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**The Evaluation of a Coal-Derived Liquid
as a Feedstock for the Production of
High-Density Aviation Turbine Fuel**

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Topical Report

**K.P. Thomas
D.E. Hunter**

August 1989

Work Performed Under Cooperative Agreement No.: DE-FC21-86MC11076

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

By
Western Research Institute
Laramie, Wyoming

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SUMMARY

The conversion of coal-derived liquids to transportation fuels has been the subject of many studies sponsored by the U.S. Department of Energy and the U.S. Department of Defense. For the most part, these studies evaluated conventional petroleum processes for the production of specification-grade fuels. Recently, however, the interest of these two departments expanded to include the evaluation of alternate fossil fuels as a feedstock for the production of high-density aviation turbine fuel. In this study, we evaluated five processes for their ability to produce intermediates from a coal-derived liquid for the production of high-density turbine fuel. These processes include acid-base extraction to reduce the heteroatom content of the middle distillate and the atmospheric and vacuum gas oils, solvent dewaxing to reduce the paraffin (alkane) content of the atmospheric and vacuum gas oils, Attapulugus clay treatment to reduce the heteroatom content of the middle distillate, coking to reduce the distillate range of the vacuum gas oil, and hydrogenation to remove heteroatoms and to saturate aromatic rings in the middle distillate and atmospheric gas oil.

The chemical and physical properties that the U.S. Air Force considers critical for the development of a high-density aviation turbine fuel are specific gravity and net heat of combustion. The target minimum values for these properties are a specific gravity of at least 0.85 and a net heat of combustion of at least 130,000 Btu/gal. In addition, the minimum hydrogen content is 13.0 wt %, the maximum freeze point is -53°F (-47°C), the maximum amount of aromatics is about 25 to 30 vol %, and the maximum amount of paraffins is 10 vol %.

To reduce the heteroatom and alkane content of those distillates that are potential feedstocks for the production of high-density turbine fuel (middle distillate, atmospheric gas oil, and vacuum gas oil) acid-base extraction and solvent dewaxing, respectively, were evaluated as processes to produce suitable intermediates. Acid-base extraction reduced the nitrogen content of all of the distillates, and reduced the oxygen content of the middle distillate. However, solvent dewaxing did not have a significant affect on the chemical properties of this very aromatic fossil fuel.

Next, Attapulugus clay treatment was evaluated as a process to produce fuel candidates suitable for evaluation. In this case, the middle distillate was the only distillate treated because it already satisfied the distillate range requirement. This treatment, even though it did reduce the heteroatom content, did not produce a fuel candidate suitable for evaluation. Primarily, this was because the heteroatom and aromatic contents were still too high, and the hydrogen content was too low.

Because the vacuum gas oil distills in a temperature range too high to be of direct use for the production of high-density turbine fuel, it was subjected to a coking process to reduce its distillate range. The distillate range and specific gravity of the coker distillate were reduced when compared to the vacuum gas oil. However, the heteroatom content was too high to warrant further evaluation of the distillate.

Because acid-base extraction and Attapulugus clay treatment did not reduce the heteroatom content of the distillates to the appropriate levels, hydrogenation was evaluated as a process to not only reduce the heteroatom content but also to saturate the aromatic rings present in the middle distillate and atmospheric gas oil. The heteroatom content of the process intermediates was reduced to the part-per-million level, but the saturation of aromatic rings and olefins was not accomplished during the application of the single-stage hydrogenation process. Consequently, evaluation of the process intermediates as fuel candidates was not conducted. In summary, the processes evaluated did not produce materials that satisfied all of the requirements of a high-density aviation turbine fuel.

In spite of our difficulties in preparing fuel candidates suitable for evaluation as high-density aviation turbine fuels, we believe that a two-stage hydrogenation process can be employed to produce a high-density turbine fuel that meets the requirements of the U.S. Air Force. This premise is based on the observation that the process intermediates from hydrogenation contain high concentrations of dicyclic alkanes and indanes/tetralins, compounds that are necessary for the production of a high-density aviation turbine fuel.

INTRODUCTION

The conversion of coal-derived liquids to transportation fuels has been the subject of many studies sponsored by the U.S. Department of Energy and the U.S. Department of Defense. For the most part, these studies evaluated conventional petroleum processes for the production of specification-grade fuels. For example, Sullivan et al. (1978) and Sullivan and Frumkin (1986) studied conventional refining processes for the production of transportation fuels from coal-derived liquids and western shale oils. Smith et al. (1988) evaluated the potential of producing conventional jet fuels from a by-product stream of the Great Plains Gasification Plant. They concluded that the production of conventional military turbine fuels, JP-4 and JP-8, is possible but only through the use of large amounts of hydrogen, 3400 scfb. They also concluded that the production of a high-density aviation turbine fuel, JP-8X, is possible but only through special processing to satisfy specific gravity and freeze point requirements. As a continuation of the screening studies conducted by Smith et al. (1988), Furlong et al. (1989) evaluated various hydrogenation schemes to produce conventional jet fuels and high-density aviation turbine fuel from the tar oil (by-product) stream. They verified their process scheme, which includes three separate hydrogenation steps, by producing two barrels of JP-8 that met all of the military specifications, except the flash point. In addition, small quantities of JP-4 and JP-8X were produced. These products met all of the specifications except the copper strip corrosion (JP-4 and JP-8X), heating value (JP-4), existent gum (JP-8X), and flash point (JP-8X). It is believed by the authors that the copper strip corrosion and existent gum specifications would have been met if the samples could have been clay-treated or additives used. As a continuation of the study reported here, Greene et al. (1989) and Greene et al. (1990) are evaluating various refinery processes to produce high-density aviation turbine fuel from coal-derived liquids. Employing a series of hydroprocessing steps they have produced fuels that exceed the net heating value requirement of a high-density aviation turbine fuel.

