to the coal hydrogenation unit. The heart of the process is a unique reactor design in which the coal-oil slurry is charged continuously with hydrogen to a reactor containing a bed of ebullated catalyst where the coal is catalytically hydrogenated and converted to liquid and gaseous products. In the ebullated bed the upward passage of the solid, liquid and gaseous materials maintains the catalyst in a fluidized state. The relative size of the catalyst and coal is such that only the unconverted coal, ash, liquid and gaseous products leave the reactor as overhead products, while the catalyst, which is coarser, is retained in the reactor. Catalyst can be added and withdrawn continuously so a constant activity can be maintained. The reactor provides a simple means of controlling reactor temperature and an effective contact between reaction species and the catalyst, permitting a satisfactory degree of reaction at reasonable operating pressure.

In the Solvent Refined Coal process, coal is pulverized and mixed with a solvent to form a slurry. The slurry is pressurized, mixed with hydrogen and heated. Nearly all of the organic matter in the coal is dissolved in the solvent. The reaction product is flashed to separate gases and the liquid is filtered to remove the mineral residue (ash and undissolved coal). The liquid is then fractionated to recover the solvent, which is recycled to slurry more feed coal. The substance remaining after the solvent has been removed is a heavy residual fuel called Solvent Refined Coal, with a melting point of about 450 K.

The samples of crudes used in this work were obtained from the following sources:

TOSCO (shale oil) - The Oil Shale Corp., Golden, CO.
PARAHO (shale oil) - Paraho Development Engr., Inc., Rifle, CO.
Synthoil (coal syncrude) - Pittsburgh Energy Research Center, ERDA, Pittsburgh, PA.

H-Coal (coal syncrude) - Hydrocarbon Research, Inc. Trenton, NJ
Southern Services (solvent refined coal) - Southern Services, Inc.
Birmingham, AL.
PAMCO (solvent refined coal) - Pittsburgh and Midway Coal Mining Co.
Dupont, WA.

EXPERIMENTAL DETERMINATION OF PROPERTIES

The densities were determined by weighing a measured amount of the liquid at the specified temperature. An H-Coal sample was not available for this measurement and the Solvent Refined Coal values were not obtained because these samples were solids at ambient temperature (with a melting point of about 450 K). The same reasons held true for the pour point measurements, which were done according to ASTM D-97, Test for Pour Point of Petroleum Oils. Viscosity measurements were attempted on the Synthoil sample and the two shale oils (TOSCO and Paraho) using standard capillary viscometric techniques, but values were not obtained by this method because there was difficulty in reading the meniscus. Values were obtained by using a vibrating sphere viscometer which is beginning to replace the capillary viscometer as a more than satisfactory alternative instrument in the procedures of ASTM D2857 and D1243.

The weight percents of carbon and hydrogen were determined by elemental analysis (Gulf Research and Development Co.) using a microcombustion technique. The nitrogen content was determined by Kjeldahl analysis and sulfur by ASTM D129, Test for Sulfur in Petroleum Products (General Bomb Method). The compositional analysis was done by the Gulf Research and Development Company using high performance liquid chromatography, giving the four group types, saturates, aromatics, polar compounds and hexane insolubles.

The distillations were accomplished according to ASTM D2892, Distillation of Crude Petroleum (15 Theoretical Plate Column) in a pressure range from about 1.33×10^3 to 6.67×10^3 newton/meter^2 (10 to 50 torr) absolute pressure. The boiling point distribution by gas chromatography was determined by the Army Fuels and Lubricants Research Lab using a linear temperature program to a maximum temperature corresponding to a C_{55} paraffin standard, boiling at 869 K. The data given has been corrected for non-volatile residue, and heavy residue boiling above about 873 K. The gel permeation chromatograms were obtained by DeBell and Richardson Testing Institute using standard gel columns.

The calculated values for molecular size were based on the angstrom values of polypropylene glycol standards and straight chain hydrocarbons.

Two methods, spark source mass spectrometry and optical emission spectrometry, were used to obtain the trace element data with both providing multielement results. In spark source mass spectrometry, the sample is compounded in a graphite or silver electrode, then ionized with a high intensity spark. A determination is then made of the intensities of the ions of various mass-to-charge ratios separated by a magnetic field. In optical emission spectrometry, the sample is excited in a spark or arc to produce line spectra of the elements. Two sets of data were obtained from mass spectrometry, one from Accu-Labs Research, Inc. and one from Ledoux and Company.

RESULTS AND DISCUSSION

Physical Properties

The results from the measurements of density, pour point, and viscosity are given in table 1. The density values are also shown in figure 1, together with a range of values usually found for shale and coal crudes. A broad range that can be found for petroleum crudes is also included, though most petroleum crudes fall within a much narrower range. The densities of the shale crudes are within the range usually found for shale, as was that of Synthoil for coal crudes. The density of the Synthoil was higher than the most dense petroleum crude. Since the properties of coal syncrudes are dependent on the degree of processing of the parent coal, it can be concluded that this particular sample of syncrude was the result of moderate processing. Additional or more severe processing would yield a less dense product.

The results from the pour point measurements, at 290 K and above, are higher than those in a typical petroleum crude which range from about 233 to about 258 K. The fluid synthetic crudes are more viscous than a typical petroleum crude. The viscosity results are plotted in figure 2 together with the range of values for some petroleum crudes. The shale crudes are slightly more viscous than a typical highly viscous petroleum crude, while the Synthoil sample is strikingly more viscous. It would be of interest to examine the viscosities of other, less dense coal syncrudes.

Chemical Composition

The results for elemental analyses for percent hydrogen, nitrogen, and sulfur by weight are given in table 1. The results for hydrogen are shown in figure 3, together with the ranges of values usually found for shale, coal and petroleum crudes, as well as coal itself. It can be seen that the hydrogen content for each of the two shale crudes are about as expected, while the value for the coal crude, Synthoil, is toward the lower end of the range, again indicating the result of mild processing of the original coal. The values for the Solvent Refined Coal samples are about as expected, remembering that the Solvent Refined Coal process yields a coal-like product. In figure 4 are plotted the results for the nitrogen content measurements, together with the ranges of values for syncrudes and petroleum crudes. The values for the shale crudes fall within the expected range, while some of those for coal do not. The value for Synthoil is within the range, but the values for the solvent refined coals are significantly higher. Since these materials are more like coal than like coal syncrude, perhaps it would not be unexpected if their properties differed from a typical crude. The results for sulfur content are plotted in figure 5 together with typical range values for shale, coal, and petroleum crudes. The values found for the TOSCO shale and the Paraho shale are within the shale range, as are the values for the coal crudes. The values for the Solvent Refined Coal Samples are toward the upper end of the coal range. All of crudes, though, fit within the range that has been found in petroleum crudes, though the usual petroleum crude has a sulfur content below 1 percent.

