NASA TECHNICAL MEMORANDUM

NASA TM X-73399

NASA TM X-73399

(NASA-TM-X-73399) SYNTHESIS AND ANALYSIS OF JET FUELS FROM SHALE CIL AND COAL SYNCRUDES (NASA) CSCL 21D

N76-21341

Unclas

G3/28 25225

SYNTHESIS AND ANALYSIS OF JET FUELS FROM SHALE OIL AND COAL SYNCRUDES

by Albert C. Antoine
Lewis Research Center
Cleveland, Ohio 44135
and
James P. Gallagher
Atlantic Richfield Company
Harvey, Illinois

TECHNICAL PAPER to be presented at
Eighty-second National Meeting of the
American Institute of Chemical Engineers
Atlantic City, New Jersey, August 29 - September 1, 1976

ABSTRACT

The purpose of this investigation was to determine the technical problems involved in converting a significant portion of a barrel of either a shale oil or coal syncrude into a suitable aviation turbine fuel. TOSCO shale oil, H-Coal and COED coal syncrudes were the starting materials. They were processed by distillation and hydrocracking to produce two (2) levels of yield (20 and 40 weight percent) of material having a distillation range of approximately 422 to 561 K (300° to 550° F). The full distillation range 311 to 616 K (100° to 650° F) materials were hydrotreated to meet two (2) sets of specifications (20 and 40 volume percent aromatics, 13.5 and 12.75 weight percent H, 0.2 and 0.5 weight percent S, and 0.1 and 0.2 weight percent N). The hydrotreated materials were distilled to meet given end point and volatility requirements. The syntheses were carried out in laboratory and pilot plant equipment scaled to produce thirty-two (32) 7.57×10^{-3} m^3 (2-gal) samples of jet fuel of varying defined specifications. Detailed analyses for physical and chemical properties were made on the crude starting materials and on the products. The work was done by Atlantic Richfield Company under NASA contract NAS3-19747.

E-8722

SYNTHESIS AND ANALYSIS OF JET FUELS FROM SHALE OIL AND COAL SYNCRUDES

by Albert C. Antoine
Lewis Research Center
Cleveland, Ohio

and

James P. Gallagher
Atlantic Richfield Company
Harvey, Illinois

E-8722

SUMMARY

The purpose of this investigation was to determine the technical problems involved in converting a significant portion of a barrel of either a shale oil or coal syncrude into a suitable aviation turbine fuel. TOSCO shale oil, H-Coal and COED coal syncrudes were the starting materials. They were processed by distillation, hydrogenation and hydrocracking in pilot plant equipment to produce thirty two 7 1/2-liter samples. The results show that these materials require substantially higher levels of processing severity than similar boiling-range fractions of petroleum. This is a result of their unusual characteristics, such as very high nitrogen and oxygen content, aromaticity or carbon-hydrogen ratio. However, if adequate processing severities are used, jet fuels of defined specifications can be produced from oil shale and coal syncrudes using readily available commercial processes.

INTRODUCTION

The purpose of this study was to investigate some of the processing factors involved in producing aviation turbine fuels from synthetic crudes. Three synthetic crude oils were used, one from shale and two from coal. They were chosen as representative of products that would be typical of those to be produced on a commercial basis when these sources are developed. From these, jet fuels of varying specifications were produced, by varying, primarily the distillation, hydrotreating and hydrocracking processes.

The syntheses of the fuels were carried out in laboratory and pilot plant equipment scaled to synthesize thirty-two different 7.57×10^{-3} m^3 (2-gal) samples of jet fuels of varying specifications. To produce this amount required about 7.57×10^{-1} m^3 (200 gal) each of shale crude oil and coal crude oil. One shale oil readily available in the required amount was that prepared at the TOSCO pilot plant facility by the Colony Development Company. This was used for the shale feedstock. Two different coal syncrudes were used because the desired material was not available in sufficient quantity. Thus, about 0.284 m^3 (75 gal) of liquid product of H-Coal syncrude prepared by the Hydrocarbon Research, Inc. was used for one set of products and the remainder was prepared from syncrude produced by the COED process, and obtained from the FMC Corporation. It was recognized that the COED process is not intended to produce maximum yields of liquid products, and thus this material may not be truly representative of a future commercial coal syncrude. A study to determine which domestic sources of synthetic crudes can be used as refinery feedstocks to produce aviation turbine fuels has recently been concluded (ref. 1).

APPARATUS AND PROCEDURE

General Process Requirements

Figure 1 shows the general process requirements that were established for this study. One requirement in the processing of the syncrudes was to obtain 2 levels of yield of material having a distillation range of approximately 422 to 561 K (300° to 550° F). One product was to have a minimum of 20 weight percent of material in this range, and the other a minimum of 40 weight percent. The 20 weight percent requirement most likely could be achieved by distillation, but hydrocracking was necessary in order to achieve the higher yield. The products were required to have a full distillation range of about 311 to 616 K (100° to 650° F), and then to be treated with hydrogen to meet two sets of specifications (maximum of 20 and 40 volume percent aromatics, minimum of 13.5 and 12.75 weight percent H, maximum of 0.2 and 0.5 weight percent S, and maximum of 0.1 and 0.2 weight percent N). Each of the hydrotreated products was then to be distilled to give maximum yields of products having the described volatility specifications. For each end point, 561 K (550° F), and 616 K (650° F), two products were required, one with a Reid vapor pressure maximum of 2×10^4 N/m^2 (3 psi), and one with a minimum flash point of 311 K (100° F). Thirty-two samples of final product thus were prepared as a result of using two syncrudes, two yield levels, two levels of hydrogenation, and four distillation ranges. TOSCO shale oil was used to prepare both yield levels from shale syncrude. H-Coal oil was used to prepare the low yield from coal syncrude; COED oil was used to prepare the high yield. Each of the 32 samples of final products was analyzed by the methods listed below.

Test	Method
Specific gravity	ASTM D-287
Distillation	D-86
Reid vapor pressure	D-323
or Flash point	D-56
Freezing point	D-2386
Viscosity at -30° F	D-445
Net heat of combustion	D-2382
Existing gum	D-381
Thermal stability	D-3241
Luminometer number	D-1740
or Smoke point	D-1322
Aromatics	D-1319
Olefins	D-1319
Total sulfur	D-1266
Mercaptan sulfur	D-1323
Hydrogen content	D-1018
Nitrogen content	Kjeldahl
Oxygen content	Modified Unterzaucher
Naphthalenes	D-1840

Shale Oil Processing

Fractionating - The shale oil crude was charged to a 20.3-cm-diam by 12.2-m, 0.946-m^3 (250-gal) batch fractionation column having 6.35-mm stainless-steel protruded packing. Material was taken at an atmospheric pressure and at pressures reduced in steps down to about 1333 N/m^2 (10-mm mercury), yielding material up to a 558 K (545° F) (converted to atmospheric pressure) overhead cut point. The 558 K (545° F) and higher bottoms from the 20.3-cm still were distilled in a 10.2-cm-diam by 4.2-m, 0.189-m^3 (50-gal) still and overhead cuts taken at a 10/1 reflux ratio and reduced pressure to a 616 K (650° F) converted cut point. Material from 616 K (650° F) to 700 K (800° F) converted cut point was taken through a side arm (Engler type) system attached to the still pot at a pressure of about 5.33×10^2 N/m^2. Bottoms products from the 10.2-centimeter still side arm distillation were vacuum flashed in a mercury vapor still to produce a 700 to 783 K (800° to 950° F) overhead fraction. The yield for each fraction (and some of the properties) are shown in Table I; the distillation curve is shown in figure 2.