Conventional aircraft turbine fuels are generally composed of high concentrations of low-density paraffins. This class of compounds is favored because of its high hydrogen content and good combustion characteristics. In addition, aromatics are limited to a maximum of 25 vol %. However, aromatics are seldom found at this concentration because of the minimum hydrogen specification and smoke point requirement. In comparison, projected requirements for a high-density aviation turbine fuel favor high concentrations of cyclic hydrocarbons and severely limit paraffin content. Table 1 lists some key specification values for fuel grades JP-4 and JP-8, the latter being the military counterpart of commercial jet fuel. Also listed are some target requirements established by the U.S. Air Force for high-density JP-8 (JP-8X) aviation turbine fuel. The specification values for JP-8 are aromatics content less than 25 vol %, hydrogen content greater than 13.5 wt %, and specific gravity between 0.775 and 0.840. To meet these specifications, a high paraffin content is required. On the other hand, to satisfy the target requirements of a high-density aviation turbine fuel, the fuel must be composed, primarily, of high-density alicyclics

and aromatics and very few paraffins. In practice, conventional fuels are easiest to make from paraffinic crude feedstocks. However, advanced or high-density fuels may be easiest to make from aromatic or naphthenic feedstocks.

The intent of this investigation is to determine the feasibility of producing a high-density aviation turbine fuel from a coal-derived liquid. The processes that are evaluated include acid-base extraction, solvent dewaxing, Attapulugus clay treatment, coking, and hydrogenation. Acid-base extraction is used to reduce the heteroatom content of the middle distillate and atmospheric and vacuum gas oils. Solvent dewaxing is used to reduce the paraffin content of the atmospheric and vacuum gas oils. Attapulugus clay treatment is used to reduce the heteroatom content of the middle distillate. Coking is used to reduce the distillate range of the vacuum gas oil, and hydrogenation is used to reduce the heteroatom content and to saturate the aromatic rings in the middle distillate and atmospheric gas oil.

EXPERIMENTAL

In April of 1989, sixteen gallons of coal-derived liquid were received from the Morgantown Energy Technology Center. The liquid was nitrogen blanketed and shipped to Western Research Institute (WRI) in a 30-gallon, stainless steel drum. During this study, the coal-derived liquid and fractions produced from it were blanketed with nitrogen to minimize oxidation. The coal-derived liquid was produced by Coalite and Chemical Products Limited of England using a low-temperature carbonization process (Needham 1961). The coal used for processing was a blend of five different English bituminous coals obtained from mines in the Midlands and South Yorkshire areas of England (B. Ashall, Managing Director, Coalite and Chem. Prod., personal communication 1991). Based upon the classification of the National Coal Board of the United Kingdom, the coals are either classified as 601 or 801, medium caking or very weakly caking coals, respectively (Francis 1961).

Sample Analysis

Routine Analysis

Numerous chemical and physical properties were determined for the whole coal-derived liquid, the distillates and residue, and the process intermediates. These analyses include carbon, hydrogen, nitrogen, sulfur, oxygen (direct), viscosity, specific gravity, molecular weight, Conradson carbon residue, pour point or freeze point, and heat of combustion. These analyses were conducted using either ASTM (1985) or standard WRI procedures. In addition, the water content of the coal-derived liquid and the naphtha was measured by Karl Fischer titration, and the ash content of the coal-derived liquid and the distillation residue was determined by combustion at 1380°F (750°C). The distillation range of the coal-derived liquid and distillates were determined by simulated distillation using either ASTM method D 2887 or a WRI procedure that involves the use of an external standard for determination of the response factor (Thomas et al. 1987).

Preparation of Distillate Fractions

The coal-derived liquid (16 gallons) was distilled to produce the following distillates and residue: IBP-350°F (IBP-177°C, naphtha), 350-550°F (177-288°C, middle distillate), 550-785°F (288-418°C, atmospheric gas oil), 785-1000°F (418-538°C, vacuum gas oil), and 1000+°F (538+°C) residue. An atmospheric-type distillation using a packed column was conducted to obtain the naphtha and middle distillate fractions. The naphtha fraction was distilled at atmospheric pressure, and the middle distillate was distilled at 20 mm of mercury vacuum. For the higher boiling distillates, a continuous vacuum still was used until a final distillate temperature of 1000°F (538°C) was reached. The maximum pot temperature for the continuous vacuum distillation was 644°F (340°C). This latter temperature was required to make the 1000°F (538°C) cut at 1 mm of mercury vacuum. No evidence of thermal cracking was observed during either of the distillations.

Preparation of Asphaltenes and Chromatographic Fractions

Asphaltenes were precipitated from 5.0 grams of each distillate using n-pentane (40 mL/g of sample). The mixture was stirred for 16 hours at ambient temperature and then filtered. The asphaltenes were washed with pentane until the washings were colorless. The asphaltenes were recovered by dissolution in hot toluene. The toluene was removed by rotary evaporation, and the asphaltenes were weighed. The pentane was removed from the maltenes using a rotary-film evaporator. In some cases, residual organic material remained after treatment with hot toluene. This material was recovered by dissolution in pyridine. The pyridine was removed by rotary evaporation. This residual organic material was then treated twice with 50-mL aliquots of toluene to ensure complete removal of pyridine through rotary evaporation. Pyridine and toluene distill as an azeotrope (22 to 78 wt %, respectively). This residual organic material is referred to as preasphaltenes.