The results for the hydrocarbon group type analysis are given in table 1. In the separation scheme used, values for saturates, aromatics, polar compounds and hexane insolubles were obtained. Since the hydrogen content values were at 11 percent and lower, it is expected that unsaturation in the crudes would be high. The highest percentages for saturates are found in the two shale crudes. The next highest is found in the Synthoil sample which, predictably, is not very high. The H-Coal sample is similar, while the Solvent Refined Coal samples are demonstrably coal-like. The polar compounds are primarily nitrogen, oxygen and sulfur heterocyclic compounds. The hexane insolubles are higher molecular weight, polycyclic compounds.

Distillation and Molecular Weight

The results for the boiling range distribution determinations are given in table 2 and figures 6 to 8. The distillation results for the three syncrudes measured are similar. About 30 percent of the crude comes off below 625 K, which is achieved at vacuum levels down to about 1.33×10^3 newton/meter^2 (10 torr). Distillation at lower pressures was not performed, but using standard procedures down to 1.33×10^2 newton/meter^2 (1 torr), would have produced material boiling about 672 K. In the usual characterization of a crude, everything above this temperature is considered residue and is largely uncharacterized. To further characterize such material, high-vacuum equipment must be used to avoid the use of high temperatures. The results from the gas chromatographic boiling point distribution show that about 80 percent comes off below 875 K. The gas chromatography system was calibrated up to a maximum temperature corresponding to a C_{55} paraffin standard, boiling at 869 K. Higher boiling point material is eluted from the column but cannot be described as to boiling point distribution because of current limitations in column maximum temperature technology. In figure 9 there is a comparison of the boiling range distribution of the synthetic crudes with the range found in typical petroleum crudes which indicates that all three are close to or exceed the usual upper limit.

The results from the gel permeation chromatographic measurements are shown in figures 10 to 16. Figure 10 shows the calibration curve used for determining the molecular size (molecular weight) distribution of the compounds in the crudes. The logarithm of the molecular size of two polypropylene glycols and two straight chain hydrocarbons are plotted against the count number, which is a measure of the elution volume. The molecular weight range encompassed is about 100 to 3000. The other figures show the chromatograms obtained for the syncrudes, where a relative concentration is plotted against the count number. All of the samples fall within the molecular size distribution encompassed by the calibration curve but, as expected, have different profiles. Crude oil chromatograms are usually unique and can serve as a "fingerprint" for the material.

Further analysis was done to determine the dispersity, i.e., the ratio of the weight-average molecular size to the number-average molecular size, which is essentially a measure of the "broadness" or relative spread in molecular sizes (ref. 3). The larger the value, the broader the distribution will be. The results shown here: Synthoil 1.50, SSSRC 1.53, Pamco SRC 1.48, TOSCO 1.71, Paraho 1.41, H-Coal 1.72 ranged from 1.41 to 1.72 for these crudes. It can be seen that the values for the two solvent-refined coal materials are about the same but the values for the two shale samples are different. For the other two coal syncrude samples, it can be seen also that the dispersity is greater for H-Coal than for Synthoil. Further work with similar measurements on other crude samples would determine the basis for the dispersity differences.

For more information for selective processing, further analysis of gel permeation chromatographic fractions can be made. By using suitable calibration plots, differences in composition can be determined.

Trace Element Determinations

The data for the trace element determinations are given in tables 3 to 11. It can be seen that in some instances the reported concentrations vary by more than an order of magnitude. The need for determining the accuracy of trace analytical methods is recognized and standard reference materials are being developed by the National Bureau of Standards. In the meantime, no single method can be relied on for all elements in any particular matrix. The concerns regarding crude oils are related to the poisoning of processing catalysts and the corrosion of equipment. The concerns regarding jet fuels are related to environmental pollution and turbine blade corrosion. The concentrations of vanadium, sodium and potassium are usually considered important due to their known deleterious effect on turbine blades. These values are given in table 3. The concentration of vanadium in the syncrudes measured here are low, with a maximum of 43 ug g^{-1}. Sodium and potassium, though, show some high concentrations. Other elements in high concentrations in both shale and coal crudes are Mg, Al, Si, Ca, and Fe. These values are given in table 4. In tables 5 to 10 are the values for the concentrations of a number of other elements determined by spark source mass spectrometry and optical emission spectrometry. Other elements reported as being below the detection limit in all of the samples were Ru, Rh, Pd, Te, Re, Os, Ir, Pt, Au, Tm, and Lu.

In table 11 are listed the concentration ranges of some elements found in petroleum crude oils. These values, from reference 4, were from four crudes which were chosen to show the wide range that occurs. Shown also in the table is the range found for the syncrudes studied in this work. As noted before, vanadium is low when compared to the amounts typically found in petroleum crudes. The values for iron are high, particularly in the coal materials. One value, >1% from the H-Coal sample, was not included in the range. This material was particularly lumpy and may not have been uniformly sampled, leading to a number of elements being listed as >1%. For a good number of the elements compared, the order of magnitude of the concentrations are the same for the petroleum and syncrudes. The maximum value for the sulfur content in the syncrudes is about an order of magnitude lower than that in the petroleum crudes. However, it should be noted that the values obtained by ASTM D129, shown in table 1, are about an order of magnitude higher than those obtained by the multi-element techniques. This kind of difference can be expected, unless the multi-element methods are optimized for specific elements, which was not the case in this study.

CONCLUDING REMARKS

The characterization of any petroleum (or synthetic) crude is relative and never complete. The usual examination of a petroleum crude includes some physical properties, distillation data, and sometimes elemental analyses for carbon and hydrogen. When needed, the percentages of nitrogen and sulfur are determined. It can be expected that with crudes of the future that the percentages of nitrogen and sulfur will always be needed. The results for nitrogen in this study show that for most of the crudes the percentage is greater than 1 percent which is substantially higher than the usual petroleum crude. It is known that nitrogen compounds are poisons for a number of processing catalysts and thus will present a specific problem to be addressed. The data for sulfur did not indicate a specific problem. In other data on chemical composition the results show that the shale crudes were more saturated than the coal crudes, approaching the level of petroleum crudes and on that basis could be integrated into existing refinery feed streams.

The distillation data for the fluid crude oils, shale and coal, showed that these materials fit within the broad range found for the petroleum crudes. The upper temperature range was determined by a gas chromatographic technique, obviating the need for vacuum distillation. By another chromatographic technique, gel permeation, unique molecular weight distribution profiles for all of the crudes were obtained, reaching into the high molecular weight region where distillation is impractical.

The results of the trace metal determinations are interesting in that it was found that the concentration of vanadium, a potentially troublesome element for turbine blade corrosion, was generally below the level found in a petroleum crude. By contrast, other elements of concern, sodium and potassium, had high concentrations, even in the shale crudes. The results also show the need for determining the accuracy of trace analytical methods, since the results in some instances differed by more than an order of magnitude.