Initial Boiling Point (IBP) - 616K (650° F) Hydrotreating. - The three fractions IBP-422, 422 to 561, 561 to 616 K (IBP-300°, 300° to 550°, and 550° to 650° F) were combined to be used as hydrotreating feedstocks for the low yield 20% 422 to 561 K (300 to 550° F) case. Prior to hydrotreating to obtain products (production run), a short experimental program was run to determine the necessary operating conditions. The nitrogen level was identified as the controlling specification for treating the shale oils, and selection of processing conditions was made on that basis. Tests were run over a range of operating severities to establish a trend for nitrogen removal. The conditions used are given in Table II. The H_2 rate chosen was one to be expected in a commercial operation designed for long catalyst life. In commercial operation, H_2 would be recycled.

The feed was treated in a 2.54-cm diameter isothermal continuous reactor over 60 g of American Cyanamid HDS-3A, a commercial 1.59-mm Ni-Mo/Al_2O_3 catalyst. The catalyst was uniformly diluted 2:1 with tabular alumina to form a 50.8-cm packed bed. The test conditions resulted in nitrogen levels of 0.0054 weight-percent or less. The results are shown in Table II. Since denitrogenation can be represented as a pseudo-first order reaction (ref. 2), these results were sufficient to establish the trends from which the conditions for the production run could be estimated. In this case, the first order trend remains valid down to about 0.0005 percent product nitrogen, at which point the residual nitrogen becomes more difficult to remove. A plot is shown in figure 3. (Severity is defined as F_T/WHSV where F_T was derived from the experimental data by plotting nitrogen removal at various levels of space velocity and temperature. Details are given in ref. 3. For the production run, a space velocity of 1.50 was chosen to provide a reasonable rate of production under moderate temperature conditions. The run was made in a 5.08-cm diameter continuous reactor over a catalyst charge of 300 g of HDS-3A at a feed rate of 450 g hr^{-1}. The catalyst bed was diluted to form a gradient to help maintain isothermal conditions. The ratio of the alumina diluent to the catalyst ranged from 5:1 at the inlet of the reactor to 1:1 at the outlet. It was found near the beginning of the production run that the overall activity of this catalyst charge was somewhat lower than the effective catalyst activity during the experimental run. This is ascribed to some differences in contacting efficiency between the 20 and 50-cm reactors. Therefore, to achieve the 0.2% nitrogen specification, it was necessary to increase the reactor temperature from about 616 K (650° F) to about 625 K (665°F).

Since the program to determine the operating conditions showed that rather low levels of nitrogen could be achieved, it was decided that the low nitrogen content samples would be prepared at about 0.02% N rather than the 0.10% N (max) specified in the requirements. To achieve this level in the production run, a temperature of about 625 K (715° F) was chosen. This result is also shown in Table II.

616 to 783 K (650° to 950° F) Hydrotreating. - The two fractions 616 to 700 K and 700 to 783 K (650° to 800° F and 800° to 950° F) were combined for use in producing the high yield 40%, 422 to 561 K (300° to 550° F) products. In order to prevent severe catalyst deactivation during the hydrocracking step, hydrodenitrogenation of this fraction was required. A short experimental program was run to determine the process conditions necessary to achieve a product nitrogen level of about 0.0200 to 0.0400 percent. This feed was hydrotreated over a 60 g sample of HDS-3A which had been charged to a 2.54-cm i.d. continuous flow isothermal reactor. The catalyst charge was diluted with tabular alumina to form a 50.8-cm packed bed. The process conditions are given in Table II.

The results are also shown. At about 666 K (740° F), product nitrogen levels of about 0.0400 and 0.0190 percent were achieved at weight hourly space velocity (WHSV) values of 0.49 and 0.34, respectively. Based on these results, process conditions for the production run, designed to hydrotreat about 7.57×10^{-1} m^3 (20 gal), were set at 666 K (740° F) and 0.43 WHSV (300 g hr^{-1} feed rate). The run was made in a 5.08-cm i.d. continuous flow reactor over 700 grams of HDS-3A catalyst. The top 1/3 of the catalyst bed was diluted with tabular alumina. Again, because of the lower catalyst activity than that noted in the experimental program, the production run was actually made at a higher temperature, 675 K (755° F), with a WHSV of 0.36 (250 g hr^{-1}) feed rate. The nitrogen content of the product was determined to be 0.0233 percent.

616 to 783 K (650° to 950° F) Hydrocracking. - The hydrocracking process was conducted in a single stage hydrocracking pilot plant, consisting of two reactors in series. The first reactor was charged with hydrodenitrogenation catalyst to further reduce the feed organic nitrogen to < 0.050 percent. The total effluent (gas and liquid) from this reactor was then passed over the hydrocracking catalyst in the second reactor where the hydrocracking reactions take place. Both catalysts employed in this process are proprietary, and are commercially available under license.

In order to determine the conditions necessary to yield a suitable organic nitrogen level in the feed to the hydrocracking reactor, and to obtain suitable hydrocracking yields, short process variable runs were made prior to the production run. The 616 to 783 K (650° to 950° F) shale gas oil had previously been denitrogenated to a level of 0.0233 percent. Process variable work was run first in the hydrotreating reactor while the hydrocracking reactor was being conditioned. The hydrocracking process variable work was then done using the complete single stage system. Only temperature was varied in this system. Pressure was fixed at 13.8×10^6 N/m^2 and space velocities were set to minimize conversion of feed to 311 K (100° F) and lighter in the hydrotreater and maximize the 311 to 616 K (100° to 650° F) yield in the hydrocracker. The process conditions for the hydrotreating runs are given in Table II. The results showed that the nitrogen level was less than 0.0050 percent at 639 K (690° F) and also that the conversion to 311 K (100° F) and lighter material was negligible. Based on the results of these tests the processing conditions in the hydrotreating reactor were set at a temperature of 639 K (690° F) and a WHSV of 1.0. The process conditions for the hydrocracking reactor in the experimental single stage tests are shown in the table, as well as the process conditions set for the production run. The production run was performed using 5.08-cm i.d. reactors; the hydrodenitrogenation reactor contained 300 grams of catalyst and the hydrocracking reactor contained 400. Both were diluted with inert tabular alumina in a linear manner to make up the required reactor volume of about 1 liter. During the production run, catalyst activity changed and the run conditions were changed accordingly. The conversion of the feed to 616 K (650° F) material and lighter was monitored throughout, together with the amounts of product in the 422 to 561 K (300° to 550° F) range and the 311 to 616 K (100° to 650° F) range. In figure 4 the yield of the 422 to 561 K (300° to 550° F) fraction found in this system is plotted as a function of conversion to 616 K (650° F) and lighter. A maximum yield appears at approximately 70 percent conversion. Figure 5 shows a plot of the 311 to 616 K (100° to 650° F) yield, again as a function of conversion to 616 K (650° F) and lighter. The yield of this fraction increased with conversion over the entire range, but not linearly. As conversion increases, losses to material lighter than 311 K (100° F) also increase. In each figure the circles represent data obtained during the production run; the triangle represents data obtained during the experimental runs. Details are given in ref. 3. Overall, the production run produced 42.29 kilograms of liquid product of 46° API gravity.

The 311 to 616 K (100° to 650° F) fraction weighed 27.39 kilograms, a yield of 52.7 weight percent of the 616 to 783 K (650° to 950° F) feed.

H-Coal Processing

Fractionating. - Figure 6 shows the distillation curve obtained by gas chromatography for the liquid product portion of the H-Coal sample furnished by Hydrocarbon Research Inc. The 422 to 561 K (300° to 550° F) fraction represents 61.4% of the liquid, and 23.9% of the total product on an ash-free basis. A portion of the liquid was fractionated on a laboratory column into IBP-422, 422 to 561, 561 to 616 K (IBP-300°, 300° to 550°, 550° to 650° F), and higher than 616 K (650° F) cuts. The analyses of the liquid composite, the distillation cuts and the vacuum bottoms as received higher than 700 K (800° F) are given in Table III.