Chromatographic separation of the distillates and maltenes was conducted using a column containing activated Davison grade 12 (250 grams) or 62 (120 grams) silica gel placed on top of activated Alcoa F-20 alumina (90 grams). The silica gels were activated at 509°F (265°C) for 16 hours, and the alumina was activated at 752°F (400°C) for 16 hours. Grade 12 silica gel was used for the separation of the middle distillate, and grade 62 silica gel was used for the separation of the atmospheric and vacuum gas oils. The grade 12 silica gel has a smaller pore diameter than the grade 62 silica gel (22 versus 140 Å). Thus, it is better suited for the separation of the smaller (lower molecular weight) molecules in the middle distillate. The adsorbents were added to the column (2.5 x 91.4 cm) as a slurry in pentane. Approximately 2.0 grams of each distillate or maltene was applied to the top of the water-jacketed column. The saturates were eluted with 1.0 L of n-pentane, the aromatics with 1.0 L of benzene, and the polar aromatics with 1.5 L of benzene-methanol (9 to 1 by volume). The cut between fractions was made when the readily visible succeeding fraction was at the silica gel-alumina interface. The solvents were removed by rotary evaporation, taking care to minimize the loss of light ends. The data reported in the tables that deal with chromatographic results are normalized to 100%

and are corrected using the results of mass spectral analysis of the saturate and aromatic fractions. The correction takes into account the fact that the chromatographic separation method did not result in a clean separation between saturate and aromatic compounds. In all cases, some aromatic compounds were identified and quantified in the saturate fractions. The correction of the saturate and aromatic chromatographic percentages was made as follows. The contribution of aromatic compounds to a saturate fraction as determined by mass spectroscopy was subtracted, and the saturate data were then normalized to an aromatic-free basis. The aromatic contribution was then added to the aromatic fraction, and these data were normalized.

Because the potential fuel candidate from Attapulugus clay treatment of the middle distillate and the coker distillate from the vacuum gas oil were very volatile and contained high concentrations of heteroatoms, a different chromatographic procedure was employed to produce hydrocarbon fractions suitable for mass spectral analysis. The chromatographic separation was conducted using a column containing 22 grams of activated Bio-Rad neutral alumina (AG-7, 100-200 mesh). The dry adsorbent was added to the column (11 x 50 mm) while tapping the column to settle the bed. Approximately 0.2 grams of distillate was applied to the column, and the first 50 mL eluting from the column with benzene as the eluant is defined as the hydrocarbon fraction. The fraction was concentrated using a rotary evaporator. Residual benzene in the hydrocarbon fraction was identified and quantified during the mass spectral analysis and was accounted for in the results.

Mass Spectral Analysis

The saturate and aromatic fractions from the middle distillate and atmospheric gas oil and the whole naphtha were analyzed using a Hewlett-Packard 5985B gas chromatograph/mass spectrometer (GC/MS) system. A 0.2 mm x 25 m fused-silica column coated with 5% (0.33 μ m thickness) methyl silicone was used for the chromatographic separation. Each sample (1 μ L) was injected using a split ratio of 100:1 at an injection port temperature of 527°F (275°C) and an oven program temperature rate of 5.4°F/min (3°C/min) from 122 to 527°F (50 to 275°C). A flow rate of 0.75 mL/min was used for the helium carrier gas. The mass spectrometer scan rate was 1.2 seconds per decade from 50-500 amu. An ionization voltage of 70 volts at an ion source temperature of 392°F (200°C) and an electron multiplier voltage of 1600 volts were used for all experiments. The mass spectral resolution was 1 in 1000. The hydrocarbon-group-type distribution of the saturate and aromatic fractions was determined using selected ions that are representative of each hydrocarbon-group type. The method relies on the gas chromatographic separation to minimize interferences from fragment ions of other hydrocarbon groups. Because the fragmentation pattern of alkenes is very similar to alkanes and monocyclic alkanes, they are included with the saturate hydrocarbons. The results from the analyses are reported as weight percentages. This proprietary method was used because it is the only available mass spectral method that differentiates between alkenes and monocyclic alkanes.

Because of their high boiling point, the saturate and aromatic fractions from the vacuum gas oil were analyzed using direct insertion into a high-resolution mass spectrometer (HRMS). The operating conditions for the ZAB 1-F mass spectrometer were ionization energy 70 volts, trap current 240 microamps, source temperature 482°F (250°C), mass resolution 1 in 5000, scan range 60-700 amu, scan time 19 seconds, interscan time 1 second, and solids probe temperature ramp 32 to 752°F (0 to 400°C) at 0.9°F/second (0.5°C/second). The samples were placed in a glass capillary tube and inserted into the solids probe. The probe was inserted into the vacuum lock, and data acquisition was initiated. The probe was fully inserted into the source by the fifth scan. Probe heating was initiated after a decline in total ion current was detected. For some samples, the probe heating rate was interrupted to prevent ion signal saturation at the detector. For these samples, the probe temperature was manually increased to 752°F (400°C) gradually to prevent signal saturation. The spectra were averaged for each sample from the onset of sample evolution from the probe until a probe temperature of 752°F (400°C) was obtained. At the chosen experimental conditions, the chromatographic fractions from each sample were not vaporized entirely during mass spectral analysis. However, at least 80% of each sample inserted into the mass spectrometer was analyzed. The averaged spectra were used for the calculations. The data were analyzed using ASTM methods D 2786 for the saturate and D 3239 for the aromatic fractions. Because the compound types identified using the GC/MS method are not exactly comparable with those identified using the HRMS method, the compound types identified by the two methods were collated according to ring size. Thus, the data can be compared across the boiling ranges. The small amounts of hexacyclic alkanes are reported separately in this report rather than being added to the pentacyclic alkanes as was done in a previous report (Thomas and Hunter 1989).