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TABLE 1. - SYNCRUDE PROPERTIES

	SYNTHOIL	TOSCO	PARAHO	H-COAL	SS SRC	PAMCO SRC
Density, g/ml (295K)	1.081	0.913	0.892	------	------	---------
Pour Point K	290	291	298	------	------	---------
Viscosity, cs (361K)	154.74	11.074	10.162	------	------	---------
Hydrogen, Weight %	7.75	11.05	11.21	------	5.76	4.70
Carbon, Weight %	87.01	84.11	83.79	------	87.04	74.39
Nitrogen, Weight %	1.07	1.96	2.15	------	2.02	1.96
Sulfur, Weight %	0.54	0.76	0.63	------	0.90	0.88
Saturates, wt. %	4.4	23.1	20.7	3.0	0.8	0.5
Aromatics, wt. %	37.0	35.4	41.5	48.3	3.8	2.7
Polar Compounds, wt. %	18.8	36.7	36.5	4.7	2.6	1.2
Insolubles (Hexane), wt.%	39.8	4.8	1.3	44.0	92.8	95.6

TABLE 2. - CRUDE OIL BOILING POINT DISTRIBUTION

(a) BY GAS CHROMATOGRAPHY

PERCENT RECOVERED	TOSCO t,K	SYNTHOIL t,K	PARAHO t,K
IBP	421	569	430
5	472	511	508
10	508	540	552
15	540	558	576
20	564	577	600
25	586	593	628
30	611	612	655
35	638	628	681
40	665	645	705
45	699	667	721
50	728	686	740
55	754	712	757
60	779	737	776
65	806	771	794
70	834	799	810
75	859	829	832
76.4	871		
80		860	854
83.1			870
83.5		877	
Residue	23.6%	16.5%	16.9%

(b) BY DISTILLATION

TOSCO		SYNTHOIL		PARAHO	
PERCENT RECOVERED	t,K	PERCENT RECOVERED	t,K	PERCENT RECOVERED	t,K
IBP	408	IBP	441	IBP	433
2.45	450	2.1	481	2.35	489
5.94	483	7.3	519	5.58	515
11.6	508	12.3	545	9.03	536
18.2	547	17.5	574	13.73	561
23.3	563	23.3	597	19.25	589
25.8	570	29.0	619	26.49	616
33.1	614			30.3	633

TABLE 3. - CONCENTRATIONS OF ELEMENTS DELETERIOUS TO TURBINE BLADES, $\mu g\ g^{-1}$

	SYNTHOIL			SS SRC			PAMCO SRC			TOSCO SHALE			PARAHO SHALE			H-COAL	
	1			2			3			4			5			6	
	SSMS	SSMS	OES	SSMS	SSMS	OES	SSMS	SSMS	OES	SSMS	SSMS	OES	SSMS	SSMS	OES	SSMS	SSMS
V	3.5	1.0	1.0	10	2	4.0	17	20	8.0	1.2	0.5	0.3	0.27	0.1	0.7	43	1
Na	350	20	0.5	320	> 200	8	600	50	9	85	500	0.5	20	10	6	650	100
K	880	100		400	20		81	500		91	200		23	10		≈0.5	200

TABLE 4. - ELEMENTS PRESENT IN HIGH CONCENTRATIONS IN BOTH SHALE AND COAL, $\mu g\ g^{-1}$

Mg	740	20	2	45	50	5	17	50	15	220	50	130	49	20	45	≈3600	50
Al	≈2100	1000	21	95	> 200	33	510	>200	210	180	>200	96	40	5	4	>1%	>200
Si	> 1%	50	23	280	50	22	260	>1000	290	890	100	220	130	5	10	>1%	200
Ca	≈1100	200	30	53	50	28	53	500	38	≈1000	500	350	55	20	40	>1%	500
Fe	400	200	13	720	500	310	≈2700	>1000	350	100	50	57	110	20	24	>1%	500

TABLE 5. - TRACE ELEMENT DETERMINATION BY SPARK SOURCE MASS SPECTROMETRY AND OPTICAL EMISSION SPECTROMETRY, $\mu g\ g^{-1}$

#1 SYNTHOIL

ELEMENT	SSMS	SSMS	OES
Li	2.0	0.1	
Be	0.66	0.05	2
B		1.0	31
F	35	2.0	
P	180	5	<2
S	260	50	
Cl	5.8	1.0	
Sc	1.9	0.5	
Ti	310	50	3
Cr	3.6	>1000	2
Mn	0.24	0.5	4
Co	0.27	0.05	<0.1
Ni	1.0	1.0	3.0
Cu	0.77	0.5	2
Zn	4.0	2.0	19
Ga	0.56	0.1	
Ge	0.50	<0.5	
As	0.72	0.5	
Se	0.08	0.05	
Br	4.4	0.05	
Rb	1.7	1.0	
Sr	26	5.0	40
Y	2.8	10.0	0.3
Zr	13	2.0	5
Nb	0.88	0.2	50
Mo	0.36	0.5	<0.05
Ag		<0.2	
Cd	0.12	<0.5	
Sn	0.13	<0.5	<1
Sb	0.06	<0.2	
I	3.1	<0.1	
Cs	0.12	0.1	
Ba	50	5.0	
La	1.8	1.0	
Hf	0.10	<1.0	
Ta	0.08	<1.0	<1
W		<1.0	<1
Hg	<0.01	<2.0	
Tl	0.06	<0.5	
Pb	0.51	0.5	<1
Bi		<0.2	
Ce	2.2	2.0	
Pr	0.55	0.1	
Nd	0.17	0.2	
Sm	0.34	<1.0	
Eu	0.05	<0.5	
Gd		<1.0	
Tb		<0.2	
Dy	0.50	<1.	
Ho		<0.2	
Er		<1.0	
Yb	0.22	<1.0	
Th	0.38	<0.2	
U	0.32	<0.2	

TABLE 6. - TRACE ELEMENT DETERMINATION BY SPARK SOURCE MASS SPECTROMETRY AND OPTICAL EMISSION SPECTROMETRY, $\mu g\ g^{-1}$