Hydrotreating. - An experimental run was made to determine the processing conditions necessary to hydrotreat the H-Coal feed to the required specifications. For this syncrude product hydrogen content is the hydrotreating specification most difficult to meet, and, therefore, processing conditions were chosen on that basis. The experimental tests were conducted in a 2.54-cm diameter continuous flow isothermal reactor over a 100 g charge of HDS 3A catalyst. The catalyst was diluted with tabular alumina on a gradient that ranged from 3 parts alumina to 1 part catalyst at the inlet of the bed to a ratio of 1:8 at the outlet. Processing conditions selected are given in Table II. It was found from these tests that the high hydrogen content specification of 13.5% could be attained at severe but practical operating conditions in a single pass operation. The relationship between product hydrogen content and operating severity is shown in figure 7. (Severity is defined as $F_T \times F_P/WHSV$ where F_T and F_P were derived from the experimental data by plotting hydrogen content at various levels of space velocity, temperature, and pressure. Details are given in ref. 3.) The production runs to hydrogenate to the two levels were conducted in a 5.08-cm diameter continuous flow reactor. The reactor was charged with 500 g of HDA-3A catalyst, diluted with tabular alumina at the same distribution gradient used for the preliminary run in the 2.54-cm reactor. The catalyst bed was about 61-cm long. The high severity (high hydrogen content) run was started at 630 K (675° F) and 0.5 WHSV, but the temperature was increased and the WHSV was lowered by the end of the run in order to maintain the required product quality. Further catalyst deactivation was observed during the low severity (low hydrogen content) hydrogenation which was run on the same catalyst charge. The starting and ending conditions are given in Table II.

COED Processing

Fractionating. - The COED syncrude, prepared from Utah coal, was found to contain about 20% water as a remarkable stable emulsion. This caused considerable difficulty in the distillation. An accurate representation of the hydrocarbon portion was obtained from the distillation curve obtained by gas chromatography on the total syncrude. The curve is shown in figure 8. The crude was charged to a 20.3-cm diameter by 12.2-m, 0.946 m^3 (250-gal) batch fractionation unit having 6.35-mm stainless steel protruded packing. The overhead was taken at a 10/1 reflux ratio and atmospheric pressure until the still bottoms reached 616 K (650° F). The pressure was then reduced and fractionation continued at a 3/1 reflux ratio until the overhead temperature indicated a 616 K (650° F) cut point. Water was separated from the fractions by decanting. Since the water gave false indications of cut point, four composites were made from the overhead products, and gas chromatograms run to determine the boiling range. Using the gas chromatogram 95% point as the cut point, yield data agreed fairly well with the gas chromatogram on the total syncrude. Bottoms from the 20.3-cm still having an initial boiling point of approximately 561 K (550° F) were run on the 10.2-cm still to a 616 K (650° F) cut point. The material above 616 K (650° F) was fractionated to a 700 K (800° F) cut point on the vacuum side arm (Engler). Yields based on total charge on a water free basis are plotted on figure 8, along with the 20.3-cm still data. Table IV also shows the results of the fractionation together with some analyses. It should be noted that the water content of the total syncrude made it necessary to determine some analyses by calculation from the fractions.

IBP - 561 K (550° F) Hydrotreating. - A quantity of COED oil in the IBP - 561 K (550° F) fraction was hydrogenated for use in producing the high yield coal syncrude jet fuel samples. All IBP - 561 K (550° F) fractions were filtered and dried to remove any remaining water prior to further processing. A short experimental program was conducted to determine the necessary operating conditions. As with the H-Coal feed, hydrogen content is the limiting factor in meeting required product quality levels. The preliminary tests were made in a 2.54-cm diameter continuous flow isothermal reactor over a 100 gram charge of American Cyanamid HDS-3A Ni-Mo/Al_2O_3 catalyst. To aid in obtaining uniform flow distribution and in controlling temperature increases resulting from the exothermic hydrogenation reactions, the 1.59-mm catalyst was diluted on a gradient, with three parts tabular alumina to one part catalyst at the inlet of the bed ranging to a 1:8 ratio at the outlet. Process conditions selected for this investigation included those given in Table II. The most severe conditions, 644 K (700° F) and 0.5 WHSV, resulted in a product meeting the higher hydrogen requirement of 13.5%. Cracking to light products, reactor volume limitations, and uniform flow considerations put these conditions near the practical operating limits of maximum temperature and minimum WHSV. If catalyst activity remains high in the production run, the high severity product can be made in a single pass.

Based on the data from this run, a correlation between hydrogen content and operating severity was developed and is presented in figure 9. The hydrotreating production run on the IBP - 561 K (550° F) COED syncrude fraction was conducted using a 5.08-cm diameter isothermal reactor charged with 500 grams of HDS-3A catalyst. The catalyst was diluted using the same distribution gradient as used for the experimental run. The high severity portion of the program was run first to take advantage of fresh catalyst activity. Based on the correlation established, the initial conditions selected were 641 K (695° F) and 0.5 WHSV. The apparent initial activity was higher for this catalyst charge than for that used during the preliminary work in the 2.54 cm reactor. Activity declined at an average rate of 11% per day during the run. To compensate, reactor temperature had to be increased to 647 K (705° F) by the end of this portion of the run.

Temperature was lowered to 616 K (650° F) and space velocity was increased to 0.8 to begin the low severity segment of the program. Failure to meet the 12.75% product hydrogen specification required an adjustment to 622 K (660° F) and 0.7 WHSV. Catalyst activity continued to decline, now at the rate of 8% per day, requiring a drop in the WHSV to 0.65 by the end of the run.

561 to 700 K (550° to 800° F) Hydrotreating. - Previous work on COED syncrude (ref. 4) showed that while not particularly high in nitrogen content, it was very difficult to denitrogenate. Thus, it was decided not to run any experimental tests, but to start a production run directly at the most severe conditions practicable. The conditions chosen are given in Table II. The initial product was analyzed and found to contain about 0.0200 percent N.

The run was made in a 5.08-cm continuous flow reactor over HDS-3A catalyst. The analysis of the feed and product is shown in Table V.

561 - 700 K (550° to 800° F) Hydrocracking. - The process configuration used in this step is the same as that used to hydrocrack the 616 to 783 K (650° to 950° F) shale oil. Two reactors are operated in series; the first contains a hydrotreating catalyst and reduces the nitrogen content to about 0.0025 percent. The total effluent (gas and liquid) from this reactor is then sent to the second reactor which contains the hydrocracking catalyst. Both of these catalysts are also proprietary and are commercially available under license. The conditions for the production run (Table II) at space velocity one (300 g hr^{-1}) were chosen to provide for 97% conversion to 616 K (650° F) and lighter. Actual conversion during the run was less due to loss of catalyst activity. Also, the temperature in the hydrocracking reactor was raised over the 330 hours of the production run to compensate for catalyst aging. This degree of rapid catalyst deactivation is highly unusual since this catalyst system gives excellent performance with petroleum-based feed stocks.

The decline in activity also affected the product distribution. The table below shows the yields of the 422 to 561 K (300° to 550° F) and 311 to 616 K (100° to 650° F) fractions at different stages of catalyst activity decline:

Test number:	1	2	3	4	5
Wt % on yield on feed					
422 to 561 K (300° to 550° F)	40.34	32.61	28.54	24.85	18.89
311 to 616 K (100° to 650° F)	88.83	75.30	74.91	69.28	66.39
Hydrocracking temperature, K	607 (634° F)	608 (635° F)	613 644° F)	633 (680° F)	626 (668° F)
% conversion	96.64	79.31	79.93	80.20	73.64

Since most of the production run was made at a constant conversion, about 80%, the component yields relative to conversion cannot be precisely defined.