Process Evaluation

The middle distillate, atmospheric gas oil, and vacuum gas oil were selected for process evaluation because these distillates have potential for being converted into high-density aviation turbine fuel. The processes included acid-base extraction, solvent dewaxing, Attapulugus clay treatment, coking, and hydrogenation. These processes address those properties of the distillates that must be modified to produce a turbine fuel; namely, heteroatom and paraffin content, molecular weight, distillation range, and aromatic content.

Acid-Base Extraction

The acid-base extraction was conducted by first dissolving 200.0 grams of the sample in about 200 mL of diethyl ether. This solution was then extracted successively with 10 wt % sulfuric acid, 2 wt % sodium bicarbonate, and 10 wt % sodium hydroxide. After each aqueous extraction, the aqueous phase was back-extracted with diethyl ether, and this solution was added to the organic phase prior to the next aqueous extraction. The diethyl ether was removed from the raffinate by rotary evaporation, and the raffinate was weighed. The extracted organic material was not recovered.

Solvent Dewaxing

The solvent dewaxing of the atmospheric and vacuum gas oils was conducted as follows. One-hundred grams of sample was dissolved in 1500 grams of acetone; the mixture was then cooled to 14°F (-10°C) and maintained at this temperature for 16 hours with occasional shaking. The mixture was filtered through Whatman glass-fiber paper (GF/A), and the wax was washed two times with cold acetone, air dried, and weighed. The solvent was removed from the dewaxed product by rotary evaporation, and the product was weighed.

Attapulqus Clay Treatment

Attapulqus clay treatment was used to remove heteroatom-containing compounds from potential fuel candidates. About 300 grams of Attapulqus clay, 50/80 A LVM, was packed dry into a glass column (2.5 x 91.4 cm). Distillate samples were poured down through the column, and the first 50 and 25 mL of the distillate eluting from the column were designated as potential fuel candidates.

Coking

Coking of the vacuum gas oil was conducted in a 5.1 x 35.6 cm vertically mounted, schedule 40 black pipe. The reactor was heated with a four-zone electric furnace, and the temperature in the reactor was monitored with type J thermocouples. The temperature at the bottom of the reactor was 900°F (482°C), and the temperature at the top of the reactor was 800°F (427°C). The experiment lasted 1.5 hours, during which gas, oil, and coke were collected. The vacuum gas oil was fed in through the top of the reactor and exited the inlet tube two-thirds of the way down inside the reactor. The produced oil vaporized from the reactor was collected in an air-cooled, 1-L vessel. The produced gas that passed through this vessel was collected and measured by water displacement. The gas was analyzed using gas chromatography. After the experiment was completed, the reactor was weighed to determine the amount of coke produced.

Hydrogenation

Hydrogenation of the middle distillate and atmospheric gas oil fractions was conducted in a bench-scale, fixed-bed system that was operated in the downflow, once-through mode. The system pressure was controlled by dome pressure regulators, and the hydrogen flow was regulated by a mass flow controller. Sample feed to the reactor was regulated with a Ruska precision pump. The reactor temperature was controlled with a four-section clamshell-type tube furnace, with each section regulated to $\pm 0.5^\circ\text{F}$ ($\pm 0.3^\circ\text{C}$) by an electronic proportioning controller. The liquid product was collected in a stainless steel receiver at room temperature and 250 psig. Produced gases were analyzed on-line by gas chromatography. The reactor used for these studies was 105.4 cm long x 2.5 cm o.d. (1.0 cm i.d.). The system was manually controlled but had computerized monitoring and data acquisition. All experiments were conducted using Shell 424 nickel-molybdenum catalyst in the presulfided form. This catalyst was chosen because it is resistant

to deactivation by nitrogen and sulfur. The catalyst bed was 20 mL and was contained in the bottom of the hot zone of the reactor. The remaining volume of the reactor was filled with the inert material, Cohart grain.

After the experimental conditions were established and sample was being fed to the top of the reactor, a typical hydrogenation run was conducted as follows. Hydrogenated product was collected for 24 hours to ensure that product composition was constant. This first product was discarded, and a second product was collected for the following six hours and retained. The conditions of the reactor were then changed, and a product was again collected for 24 hours to ensure that the composition was constant. This product was also discarded, and a second product at the new conditions was collected and retained. The two retained products or process intermediates were then washed with cold water to remove hydrogen sulfide and ammonia. The process intermediates were dried by stirring for 16 hours with anhydrous magnesium sulfate, and the salt was removed by filtration.

RESULTS AND DISCUSSION

Whole Coal-Derived Liquid and its Distillates and Residue

The chemical and physical properties of the whole coal-derived liquid and its distillates and residue are listed in Table 2. As is typical of coal-derived liquids, the whole oil is fairly aromatic having a hydrogen-to-carbon ratio of 1.25; it also contains modest amounts of nitrogen and sulfur (1.1 wt % each) and a rather large amount of oxygen (6.2 wt %). The specific gravity is greater than one (1.0407), also reflecting its aromatic character. The coal-derived liquid as delivered to WRI contained 1.8 wt % water and no detectable ash; it also had a viscosity of 67.8 cP at 100°F (38°C) and a Conradson carbon residue of 4.3 wt %. Nitrogen increases with increasing distillate range from 0.3 to 1.7 wt %. Sulfur varies from 0.7 to 1.5 wt %. The naphtha has the highest amount of sulfur, probably thiophenes. Oxygen varies from 2.0 to 7.3 wt %. The middle distillate has the highest amount of oxygen, probably phenols. As expected, the hydrogen-to-carbon ratio decreases with increasing distillate range, and the viscosity, specific gravity, molecular weight, and pour point increase with increasing distillate range. Note that the molecular weight of the vacuum gas oil was determined in pyridine rather than the customary solvent, toluene, because of the presence of preasphaltenes. The residue contained 0.4 wt % ash, which probably resulted from the carry over of coal fines during the coal carbonization process.