#2 - SOUTHERN SERVICES SOLVENT REFINED COAL

ELEMENT	SSMS	SSMS	OES
Li	0.02		
Be	1.3	0.2	1
B		1	25
F	1.6	0.5	
P	14	1	< 2
S	400	10	
Cl	20	1	
Sc	0.11	0.5	
Ti	150	50	60
Cr	6.5	10	6
Mn	14	10	12
Co	0.28	0.2	< 0.1
Ni	1.1	1	4
Cu	0.30	2	< 0.1
Zn	3.2	0.5	< 2
Ga	0.12	1	
Ge	0.46	< 0.5	
As	< 0.17	1	
Se		0.05	
Br	0.40	< 0.05	
Rb		0.1	
Sr	0.47	1	28
Y	0.12	0.1	
Zr	0.32	10	< 0.2
Nb	0.34	0.2	
Mo	< 0.09	0.5	< 0.05
Ag		< 0.2	
Cd		< 0.5	
Sn		0.5	< 1
Sb		< 0.2	
I	0.61	< 0.1	
Cs		< 0.1	
Ba	0.21	0.2	
La		0.1	
Hf	< 0.15	< 1	
Ta	0.30	< 1	< 1
W	< 0.09	< 1	< 1
Hg	< 0.01	< 2	
Tl		< 0.5	
Pb	0.14	1	< 1
Bi	< 0.06	< 0.2	
Ce		0.2	
Pr		< 0.2	
Nd		< 1	
Sm	< 0.19	< 1	
Eu		< 0.5	
Gd		< 1	
Tb		< 0.2	
Dy	< 0.06	< 1	
Ho		< 0.2	
Er		< 1	
Yb	< 0.25	< 1	
Th	< 0.09	0.2	
U	< 0.08	0.2	

TABLE 7. - TRACE ELEMENT DETERMINATION BY SPARK SOURCE MASS SPECTROMETRY AND OPTICAL EMISSION SPECTROMETRY $\mu g\ g^{-1}$

#3 - PAMCO SOLVENT REFINED COAL

ELEMENT	SSMS	SSMS	OES
Li	0.15	0.2	
Be	0.85	0.1	5
B		5	47
F	8.9	2	
P	27	100	<2
S	820	100	
Cl	9.9	1	
Sc	<0.13	1	
Ti	270	200	55
Cr	3.1	10	2
Mn	30	10	15
Co	0.23	1	<0.1
Ni	2.0	1	7.0
Cu	2.6	2	5
Zn	13	10	29
Ga	0.23	1	
Ge		0.5	
As	0.74	2	
SE		0.1	
Br	7.7	0.05	
Rb	0.20	1	
Sr	3.5	5	2
Y	1.5	5	
Zr	4.9	5	<0.2
Nb	0.23	0.5	
Mo	0.37	0.5	<0.05
Ag		<0.2	
Cd		<0.5	
Sn		0.2	<1
Sb		<0.2	
I	2.3	<0.1	
Cs		<0.1	
Ba	2.7	2	
La	0.28	2	
Hf	<0.23	<1	
Ta	0.17	<1	<1
W	<0.13	<1	<1
Hg	<0.01	<2	
Tl		<0.5	
Pb	0.88	1	<1
Bi		<0.2	
Ce	0.23	5	
Pr		0.2	
Nd		0.2	
Sm	<0.28	<1	
Eu		<0.5	
Gd		<1	
Tb		<0.2	
Dy		<1	
Ho		<0.2	
Er		<1	
Yb	<0.38	<0.2	
Th	<0.13	0.5	
U	<0.11	0.5	

TABLE 8. - TRACE ELEMENT DETERMINATION BY SPARK SOURCE MASS SPECTROMETRY AND OPTICAL EMISSION SPECTROMETRY, $\mu g\ g^{-1}$

#4 - TOSCO SHALE

ELEMENT	SSMS	SSMS	OES
Li	0.67	A[a]	
Be		< 0.5	0.02
B		0.2	< 20
F	6.0	2	
P	68	28	< 2
S	110	200	
Cl	0.22	1	
Sc	0.05	0.2	
Ti	16	5	1.0
Cr	0.32	5	0.1
Mn	1.4	0.5	0.3
Co	0.95	0.5	1
Ni	10	1	0.5
Cu	0.62	1	0.2
Zn	13	1	4
Ga	0.08	< 0.1	
Ge		< 0.5	
As	19	2	
Se	0.10	0.05	
Br		< 0.05	
Rb	0.18	0.2	
Sr	2.1	2	3
Y		< 0.1	
Zr	0.49	0.5	0.2
Nb	0.09	< 0.2	
Mo	0.37	0.5	< 0.05
Ag	0.07	< 0.2	
Cd		0.2	
Sn	0.26	0.5	< 1
Sb	0.11	< 0.2	
I		< 0.1	
Cs		< 0.1	
Ba	2.9	1	
La	0.28	0.1	
Hf		< 1	
Ta		< 1	< 1
W	0.11	< 1	< 1
Hg	0.03	< 2	
Tl		< 0.5	
Pb	0.37	1	< 1
Bi		0.1	
Ce	0.21	0.5	
Pr	0.13	< 0.2	
Nd	0.19	< 1	
Sm		< 1	
Eu		< 0.5	
Gd		< 1	
Tb		< 0.2	
Dy		< 1	
Ho		< 0.2	
Er		< 1	
Yb		< 1	
Th	0.10	< 0.2	
U	0.05	< 0.2	

[a] Matrix interference.

TABLE 9. - TRACE ELEMENT DETERMINATION BY SPARK SOURCE MASS SPECTROMETRY AND OPTICAL EMISSION SPECTROMETRY, $\mu g\ g^{-1}$
#5 - PARAHO SHALE

ELEMENT	SSMS	SSMS	OES
Li	0.15	0.1	
Be		< 0.05	< 0.01
B		0.05	< 20
F	1.4	1	
P	4.6	1	< 2
S	48	20	
Cl	0.10	0.5	
Sc		0.1	
Ti	1.7	1	0.5
Cr		0.5	0.04
Mn	1.8	0.2	0.4
Co	1.4	0.5	0.3
Ni	6.1	1	0.8
Cu	0.09	0.5	0.1
Zn	2.5	0.5	2
Ga		< 0.1	
Ge		< 0.5	
As	30	2	
Se		< 0.05	
Br		< 0.05	
Rb		< 0.2	
Sr	0.29	< 1	0.2
Y		< 0.1	
Zr		< 0.5	0.1
Nb		< 0.2	
Mo	0.08	1	0.08
Ag		< 0.2	
Cd		< 0.5	
Sn		< 0.5	< 1
Sb		< 0.2	
I		< 0.1	
Cs		< 0.1	
Ba	0.20	< 0.5	
La		< 0.2	
Hf		< 1	
Ta		< 1	< 1
W		< 1	< 1
Hg	< 0.01	< 2	
Tl		< 0.5	
Pb	0.09	0.5	< 1
Bi		< 0.2	
Ce		< 0.2	
Pr		< 0.2	
Nd		< 1	
Sm		< 1	
Eu		< 0.5	
Gd		< 1	
Tb		< 0.2	
Dy		< 1	
Ho		< 0.2	
Er		< 1	
Yb		< 1	
Th		< 0.2	
U		< 0.2	