RESULTS AND DISCUSSION

It has been shown in this study that jet fuels of defined specifications can be made from oil shale and coal syncrudes using readily available commercial processes. The specifications of the fuels produced are approximately those found in the following: (1) JP-4 (Jet B) with a 561 K (550° F) end point and 20.7×10^3 N/m^2 (3 psi) maximum Reid vapor pressure, (2) JP-5 (Jet A) with 561 K (550° F) end point and a 311 K (100° F) minimum flash point, (3) a broad specification fuel incorporating the volatility of a JP-4 20.7×10^3 N/m^2 (3 psi RVP) and the end point of a diesel No. 2, 616 K (650° F), (4) Diesel No. 2 with a 616 K (650° F) end point and a 311 K (100° F) minimum flash point. Certain problem areas have been identified. It was noted in the introduction that the COED process was not intended to maximize liquid product yield, and thus may not be truly representative of a future commercial coal syncrude. Further, a problem with the COED oil was the rapid catalyst deactivation seen in all of the hydrotreating and hydrocracking. This has been observed before with COED syncrude (ref. 4). It appears to be true for the hydrotreating of H-Coal seen in this study. The cause of the deactivation is not apparent. Petroleum stocks of equivalent aromaticity can be readily hydrotreated or hydrocracked without excessive catalyst deactivation. In regard to the H-Coal, the initial preparation of the crude would have a determining effect on the level of yield of jet fuel in the 422 to 561 K (300° to 550° F) range, for example. From examining the material used in this study, it appears that it was a representative sample of H-Coal syncrude produced at moderate severity conditions. The liquid product is seen to have a 95% true boiling point of 616 K (650° F) so that is would not be possible to produce the high yield of the 422 to 561 K (300° to 550° F) fraction without processing of the vacuum bottoms. The vacuum bottoms contain only about 8% of material lower than 700 K (800° F) which could be hydrocracked to increase yield. Processing of material higher than 700 K (800° F) appears highly impractical. A similar problem of initial preparation was seen in the case of the shale oil crude also. It was originally estimated that yields of more than 20 and 40 weight percent, 422 to 561 K (300° to 550° F) material could be readily obtained from what was considered to be a typical product from a commercial shale oil installation. For example, based on the 783 K (950° F) and lower portion, estimates of the 422 to 561 K (300° to 550° F) yields were 28.4 and 40.2 weight percent. The shale oil obtained for the present study appeared to be atypical in that it contained a very large quantity of high boiling material, 35% greater than 783 K (950° F). Thus, the low yield of the

422 to 561 K (300° to 550° F) fraction was 21.4% and the high yield 29.4%. In order to achieve a 40% yield of 422 to 561 K (300° to 550° F), 72% of the 616 to 783 K (650° to 950° F) fraction would have to be converted to 422 to 561 K (300° to 550° F) product, which was not technically feasible, as shown in figure 4. (It should be noted that commercial shale processing would include a delayed coker to process material higher than 783 K (950° F) into lower boiling material. Yields of about 40% of 422 to 561 K material would then be obtainable.)

Table VI shows the properties of the 32 samples prepared to the required specifications. The results of the thermal stability tests will be reported in the future.

SUMMARY OF RESULTS

In all instances the requirement for limits on aromatics (<20%, <40%) was met. The requirement for percent H was met for all of the shale products, and for most of the coal products. The requirements for percent S were met for all of the products. And, with one or two exceptions, the requirements for percent N were met for all of the products.

The low level of yield requirement was met for the shale oil, being 21.4; but the high level of yield was 29.4%, below the required amount. The low level of yield, from coal syncrude from H-Coal, was 17.46% of 422 to 561 (300° to 550° F) material, based on total syncrude. On an ash free basis, the percentage was 23.89. For the high yield, from COED, the figure was about 40%.

REFERENCES

1. Shaw, H., C. D. Kalfadelis, and C. E. Jahnig, Technical Report AFAPL-TR-75-10, March 1975.
2. Jacobs, H. E., Jones, J. F., and Eddinger, R. T., Ind. Eng. Chem. Proc. Des. Develop., 10, 558 (1971).
3. Gallagher, J. P., Atlantic Richfield Contractor Report, NASA contract NAS3-19747, to be published.
4. Greene, M. I., L. J. Scotti, and J. F. Jones, presentation at the American Chemical Society Meeting, Division of Fuel Chemistry, Los Angeles, California, April 1974.

TABLE I. - TOSCO SHALE OIL COMPOSITE FEED AND FRACTIONS

	FEED	IBP-422 K (IBP-300° F)	422 to 561 K (300° to 550° F)	561 to 616 K (550° to 650° F)	616 to 700 K (650° to 800° F)	700 to 783 K (800° to 850° F)
Wt % on whole shale	100.0	9.4	18.4	6.6	12.1	18.3
°API gravity	19.1	51.1	32.8	22.3	19.4	----
% Sulfur	0.683	0.770	0.735	0.673	0.643	----
% Carbon	83.88	86.83	84.58	84.68	85.38	----
% Hydrogen	10.74	13.17	12.14	11.37	11.32	----
% Nitrogen	2.10	0.39	1.39	2.12	1.96	----

TABLE II. - HYDROTREATING PROCESS CONDITIONS

	Temperature, K	(°F)	Pressure, N/m^2	(psi)	WHSV g/feed/hr / g/catalyst	H_2 rate m^3/m^3	(SCF/B)	Product nitrogen wt %
Shale oil:								
IBP-616 K (650° F) hydrotreating:								
Experimental	630	(675)	10.3×10^6	(1500)	1.03	1.42×10^3	(8000)	0.0054
	644	(699)	↓	↓	1.00	↓	↓	0.0004
	650	(711)	↓	↓	1.03	↓	↓	0.0004
	659	(726)	↓	↓	0.99	↓	↓	0.0003
	658	(725)	↓	↓	0.50	↓	↓	0.0002
Production	617	(651)	↓	↓	1.50	↓	↓	0.3099
	622	(660)	↓	↓	1.52	↓	↓	0.2218
	626	(667)	↓	↓	1.50	↓	↓	0.1752
	654	(717)	↓	↓	1.52	↓	↓	0.0118
616 to 783 K (650 to 950° F) hydrotreating:								
Experimental	644	(699)	13.8×10^6	(2000)	0.78	1.42×10^3	(8000)	0.4821
	644	(700)	↓	↓	0.49	↓	↓	0.2666
	656	(721)	↓	↓	0.52	↓	↓	0.1477
	666	(739)	↓	↓	0.49	↓	↓	0.0399
	666	(740)	↓	↓	0.34	↓	↓	0.0188
Production	666	(740)	↓	↓	0.43	↓	↓	0.0300
	675	(755)	↓	↓	0.36	↓	↓	0.0233
616 to 783 K (650 to 950° F) hydrocracking:								
Experimental								
hydrotreating reactor	619	(655)	13.8×10^6	(2000)	1.00	1.78×10^3	(10 000)	0.0082
	639	(690)	↓	↓		↓	↓	0.0029
	652	(715)	↓	↓		↓	↓	0.0021
hydrocracking reactor	616	(650)	↓	↓		↓	↓	
	630	(675)	↓	↓		↓	↓	
	644	(700)	↓	↓		↓	↓	
Production			↓	↓		↓	↓	
hydrotreating reactor	639	(690)	↓	↓	1.00	↓	↓	
hydrocracking reactor	622	(660)	↓	↓	0.75	↓	↓	
H-Coal								
Experimental	616	(650)	13.8×10^6 to 17.2×10^6	(2000 to 2500)	0.33	1.42×10^3	(8000)	
	630	(675)			0.66	↓	↓	
	644	(700)			1.00	↓	↓	
Production						↓	↓	
high hydrogen content	630	(675)*	17.2×10^6	(2500)	0.50*	↓	↓	
	636	(685)**			0.45**	↓	↓	
low hydrogen content	611	(640)*	13.8×10^6	(2000)	0.50	↓	↓	
	614	(646)**						
COED								
IBP-561 K (550° F) hydrotreating								
Experimental	616	(650)	13.8×10^6	(2000)	0.50	1.42×10^3	(8000)	
	630	(675)	↓	↓	1.00	↓	↓	
	644	(700)	↓	↓		↓	↓	
Production			↓	↓		↓	↓	
high hydrogen content	641	(695)*	↓	↓	0.50	↓	↓	
	647	(705)**	↓	↓		↓	↓	
low hydrogen content	616	(650)*	↓	↓	0.80*	↓	↓	
	622	(660)**	↓	↓	0.65**	↓	↓	
561 to 700 K (550° to 800° F) hydrotreating			↓	↓		↓	↓	
Production	658	(725)	↓	↓	0.70	↓	↓	
561 to 700 K (500° to 800° F) hydrocracking			↓	↓				
Production			↓	↓				
hydrotreating reactor	644	(700)	↓	↓	1.00	1.78×10^3	(10 000)	
hydrocracking reactor	607	(634)*	↓	↓				
	631	(676)**	↓	↓				