The results of simulated distillation analysis of the whole oil and its distillates are listed in Table 3. The whole oil is fairly light with about 76 wt % boiling in the middle distillate/atmospheric gas oil range (350-800°F/177-427°C). Simulated distillation analysis of the distillates was conducted as a measure of the efficiency of the large-scale distillation. Apparently, some foaming of the oil and water occurred during the distillation of the naphtha fraction. Only 71 wt % of the sample distills in the desired boiling range, and the remaining

29 wt % of the sample is the result of carry-over of the higher boiling middle distillate fraction. In a similar investigation (Thomas and Hunter 1989), western shale oil containing only about 0.2 wt % water was distilled by a similar process. The result was that the naphtha contained more than 95 wt % of material distilling in the desired temperature range. The middle distillate and atmospheric gas oil fractions from the coal-derived liquid contained about 92 and 88 wt %, respectively, distilling in the desired temperature range. During the vacuum distillation to produce the vacuum gas oil, the filter on the feed pump plugged repeatedly with solid material, apparently the coal fines mentioned earlier. This resulted in excessive temperature fluctuations during the subsequent shutdowns and restarts. Consequently, only 35 wt % of the fraction distills in the desired range. This sample is also composed of about 54 wt % distilling in the atmospheric gas oil temperature range. The vacuum gas oil fraction from western shale oil was composed of about 63 wt % distilling in the desired temperature range and only 25 wt % distilling in the atmospheric gas oil range (Thomas and Hunter 1989). This rather large amount of material (54 wt %) distilling in the 550-800°F (288-427°C) range occurred, in part, because the distillation to produce the atmospheric gas oil was inadvertently stopped about 15°F (9°C) short of the desired 800°F (427°C). This mistake was not discovered until well into the succeeding distillation to produce the vacuum gas oil. Thus, the cut point between the atmospheric and vacuum gas oil fractions is 785°F (418°C) rather than the desired 800°F (427°C). Another reason for the poor separation efficiency is because a continuous vacuum distillation process does not have the separation efficiency of an atmospheric distillation process that uses a packed column.

Because the middle distillate, atmospheric gas oil, and vacuum gas oil can be feedstocks for the production of high-density aviation turbine fuel, these distillates were investigated in detail. The results of the chromatographic separation of these three distillates are listed in Table 4. Because the saturates resulting from the separation contained some aromatics that were subsequently identified and quantified by mass spectroscopy, the data for the saturates and aromatics listed in this table were corrected based on the mass spectral results. This correction was applied to all chromatographic data contained in this report. With increasing boiling point, the weight percentage of saturates decreases from 40.0 to 6.5 wt %. The atmospheric gas oil contains the largest percentage of aromatics, and the vacuum gas oil contains a very large percentage of asphaltenes (49.1 wt %) and some preasphaltenes (1.5 wt %). The saturates and aromatics resulting from the chromatographic separation of the middle distillate and the atmospheric and vacuum gas oils and the whole naphtha were investigated by mass spectrometry. The results of the hydrocarbon-group-type analysis of these four distillates are listed in Table 5. The data obtained on the chromatographic fractions have been normalized to a whole sample basis. All of the distillates contain alkanes with the middle distillate containing the most, 23.4 wt %. In addition, the distillates contain alkenes and alicyclics with the monocyclic alkanes concentrating in the naphtha fraction. Low levels of mono- through tetracyclic alkanes are present in the other distillates except the atmospheric gas oil. The alkenes in the vacuum gas oil are accounted

for in the monocyclic alkanes. The naphtha and middle distillate contain monoaromatics, whereas the atmospheric gas oil contains di- and triaromatics, and the vacuum gas oil contains mono- through pentaaromatics and some thiopheno aromatics. In general, the percentage of saturates decreases with increasing boiling range except for the middle distillate. This fraction contains the highest percentage of saturates, 40.0 wt %, primarily, alkanes. The percentage of aromatics is approximately constant except for the naphtha fraction. This fraction contains a very large amount of aromatics, 69.9 wt %, exclusively, monoaromatics. As expected, the percentage of total hydrocarbons decreases with increasing boiling range. This parallels the decrease in H/C ratio.

Raffinates from Acid-Base Extraction

The middle distillate, atmospheric gas oil, and vacuum gas oil were treated by acid-base extraction to decrease the heteroatom content of the distillates. The percentage of raffinate recovered for the three distillates was 62.5, 83.9, and 84.2 wt %, respectively. The chemical and physical properties of the raffinates are listed in Table 6. For the middle distillate, the percentages of nitrogen and sulfur were reduced by about 50%. This resulted in an increase in H/C ratio from 1.35 to 1.41, a decrease in viscosity and specific gravity, and a slight decrease in molecular weight. The predominant compound type extracted from this fraction is probably phenols. The atmospheric gas oil also experienced reductions in the percentages of nitrogen and oxygen. This resulted in an increase in the H/C ratio from 1.27 to 1.49, a decrease in the viscosity, and slight increases in the specific gravity and molecular weight. For the vacuum gas oil, only small reductions were noted for nitrogen and oxygen. These reductions resulted in a decrease in the viscosity and specific gravity, and an increase in the molecular weight. The distillate range (Table 7) of the middle distillate and vacuum gas oil was only slightly affected by the acid-base extraction process. In both cases, the range was increased due to the loss of lower boiling components.