TABLE 10. - TRACE ELEMENT DETERMINATION BY SPARK SOURCE MASS SPECTROMETRY, $\mu g\ g^{-1}$

ELEMENT	SSMS	SSMS
Li	21	A[a]
Be	1.6	0.1
B		5
F	430	2
P	140	2
S	630	20
Cl	330	2
Sc	4.7	0.2
Ti	470	10
Cr	22	5
Mn	310	5
Co	40	1
Ni	10	1
Cu	5.7	1
Zn	100	1
Ga	0.94	0.2
Ge	1.2	0.2
As	1.0	0.1
Se	0.61	0.05
Br	4.8	< 0.05
Rb	9.7	1
Sr	22	2
Y	3.3	0.5
Zr	22	1
Nb	2.1	< 0.2
Mo	2.7	0.2
Ag	0.05	< 0.2
Cd	1.0	< 0.5
Sn	11	0.2
Sb	0.23	0.1
I	1.1	< 0.1
Cs	1.1	< 0.1
Ba	21	1
La	7.2	0.5
Hf	0.30	< 1
Ta	0.09	< 1
W	0.70	< 1
Hg	< 0.01	< 2
Tl	0.22	< 0.5
Pb	2.8	2
Bi		< .2
Ce	14	1
Pr	0.49	0.1
Nd	2.4	0.1
Sm	1.2	< 1
Eu	0.18	0.5
Gd	0.14	< 1
Tb	0.23	< 0.2
Dy		< 1
Ho	0.06	< 0.2
Er	0.06	< 1
Yb	0.35	< 1
Th	2.1	< 0.2
U	0.61	< 0.2

[a] Matrix interference.

TABLE 11. - COMPARISON OF CONCENTRATION RANGES OF SOME ELEMENTS IN PETROLEUM AND SYNTHETIC CRUDES
[CONCENTRATION, $\mu g\ g^{-1}$.]

ELEMENT	TRACE ELEMENT CONTENTS OF SOME PETROLEUM CRUDE OILS (BY NEUTRON ACTIVATION ANALYSIS) FROM 4 CRUDES TO SHOW WIDE CONCENTRATION RANGE REF. 4	TRACE ELEMENT CONTENTS OF SOME SYNTHETIC CRUDES - THIS WORK
V	.68 - 1100	.27 - 43
Cl	1.47 - 25.5	.10 - 330
I	1.36	< .1 - 3.1
S	9.90 - 4694	10 - 820
Na	2.92 - 20.3	10 - 650
K	4.93	10 - ≈ 5,000
Mn	.048 - 1.20	0.2 - 310
Cu	0.19 - 0.93	0.30 - 2.6
Ga	.01 - 0.30	0.08 - 0.94
As	.0024 - 0.655	0.1 - 30
Br	.072 - 1.33	< .05 - 7.7
Mo	7.85	< .09 - 2.7
Cr	.0023 - 0.640	0.32 - 22
Fe	0.696 - 68.9	20 - ≈ 2700
Hg	.027 - 23.1	< .01 - 0.03
Se	.0094 - 1.10	< .05 - 0.61
Sb	.055 - .303	.06 - 0.23
Ni	.609 - 117	1 - 10
Co	.0027 - 13.5	.05 - 40
Zn	.670 - 62.9	0.5 - 100
Sc	.000282 - .0088	.05 - 4.7
U	.015	.05 - .61

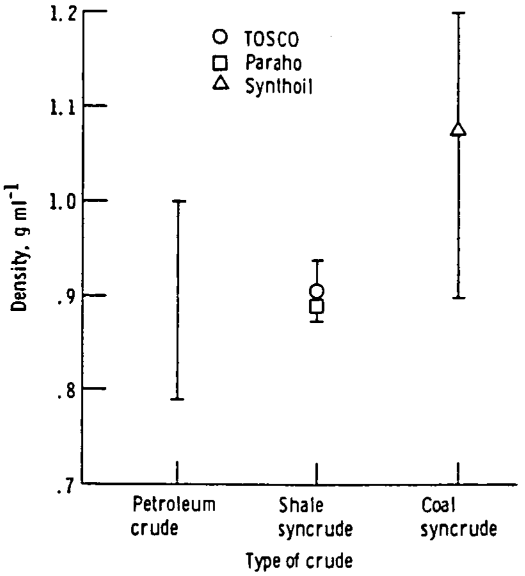

Figure 1. - Comparison of synthetic crude densities to petroleum crude densities. Vertical bars indicate normal range of variability for each type of crude.

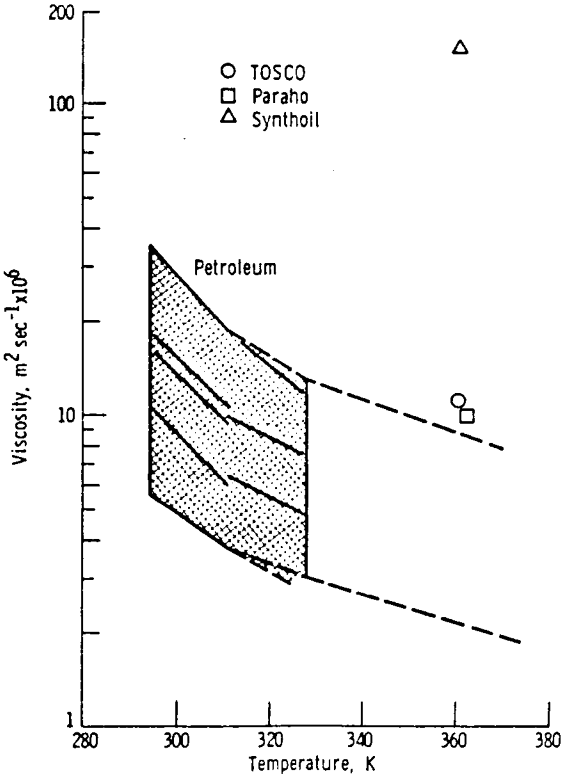

Figure 2. - Comparison of viscosities of some synthetic crudes to petroleum crudes.

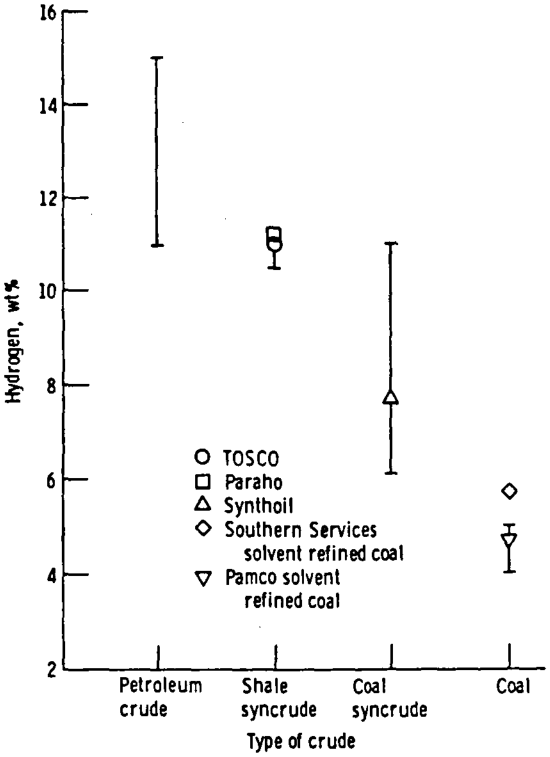

Figure 3. - Comparison of hydrogen content of synthetic crudes to petroleum crudes. Vertical bars indicate normal range of variability for each type of crude.