* Start

**end

TABLE III. - H-COAL COMPOSITE FEED AND FRACTIONS

	FEED	IBP-422 K (IBP-300° F)	422 to 561 K (300° to 550° F)	561 to 616 K (550° to 650° F)	616 K+ (650° F+)	Vacuum bottoms
Wt % of total liquid	100	25	61.4	8.1	5.2	-----
Wt % of total syncrude	28.44	7.11	17.46	2.30	1.48	71.56
Wt % of total syncrude, ash free	38.91	9.73	23.89	3.15	2.02	61.09
API gravity	31.0	50.3	27.5	14.5	5.4	-----
% Hydrogen	11.8	13.3	11.2	10.0	9.0	5.75
% Carbon	87.1	86.6	87.2	89.2	89.2	74.39
% Sulfur	0.170	0.129	0.073	0.110	0.199	1.93
% Nitrogen	0.1722	0.0659	0.1749	0.1651	0.5044	1.16
% Oxygen	0.48	0.61	1.00	0.49	1.34	4.60
% Ash	0.0	------	------	------	------	14.62

TABLE IV. - COED OIL COMPOSITE FEED AND FRACTIONS

	FEED	IBP-422 K (IBP-300° F)	422 to 561 K (300° to 550° F)	561 to 616 K (550° to 650° F)	616 to 700 K (650° to 800° F)	700 K+ (800° F+)
% Total syncrude	100	4.0	32.5	18.0	27.0	18.5
API gravity	18.2	47.8	25.2	18.0	16.5	9.6
% Hydrogen	10.94*	14.8	11.23	10.58	10.86	10.09
% Carbon	87.48	85.2	86.45	87.9	88.10	87.54
% Sulfur	0.023*	0.027	0.021	0.016	0.032	<0.02
% Nitrogen	0.3853	0.0677	0.3696	0.3726	0.3399	0.4285
% Oxygen	0.98*	0.34	1.31	0.86	0.74	1.02
% Ash	0.05	------	------	<0.001	<0.02	0.03

*Back calculated from analyses of fractions

TABLE V. - HYDROTREATING OF 561 to 700 K (550° to 800° F) COED OIL FEED AND PRODUCT ANALYSES

	FEED	Product
Gravity, °API	17.2	22.9
% Hydrogen	10.63	11.91
% Sulfur	0.025	0.002
% Nitrogen	0.3578	0.0237

TABLE VI. - FINAL PRODUCT INSPECTIONS

(a) Low yield shale products

	Low severity				High severity			
	Boiling range, K (^{o}F)							
	IBP-616 (IBP-650)	394 to 616 (250 to 650)	394 to 561 (250 to 550)	IBP-561 (IBP-550)	IBP-616 (IBP-650)	394 to 616 (250 to 650)	394 to 561 (250 to 550)	IBP-561 (IBP-550)
Specific gravity	0. 8040	0. 8170	0. 8068	0. 7945	0. 7977	0. 8081	0. 8022	0. 7914
Reid vapor pressure, kN/m^2	1. 1	------	------	0. 34	2. 8	------	------	1. 1
(psi)	(0. 15)	------	------	(0. 05)	(0. 40)	------	------	(0. 15)
Flash point, K	-------	315	311	------	------	312	312	------
(^{o}F)	-------	(108)	(100)	------	------	(102)	(102)	------
Freezing point, K	255	258	229	225	255	258	231	229
(^{o}F)	(0)	(+5)	(-47)	(-54)	(+1)	(+5)	(-44)	(-47)
Viscosity at 239 K (-30^{o} F)cS	(a)	(a)	6. 781	4. 736	(a)	(a)	6. 990	5. 059
Net heat of combustion, cal/g	10, 477	10, 433	10, 545	10, 428	10, 545	10, 482	10, 466	10, 499
Existing gum, mg	16. 2	51. 4	40. 2	32. 2	0. 8	19. 2	8. 6	9. 0
Smoke point	21	20	21	22	26	26	24	26
Aromatics, %	21. 9	25. 9	22. 2	19. 0	13. 7	17. 4	17. 1	13. 5
Olefins, %	1. 1	0. 8	1. 1	1. 0	0. 8	1. 0	1. 2	0. 9
Naphthalenes, %	1. 0	1. 2	0. 5	0. 5	0. 4	0. 4	0. 2	0. 2
Hydrogen, %	13. 64	13. 66	13. 68	13. 73	13. 82	13. 86	13. 95	13. 76
Nitrogen, %	0. 1954	0. 2233	0. 2011	0. 1750	0. 0161	0. 0168	0. 0152	0. 0132
Total sulfur, %	0. 0010	0. 0044	0. 0006	0. 0006	0. 0009	0. 0003	0. 0001	0. 0002
Mercaptans, %	0. 0002	0. 0002	0. 0002	0. 0002	0. 0003	0. 0002	------	------
Oxygen, %	0. 03	0. 05	0. 06	0. 04	0. 03	0. 05	0. 09	0. 09

[a] Solid

TABLE VI. - Continued.

(b) High yield shale products

	Low severity				High severity			
	Boiling range, K (°F)							
	IBP-616 (IBP-650)	394 to 616 (250 to 650)	394 to 561 (250 to 550)	IBP-561 (IBP-550)	IBP-616 (IBP-650)	394 to 616 (250 to 650)	394 to 561 (250 to 550)	IBP-561 (IBP-550)
Specific gravity	0.7972	0.8146	0.8054	0.7874	0.7936	0.8100	0.8035	0.7874
Reid vapor pressure, kN/m^2	7.6	------	------	6.9	8.6	------	------	7.6
(psi)	(1.10)	------	------	(1.00)	(1.25)	------	------	(1.10)
Flash point, K	------	314	312	------	------	312	309	------
(°F)	------	(106)	(102)	------	------	(102)	(96)	------
Freezing point, K	251	255	227	222	250	254	226	223
(°F)	(-8)	(-1)	(-50)	(-59)	(-9)	(-3)	(-52)	(-58)
Viscosity at 239 K (-30° F)cS	(a)	(a)	6.918	4.093	------	------	7.060	4.326
Net heat of combustion, cal/g	10,565	10,531	------	10,622	10,595	10,488	10,532	10,605
Existing gum, mg	26.8	61.8	23.4	17.0	9.2	32.8	16.0	16.6
Smoke point	23	20	22	25	26	25	25	27
Aromatics, %	15.7	20.3	17.9	13.7	12.1	15.4	13.2	11.4
Olefins, %	0.8	0.9	1.3	0.8	0.6	1.0	1.0	0.8
Naphthalenes, %	0.75	0.93	0.42	0.33	0.3	0.35	0.21	0.17
Hydrogen, %	13.82	13.37	13.80	13.70	13.98	13.95	13.95	13.98
Nitrogen, %	0.1305	0.1581	0.1397	0.1138	0.0101	0.0144	0.0076	0.0088
Total sulfur, %	0.0014	0.0012	0.0006	0.0005	0.0011	0.0002	0.0002	0.0002
Mercaptans, %	0.0001	------	------	------	<0.0001	------	------	------
Oxygen, %	0.08	0.14	0.14	0.13	0.11	0.10	0.07	0.10

[a] Solid

TABLE VI. - Continued.