The results of the chromatographic separation of the three raffinates are listed in Table 8. As observed for the distillates, the percentages of saturates and aromatics decrease with increasing boiling point, and, as one would expect, the percentage of saturates was increased in the gas oil raffinates as a result of the acid-base extraction process. However, for some unknown reason, the percentage of saturates was decreased in the middle distillate raffinate. The acid-base extraction process also resulted in a reduction in the percentage of asphaltenes and preasphaltenes in the gas oil raffinates. Table 9 lists the results of the hydrocarbon-group-type analysis of the raffinates. Other than a decrease in the percentage of alkanes in the middle distillate and an increase in the percentage of tetracyclic alkanes in the vacuum gas oil, the composition of the saturate fractions from the raffinates are comparable to that of the original distillates. With respect to the aromatics, the compositions of the raffinates are also similar to the compositions of all the original distillates except, the middle distillate. For this sample, the percentage of monoaromatics is increased with respect to that of the distillate (30.1 versus 22.1 wt

%). This increase parallels the increase in aromatics isolated by chromatography from this sample. Because the raffinate from the middle distillate contained too high a concentration of heteroatoms, alkanes and alkenes, it was not suitable for evaluation as a fuel candidate. The high distillate range and composition of the raffinates from the gas oils precluded them from evaluation as fuel candidates.

Products from Solvent Dewaxing

The atmospheric and vacuum gas oils were solvent dewaxed to remove alkanes. The percentage of dewaxed product recovered from these two distillates was 97.3 and 98.2 wt %, respectively. The chemical and physical properties of the dewaxed products are listed in Table 10. Because so little wax was removed from these two distillates, little change was observed in the properties of the dewaxed products. The only meaningful changes were an increase in the viscosity and specific gravity and a decrease in the pour point of the dewaxed product from the atmospheric gas oil. For the dewaxed product from the vacuum gas oil, the only meaningful change was an increase in the viscosity from 97,800 to 317,000 cP at 100°F (38°C). The distillate range (Table 11) of the dewaxed products was not affected by the dewaxing process.

The results of the chromatographic separation of the dewaxed products are listed in Table 12. Again, very little change is observed in the distribution of the chromatographic fractions when they are compared with those of the original distillates. In addition, the results of the hydrocarbon-group-type analysis (Table 13) are comparable to those of the original distillates. These products were not evaluated as fuel candidates because they were not in the appropriate boiling range and they also contained too high of a concentration of heteroatoms.

Fuel Candidates from Attapulqus Clay Treatment

Because the chemical and physical properties of the products from the acid-base extraction process (raffinates) and from the dewaxing process were not suited for evaluation as fuel candidates, the original middle distillate was used for the preparation of fuel candidates. This distillate was chosen because it already satisfied the distillate range requirement of a high-density aviation turbine fuel. The potential fuel candidates were prepared by passing the middle distillate through an Attapulqus clay column and collecting the first 50 mL of eluant (test fuel #1) and the first 25 mL of eluant (test fuel #2).

The chemical and physical properties of the fuel candidates are listed in Table 14. Test fuels #1 and #2 do not satisfy the requirements of a high-density aviation turbine fuel. Both fuels contain higher than acceptable levels of heteroatoms. Even though there are no listed requirements for nitrogen and oxygen, 0.2 wt % for nitrogen and about 6 wt % for oxygen are higher than acceptable for a finished turbine fuel. In addition, the percentage of hydrogen for the fuels is below the 13.0 wt % required. The specific gravities of the fuels are higher than the requirement, about 0.96, but this is probably because of the high concentration of heteroatoms and aromatics present

in the fuels. The pour point of test fuel #2 was determined to be -24°F (-31°C). The freeze point could not be determined for this sample because the fuel was too highly colored. The net heat of combustion of the fuels is fairly high but does not meet the requirement of 130,000 Btu/gal. As determined previously, the test fuels satisfy the requirement for distillate range (Table 15).

Because test fuel #2 was somewhat better than test fuel #1, as far as meeting the requirements of a turbine fuel, a hydrocarbon-group-type analysis was performed on the sample. Before analysis, the sample was passed through neutral alumina to remove heteroatomic compounds. This resulted in 62.3 wt % of the sample being rejected. The mass spectral data reported in Table 16 are normalized to 100%. As expected, the hydrocarbon fraction contains a very high percentage of aromatics (77.8 wt %), primarily, indanes/tetralins (55.0 wt %) and naphthalenes (19.4 wt %). However, the sample is relatively low in alkanes (15.1 wt %) and alkenes (6.6 wt %). The types of compounds identified in this hydrocarbon fraction suggest that the middle distillate from this coal-derived liquid has the potential to be a feedstock for the production of high-density aviation turbine fuel. However, it appears that the processing steps will need to address the very high aromatic content of the feed. The usual procedure is catalytic hydrogenation. Of course, upon hydrogenation, the alkenes may be converted to alkanes, which would result in an excessive amount of this class of compound. However, upon hydrogenation, the indanes/tetralins will be converted to dicyclic alkanes, which are necessary components for the production of a high-density aviation turbine fuel. In addition, through hydrogenation the heteroatom content will be reduced to acceptable levels.

Coker Distillate from Coking

The vacuum gas oil distills above the appropriate temperature range for direct use in the production of high-density aviation turbine fuel. Consequently, it was subjected to a coking process to reduce its distillate range by converting high boiling compounds to low boiling ones. The reactor conditions, yield data, and chemical and physical properties of the coker distillate are listed in Table 17. The recovery for this coking experiment was 93.3 wt %, with 57.6 wt % being coker distillate. The percentage of coke produced during this experiment (29.2 wt %) was greater for this aromatic feed than it was for the more paraffinic western shale oil (19.5 wt %) (Thomas and Hunter 1989). Even though the distillate range and the specific gravity of the vacuum gas oil were reduced, the heteroatom content was not significantly affected. However, the H/C ratio was slightly increased due to the coking process. Apparently, the conversion of aromatic compounds to coke resulted in the observed increase in H/C ratio of the coker distillate. The original distillate contained only 56 wt % distilling below 800°F (427°C), after treatment almost 91 wt % of the sample distilled below 800°F (427°C), and the specific gravity was reduced from 1.1080 to 1.0408.