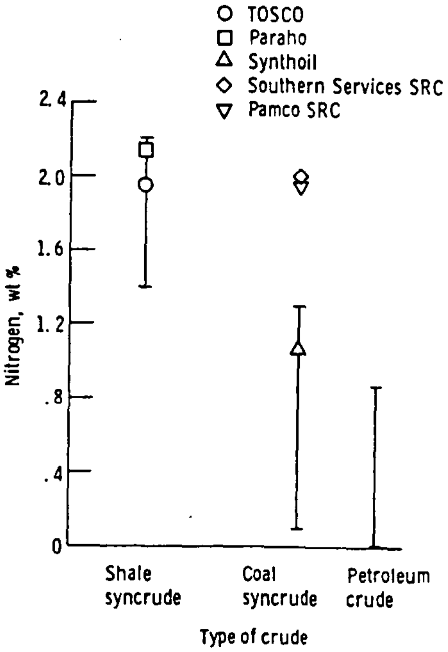

Figure 4. - Comparison of nitrogen content of synthetic crudes to petroleum crudes. Vertical bars indicate normal range of variability for each type of crude.

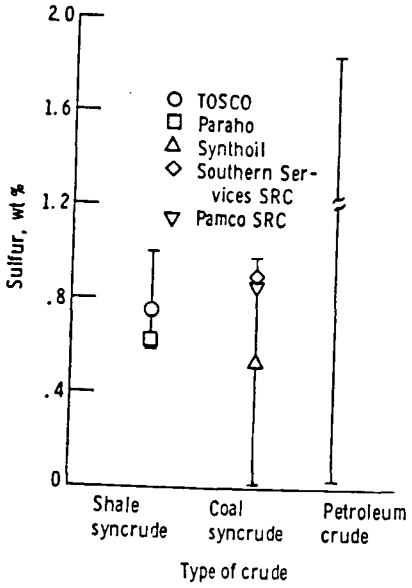

Figure 5. - Comparison of sulfur content of synthetic crudes to petroleum crudes. Vertical bars indicate normal range of variability for each type of crude.

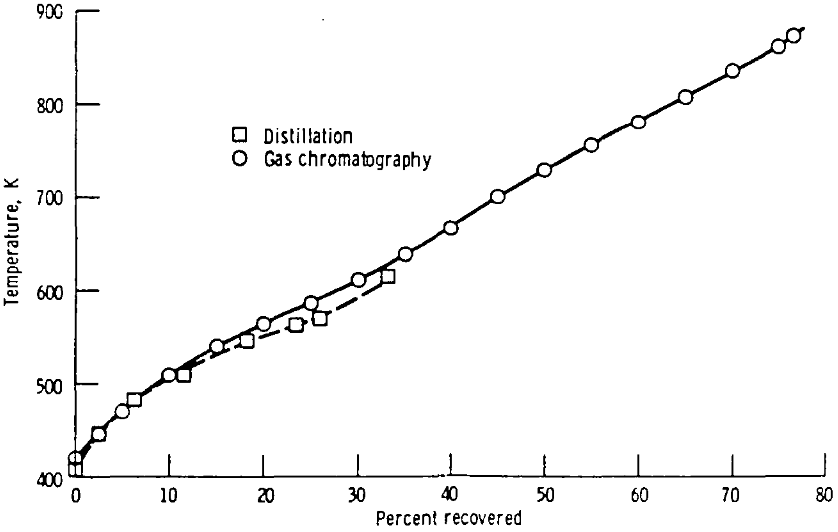

Figure 6. - Boiling range distribution of TOSCO crude oil.

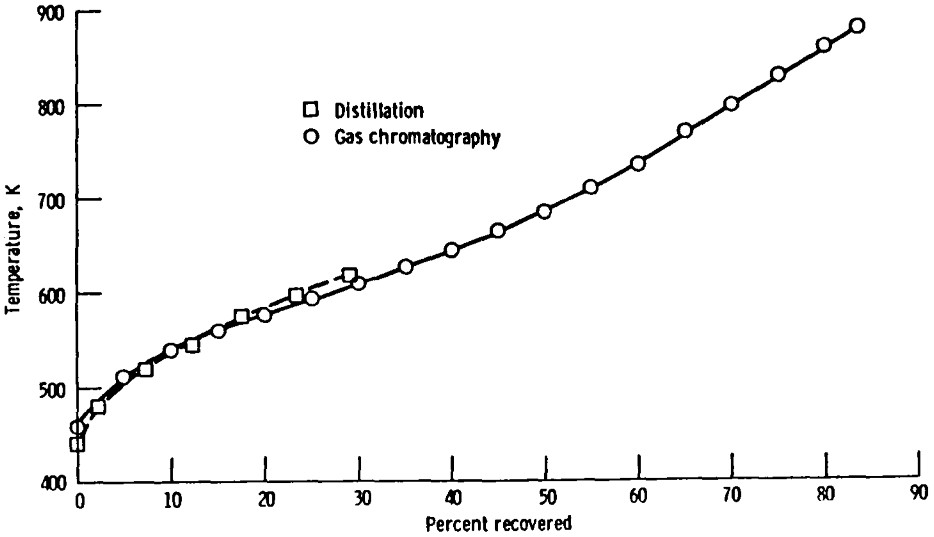

Figure 7. - Boiling range distribution of Synthoil crude oil.

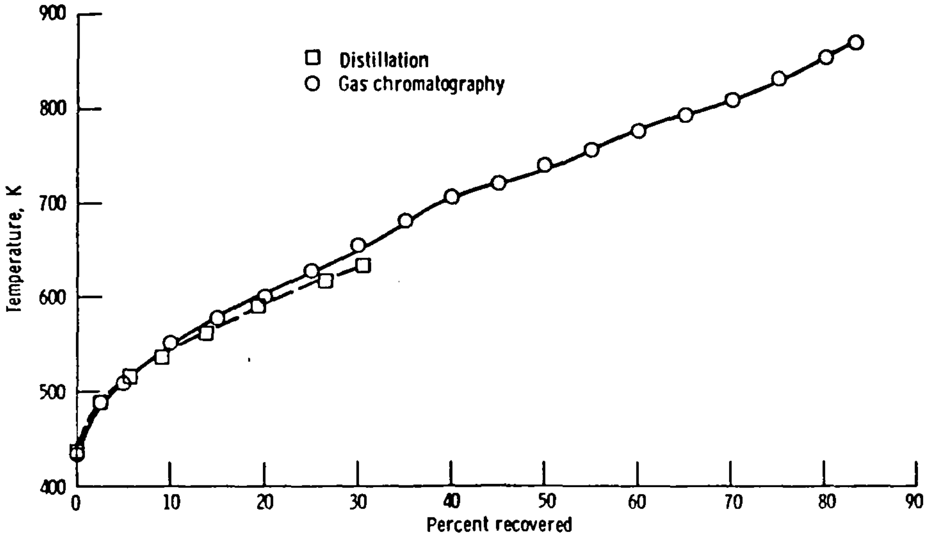

Figure 8. - Boiling range distribution of Paraho crude oil.