(c) Low yield H-Coal products

	Low severity				High severity			
	Boiling range, K (°F)							
	IBP-616 (IBP-650)	394 to 616 (250 to 653)	394 to 561 (250 to 550)	IBP-561 (IBP-550)	IBP-616 (IBP-650)	394 to 616 (250 to 650)	394 to 561 (250 to 550)	IBP-561 (IBP-550)
Specific gravity	0.8493	0.8654	0.8565	0.8413	0.8338	0.8488	0.8468	0.8314
Reid vapor pressure, kN/m^2	1.4	------	------	1.1	1.7	------	------	3.1
(psi)	(0.20)	------	------	(0.15)	(0.25)	------	------	(0.45)
Flash point, K	------	312	309	------	------	312	314	------
(°F)	------	(102)	(96)	------	------	(102)	(106)	------
Freezing point, K	251	237	217	211	255	246	225	207
(°F)	(-8)	(-32)	(-68)	(-79)	(0)	(-17)	(-54)	(-86)
Viscosity at 239 K (-30° F)cS	------	16.99	6.785	5.162	9.757	15.91	9.102	6.264
Net weight of combustion, cal/g	10,363	10,248	10,303	10,340	10,450	10,462	10,462	10,421
Existing gum, mg	6.0	74.0	92.0	10.2	4.8	110.8	11.2	9.8
Smoke point	14	15	15	16	24	21	24	25
Aromatics, %	29.7	33.8	30.9	26.3	5.9	6.7	5.8	5.5
Olefins, %	1.2	1.8	1.4	1.2	1.3	1.4	1.0	0.9
Naphthalenes, %	0.54	0.66	0.31	0.27	0.064	0.077	0.065	0.055
Hydrogen, %	12.73	12.47	12.64	12.79	13.56	13.26	13.31	13.73
Nitrogen, %	0.0005	0.0006	0.0006	0.0001	<0.0001	<0.0001	<0.0001	0.0001
Total sulfur, %	0.0004	0.0004	0.0001	0.0001	0.0005	0.0005	<0.0001	0.0001
Mercaptans, %	------	------	------	------	------	------	------	------
Oxygen, %	0.11	0.09	0.06	0.10	0.04	0.06	0.03	0.04

TABLE VI. - Concluded.

(d) High yield COED products

	Low severity					High severity		
	Boiling range, K (°F)							
	IBP-616 (IBP-650)	394 to 616 (250 to 650)	394 to 561 (250 to 550)	IBP-561 (IBP-550)	IBP-616 (IBP-650)	394 to 616 (250 to 650)	394 to 561 (250 to 550)	IBP-561 (IBP-550)
Specific gravity	0.8255	0.8458	0.8368	0.8165	0.8358	0.8586	0.8493	0.8270
Reid vapor pressure, kN/m^2	5.8	------	------	5.8	5.8	------	------	7.2
(psi)	(0.85)	------	------	(0.85)	(0.85)	------	------	(1.05)
Flash point, K	------	313	314	------	------	319	313	------
(°F)	------	(104)	(106)	------	------	(114)	(104)	------
Freezing point, K	242	239	220	215	256	256	221	217
(°F)	(-23)	(-30)	(-64)	(-72)	(-23)	(+2)	(-62)	(-70)
Viscosity at 239 K (-30° F)cS	(a)	19.25	9.676	5.565	(a)	(a)	9.851	5.586
Net heat of combustion, cal/g	10,484	10,534	10,484	10,547	10,328	10,427	10,401	10,486
Existing gum, mg	0.8	23.0	6.6	7.6	1.6	21.2	2.4	3.2
Smoke point	20	20	24	27	16	14	16	19
Aromatics, %	9.3	11.6	7.2	5.4	22.4	28.5	25.2	20.1
Olefins, %	0.7	1.1	0.9	0.5	0.6	1.2	0.8	0.5
Naphthalenes, %	0.49	0.62	0.13	0.11	0.68	0.86	0.38	0.31
Hydrogen, %	13.6	13.44	13.63	13.69	13.07	12.88	12.96	13.24
Nitrogen, %	0.0002	0.0002	0.0002	0.0002	0.0003	0.0002	0.0002	0.0002
Total sulfur, %	0.0003	0.0003	0.0001	0.0001	0.0003	0.0001	0.0001	0.0001
Mercaptans, %	------	------	------	------	------	------	------	------
Oxygen, %	0.05	0.05	0.05	0.03	0.03	0.03	0.03	0.03

[a] Solid

E-8722

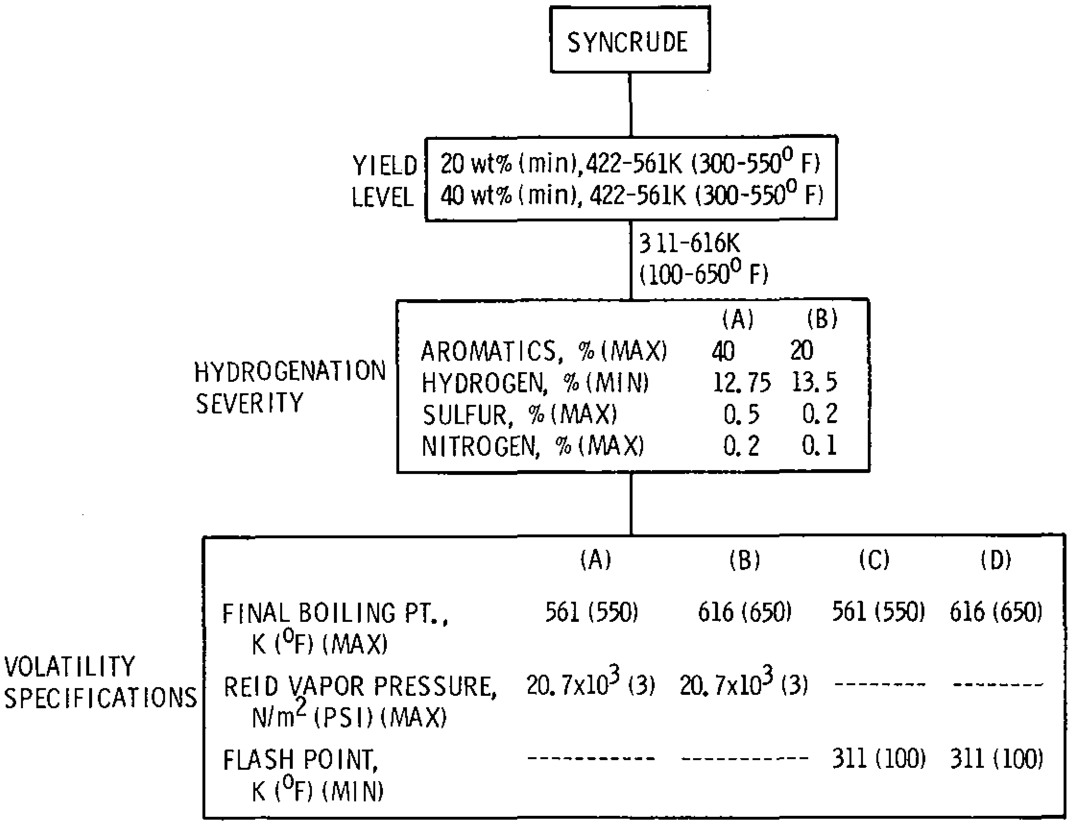

Figure 1. - General process requirements.