Results of the hydrocarbon-group-type analysis (Table 18) show that the percentage of alkanes is increased somewhat from 3.6 to 7.5 wt %. However, the increase of aromatics, primarily mono- through triaromatics is significant. In addition, now 47.5 wt % of the sample is in the

hydrocarbon fraction, up from 33.3 wt %. Notice that there is a slight reduction in heteroatom content. In spite of its improvements, the coker distillate was still not suitable for further evaluation because of its high heteroatom and aromatic content and its low saturate content.

Process Intermediates from Hydrogenation

Hydrogenation experiments were conducted on the middle distillate and atmospheric gas oil to remove heteroatoms and to saturate aromatic rings. The process conditions and properties of the process intermediates are listed in Table 19. Each distillate was hydrogenated at two different temperatures. This was done to estimate the level of severity that might be appropriate for conversion of the distillates to high-density aviation turbine fuel intermediates.

The middle distillate was hydrogenated at a pressure of 1750 psig, a liquid hourly space velocity of 1, a hydrogen feed ratio of 8000 scfb, and at temperatures of 635 and 650°F (335 and 343°C). The hydrogen consumption increased with reactor severity from 2681 to 2835 scfb. The amount of nitrogen and sulfur was reduced to the part-per-million level in the two process intermediates, and the specific gravity decreased with increasing reactor temperature. The distillate range and hydrocarbon-type distribution were not significantly affected by the increase in reactor temperature.

The atmospheric gas oil was hydrogenated at a pressure of 2000 psig, a liquid hourly space velocity of 1, a hydrogen feed ratio of 8000 scfb, and at temperatures of 700 and 715°F (371 and 379°C). The hydrogen consumption increased with reactor severity from 2269 to 2559 scfb. The amount of nitrogen and sulfur in the intermediates decreased with increasing reactor temperature, and the specific gravity was only slightly reduced with increasing reactor temperature. The distillate range was not significantly affected by the increase in reactor temperature, and the percentage of saturates increased slightly with respect to aromatics. This is due, primarily, to an increase in alkanes.

During the hydrogenation process, the heteroatom content and the distillate range of all intermediates significantly decreased with respect to the original distillates. The total heteroatom content was reduced from the 5.7 to 8.5 wt % level to the part-per-million level. A significant amount of thermal cracking occurred during the hydrogenation of the distillates. For the middle distillate, the conversion in distillate range was significant, the process intermediates contain about 50 wt % distilling below 350°F (177°C) rather than the original 3 wt %. For the atmospheric gas oil, a rather significant reduction in the distillate range was also the result of the hydrogenation process. More than one-third of the material distilling in the 550-800°F (288-427°C) range was converted to the next lower reported distillate range. The specific gravity of the process intermediates was decreased with respect to the original distillates. The specific gravity of the distillates ranged from 0.9750 to 1.0313, whereas the specific gravity of the process intermediates ranged from 0.9178 to 0.9598.

Hydrocarbon-group-type analysis of the process intermediates produced from the middle distillate contained less alkanes than the original distillate. However, the percentage of alkenes in the intermediates doubled because of the processing. Monocyclic alkanes were also significantly increased. The percentage of saturates increased from 40 to about 75 wt %. The percentage of aromatics remained about the same as that in the original distillate, about 25 wt %. The aromatics were composed of, primarily, indanes/tetralins and some alkylbenzenes. The process intermediates from the atmospheric gas oil contained about the same amount of alkanes and three times the amount of alkenes as the original distillate. In addition, they contained significant amounts of monocyclic alkanes. The percentage of saturates increased from 19.7 wt % to about 48 wt %. The percentage of aromatics also increased, in this case, from 38.1 wt % to about 52 wt %. As observed for the intermediates from the middle distillate, the aromatics from the atmospheric gas oil were composed of, primarily, indanes/tetralins and some alkylbenzenes. Even though the hydrogenation process reduced the heteroatom content to the part-per-million level and the alkane content was low, the intermediates were not suitable for evaluation as high-density turbine fuels because their alkene contents were too high and, for those intermediates from the atmospheric gas oil, the aromatic contents were too high. However, the high concentration of indanes/tetralins does seem to suggest that this coal-derived liquid may be a suitable feedstock for the production of high-density aviation turbine fuel.

Table 20 lists the results of the hydrocarbon-group-type analysis of a FCC light cycle oil and a prototype high-density aviation turbine fuel. This prototype high-density turbine fuel was prepared by hydrogenation of the light cycle oil and met most of the target values established by the U.S. Air Force. Only the freeze point and the hydrogen content were not met. These values were -17°F (-27°C) and 12.9 wt %, respectively. Distillation of this product to approximately that of JP-8 resulted in a product that met all of the target values of a high-density aviation turbine fuel. This information is presented to give an indication of what the composition of the feedstock should be so that a high-density aviation turbine fuel can be produced from it through hydrogenation.