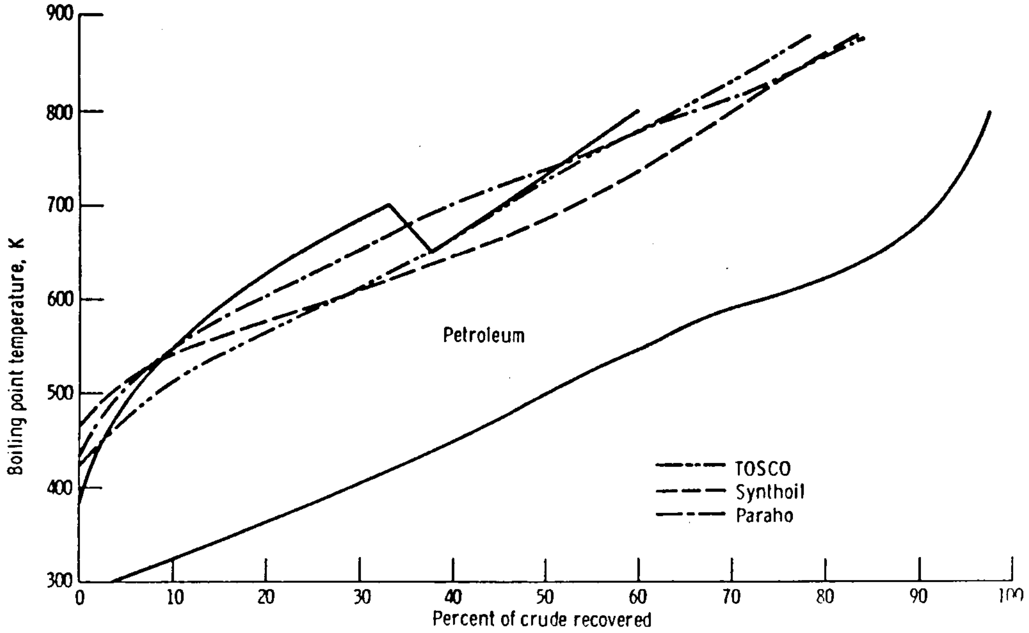

Figure 9. - Comparison of boiling range distribution.

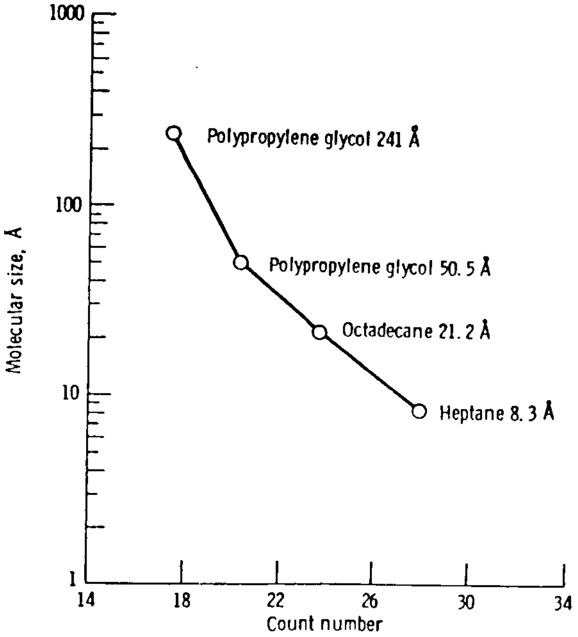

Figure 10. - Gel permeation chromatography calibration curve.

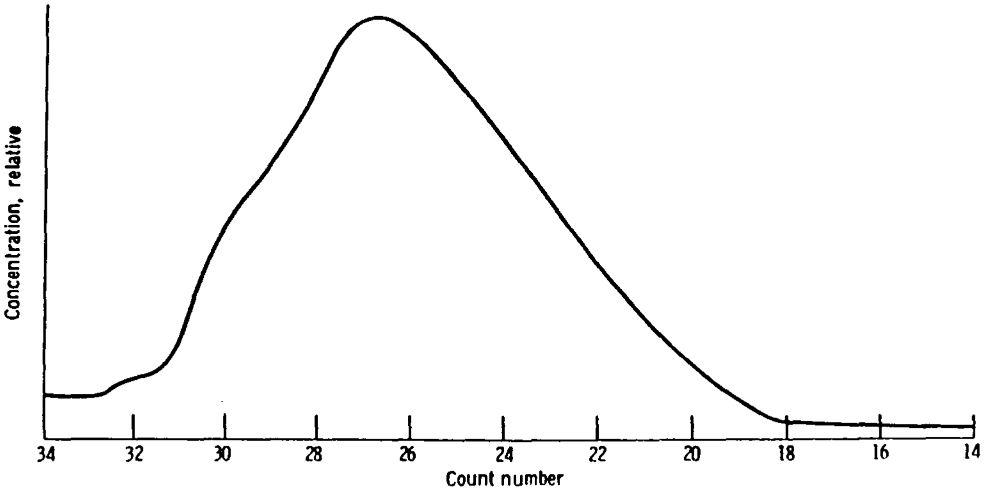

Figure 11. - Gel permeation chromatogram - Synthoil crude oil.

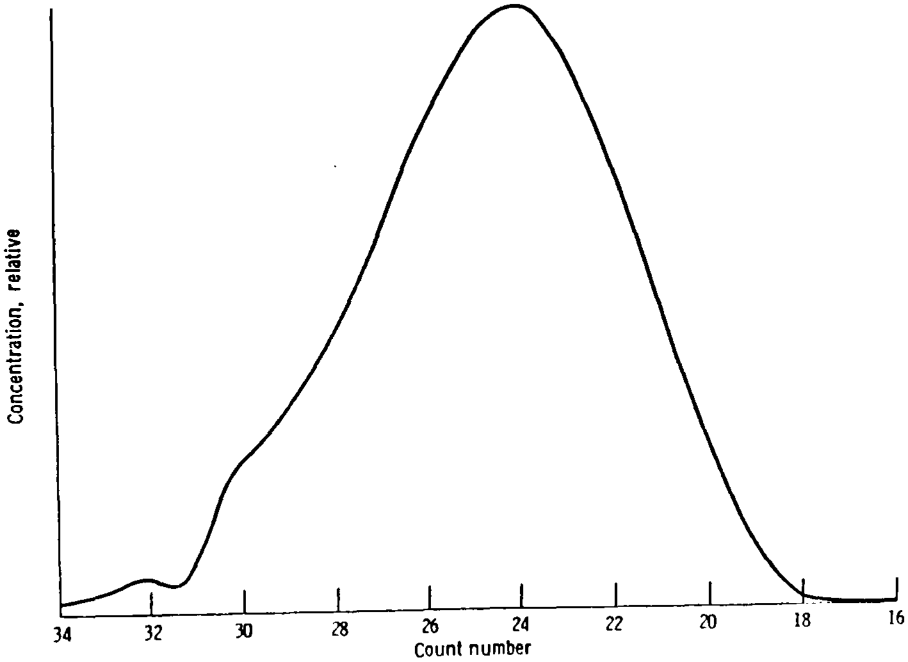

Figure 12. - Gel permeation chromatogram - Southern Services solvent refined coal.