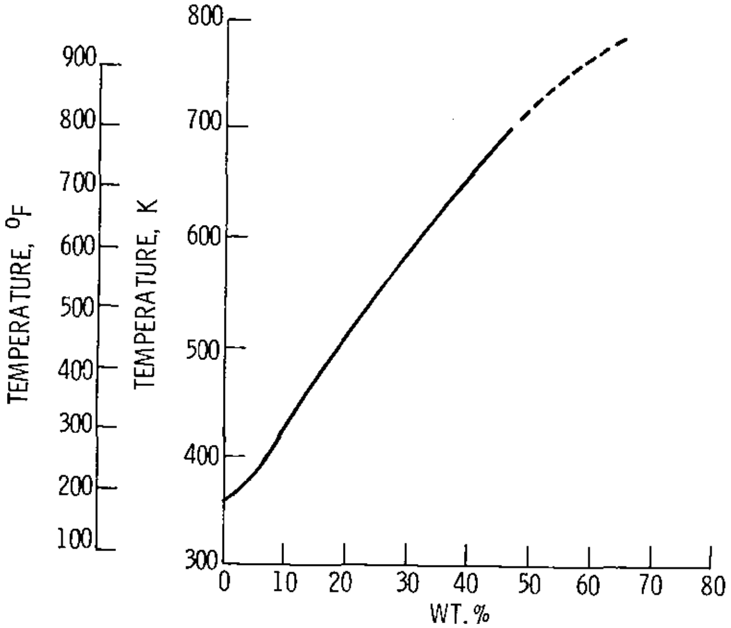

Figure 2. - TOSCO shale oil distillation curve.

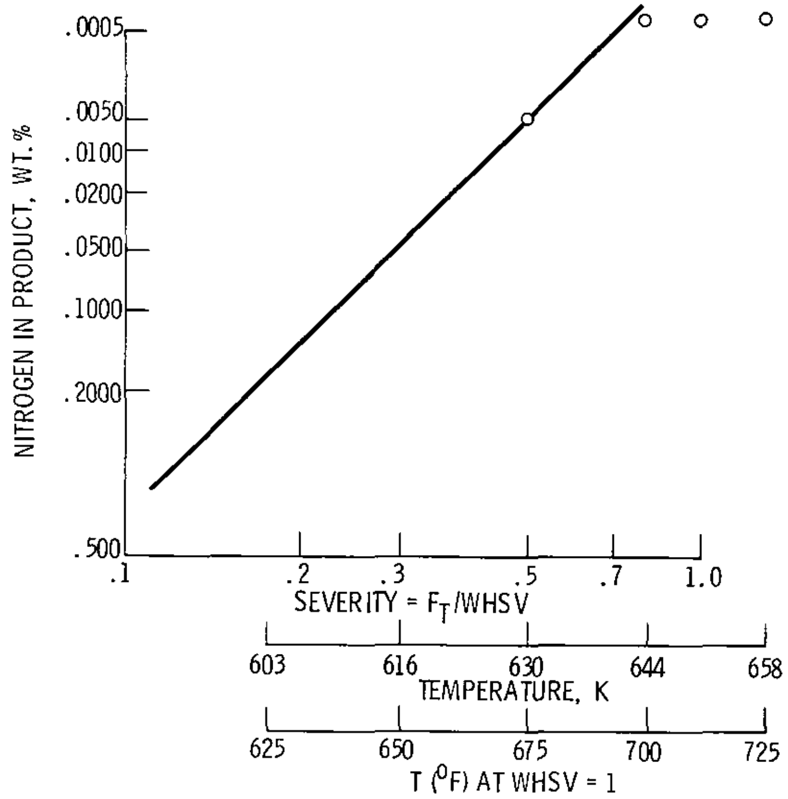

Figure 3. - Shale oil hydrotreating; IBP-616 K (650° F) cut.

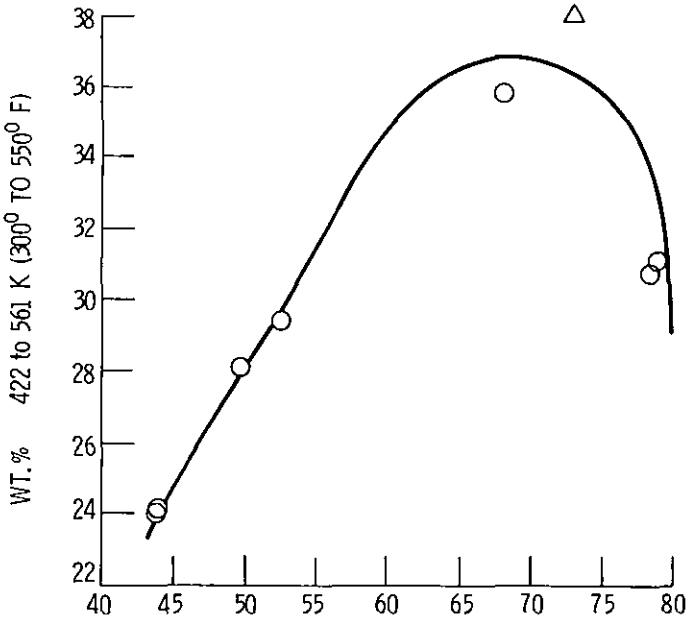

Figure 4. - Single stage hydrocracking 616 to 783 K (650° to 950° F) shale gas oil.

27

REPRODUCIBILITY OF THE ORIGINAL PAGE IS POOR

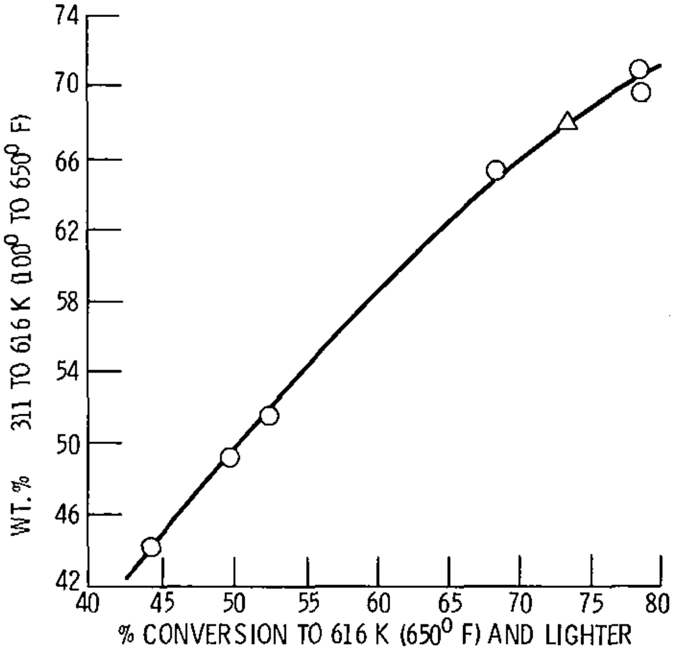

Figure 5. - Single stage hydrocracking 616 to 783 K (650° to 950° F) shale gas oil.