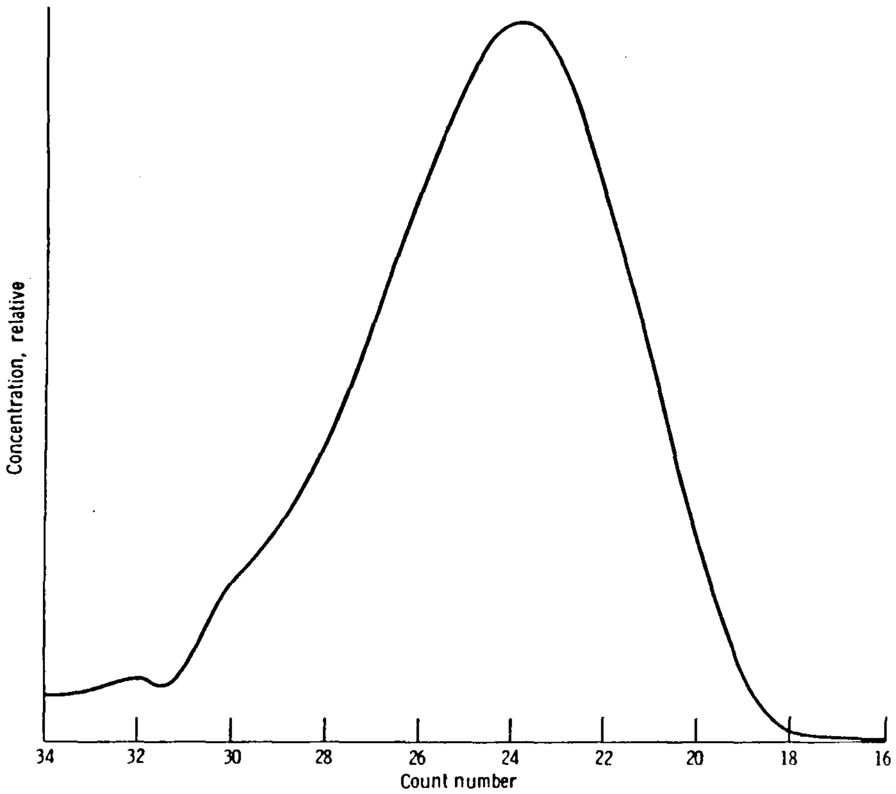

Figure 13. - Gel permeation chromatogram-Pamco solvent refined coal.

Figure 14. - Gel permeation chromatogram - TOSCO shale oil.

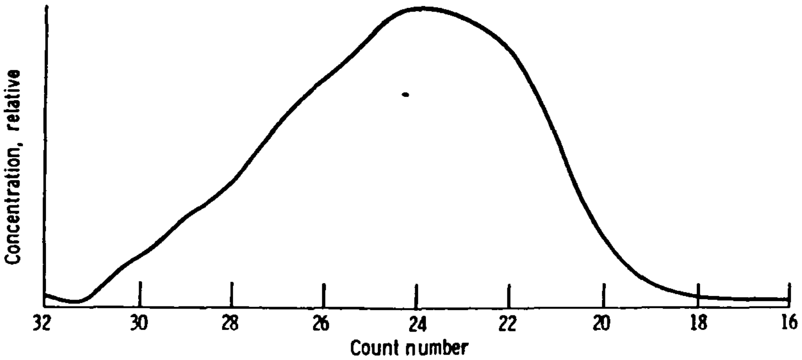

Figure 15. - Gel permeation chromatogram - Paraho shale oil.

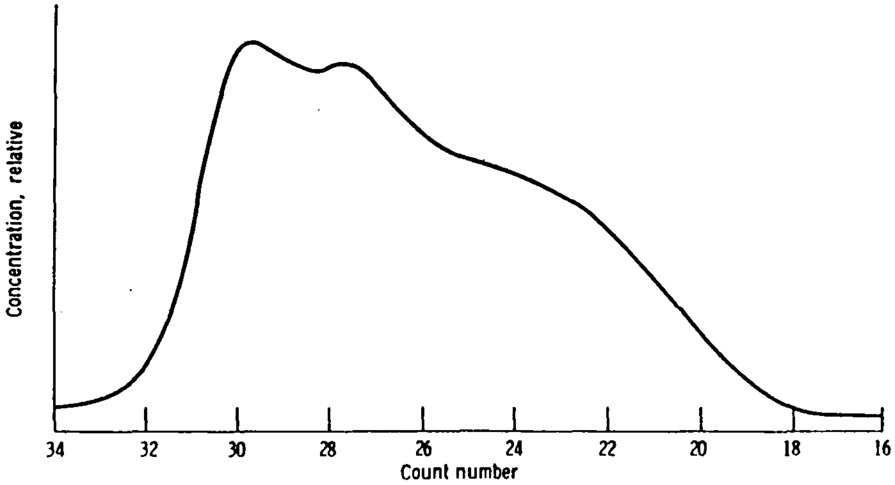

Figure 16. - Gel permeation chromatogram - H-coal crude oil.

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16. Abstract

Physical properties and chemical compositions of six (6) synthetic crudes were determined. The results were compared to those of typical petroleum crudes, with the interest being the feasibility of making jet fuels from oil shale and coal syncrudes. The specific gravity, viscosity, and pour point were measured, showing that these crudes would be described as "heavier" rather than "lighter" crudes. The boiling range distribution of the crudes was determined by distillation and by gas chromatography. In addition, gel permeation chromatograms were obtained, giving a unique molecular weight distribution profile for each crude. Analyses for carbon, hydrogen, nitrogen and sulfur concentrations were performed, as well as for hydrocarbon group type and trace element concentrations. It was found that the range in concentration of vanadium, an element whose presence in turbine fuels is of major concern, was lower than that of petroleum crudes. Sodium and potassium, other elements of concern, were present in comparatively high concentrations.

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