E-8722

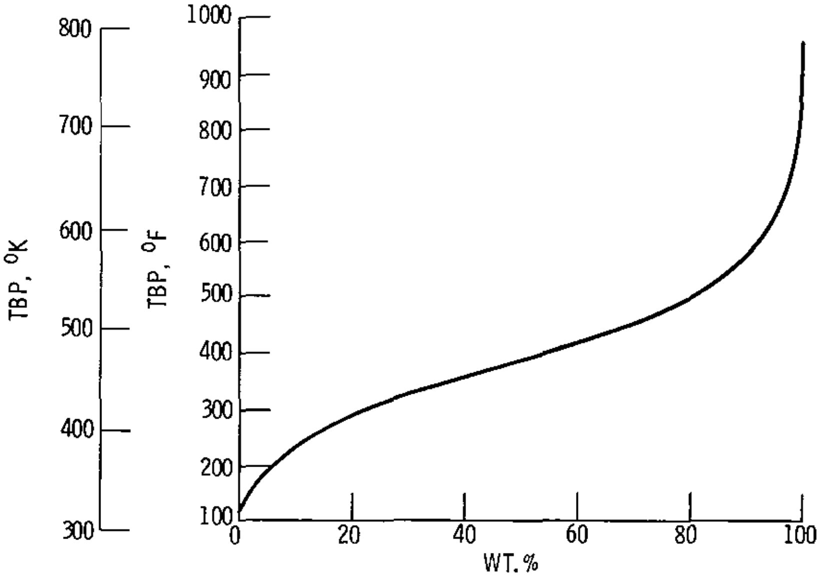

Figure 6. - H-Coal liquid product distillation curve.

2B

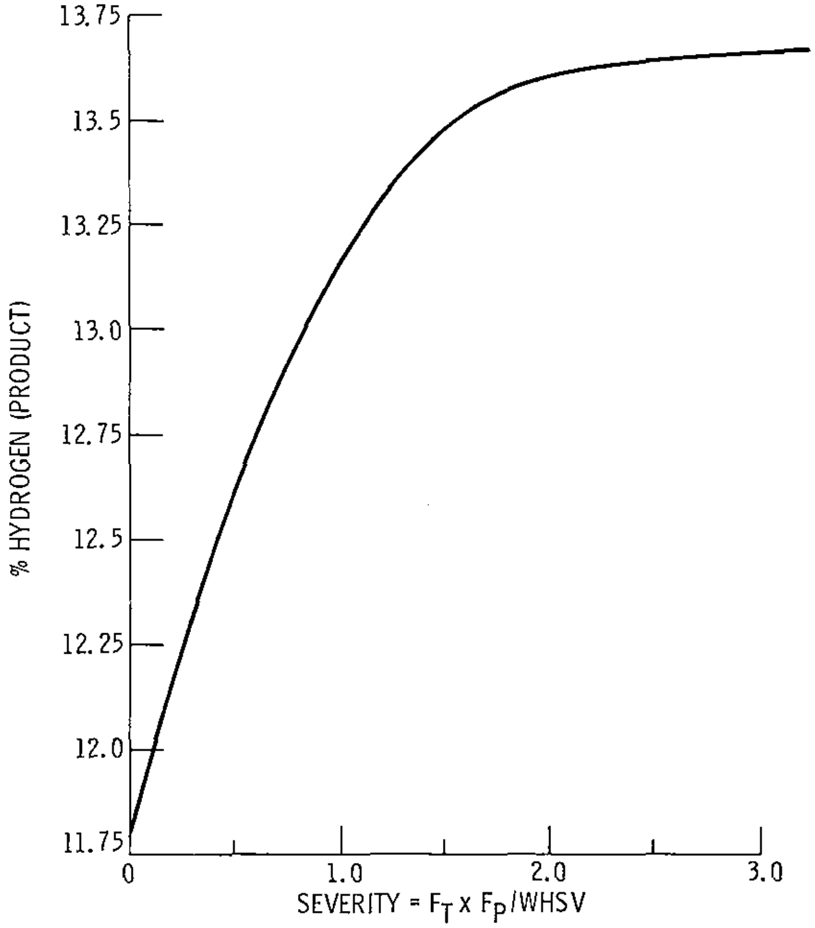

Figure 7. - H-Coal hydrotreating.

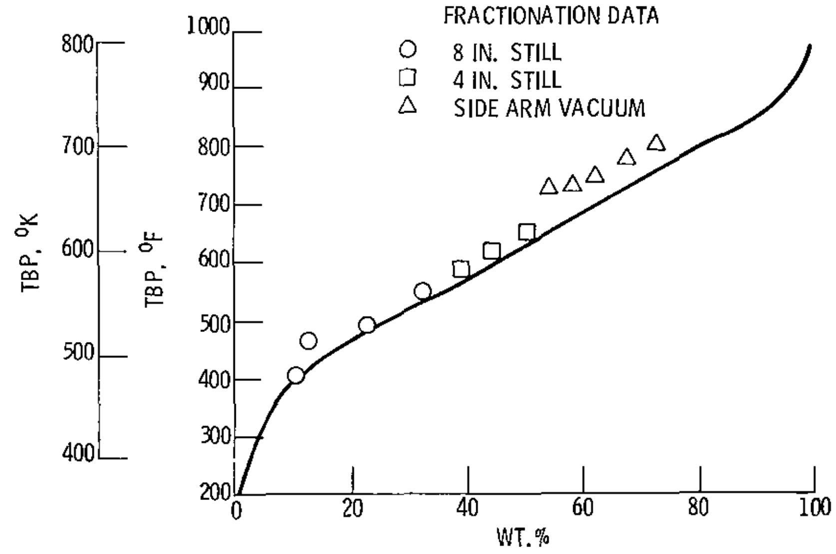

Figure 8. - COED oil distillation curve.

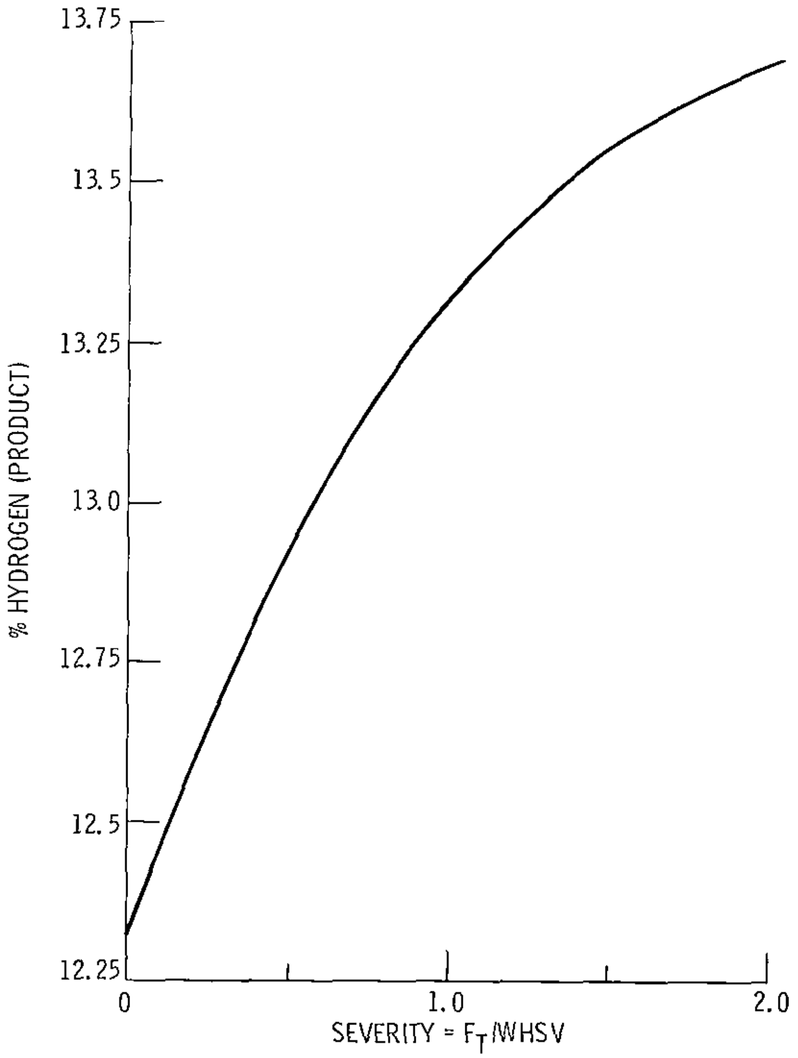

Figure 9. - COED oil hydrotreating; IBP to 561 K (550° F).

3p