The hydrogenation studies reported here parallel those of Smith et al. (1988). The combined results of the two studies demonstrate that during the hydrogenation of a coal-derived liquid containing high concentrations of heteroatoms, in particular oxygen, the reactions occur in the following order: sulfur removal, oxygen removal, and nitrogen removal and ring opening. Saturation of double bonds competes with these processes and results in products that are either partially hydrogenated or reflect ring-opening reactions. If these results are compared with earlier work (Smith et al. 1986) on FCC light cycle oil and pyrolysis fuel oil, there is almost complete conversion of naphthalene to dicyclic alkanes. However, the higher ring-number structures are not exclusively converted to their saturate analogs. These structures also undergo ring opening and alkyl chain cleavage to yield tetralin-type structures. It appears that two-stage hydrogenation is necessary, but the first stage must be relatively mild with the goal

being the removal of heteroatoms, in particular oxygen. The second stage is then more severe, with the goal being the saturation of alkenes and aromatic rings. If the processing is not conducted using this two-stage approach, a single-stage process will result in the opening of one of the rings of the dicyclic structures to produce monocyclic structures.

Table 1. Specifications of Jet Fuels

Property	JP-4	JP-8	Near-Term JP-8X
Specific Gravity, 60°F	0.751-0.802	0.775-0.840	0.850 min
Hydrogen, wt %	13.6 min	13.5 min	13.0 min
Boiling Range, °F (ASTM D-2887)	Report-608	Report-626	300-653
Net Heat of Combustion, Btu/gal x 10 ⁻³	115.2 min	118.9 min	130 min
Freeze Point, °F	-72 max	-58 max	-53 max
Aromatics, vol %	25.0 max	25.0 max	30.0 max
Paraffins, vol %	Not Specified	Not Specified	10.0 max

Table 2. Chemical and Physical Properties of a Coal-Derived Liquid and its Distillates and Residue

Property	Whole Oil	Naphtha	Middle Distillate	Atmospheric Gas Oil	Vacuum Gas Oil	Residue
Elemental Composition, wt %						
Carbon	82.9	84.6	82.2	85.2	85.0	86.1
Hydrogen	8.7	11.6	9.3	9.1	8.0	6.5
Nitrogen	1.1	0.3	0.5	1.1	1.4	1.7
Sulfur	1.1	1.5	0.7	0.8	1.0	0.9
Oxygen ^a	6.2	2.0	7.3	3.8	4.6	4.8
Hydrogen-to-Carbon Atomic Ratio						
	1.25	1.63	1.35	1.27	1.12	0.90
Viscosity, cP						
100°F	67.8	-	42.0	83.2	97,800	-
190°F	7.0	-	-	-	-	-
Specific Gravity, 60°F						
	1.0407	0.8453	0.9750	1.0313	1.1080	-
Molecular Weight						
	180	-	190	230	270 ^b	-
Water, wt %						
	1.82	0.46	-	-	-	-
Ash, wt %						
	0.0	-	-	-	-	0.42
Conradson Carbon Residue, wt %						
	4.3	-	-	-	-	-
Pour Point, °F						
	-	-	-29	57	97	-

^a Oxygen determined directly, elemental composition then normalized to 100 wt %.

^b Molecular weight determined in pyridine, all other molecular weights determined in toluene.

Table 3. Results of Simulated Distillation Analysis of a Coal-Derived Liquid and its Distillates, vol %

Boiling Range, °F	Whole Oil ^a	Naphtha	Middle Distillate	Atmospheric Gas Oil	Vacuum Gas Oil ^a
IBP-350	2.4	71.3	2.9	0	0
350-550	31.9	28.7	92.4	6.1	2.2
550-800	43.9	0	4.7	88.4	54.3
800-1000	13.1	0	0	5.5	34.9
Residue	8.7	0	0	0	8.6

^a Data reported as weight percent as determined by the method.

Table 4. Results^a of Chromatographic Separation of Distillates from a Coal-Derived Liquid, wt %

Chromatographic Fraction	Middle Distillate	Atmospheric Gas Oil	Vacuum Gas Oil
Saturates	40.0	19.7	6.5
Aromatics	27.2	38.1	26.8
Polar Aromatics	32.8	33.1	16.1
Asphaltenes	0	9.1	49.1
Preasphaltenes	0	0	1.5

^a Chromatographic data corrected using mass spectral results.

Table 5. Results of Hydrocarbon-Group-Type Analysis of the Distillates from a Coal-Derived Liquid, wt %

Hydrocarbon Type	Naphtha	Middle Distillate	Atmospheric Gas Oil	Vacuum Gas Oil
Alkanes	8.2	23.4	14.0	3.6
Alkenes	9.8	15.2	5.7	-
Monocyclic Alkanes	12.0	0.1	0	0.6
Dicyclic Alkanes	0	0.3	0	0.5
Tricyclic Alkanes	0.1	1.0	0	1.5
Tetracyclic Alkanes	0	0	0	0.3
Pentacyclic Alkanes	0	0	0	0
Hexacyclic Alkanes	<u>0</u>	<u>0</u>	<u>0</u>	<u>0</u>
Total Saturate Hydrocarbons	30.1	40.0	19.7	6.5
Monoaromatics	69.9	22.1	0.7	5.4
Diaromatics	0	5.1	22.0	7.5
Triaromatics	0	0	15.4	5.7
Tetraaromatics	0	0	0	5.5
Pentaaromatics	0	0	0	0.1
Thiopheno Aromatics	ND	ND	ND	0.5
Unidentified Aromatics	<u>ND</u>	<u>ND</u>	<u>ND</u>	<u>2.1</u>
Total Aromatic Hydrocarbons	69.9	27.2	38.1	26.8
Total Hydrocarbons	100.0	67.2	57.8	33.3

ND = not determined

Table 6. Chemical and Physical Properties of the Raffinates from the Acid-Base Extraction of Distillates from a Coal-Derived Liquid

Property	Middle Distillate	Atmospheric Gas Oil	Vacuum Gas Oil
Elemental Composition, wt %			
Carbon	84.4	84.8	85.7
Hydrogen	10.0	10.6	8.0
Nitrogen	0.2	0.4	0.8
Sulfur	0.9	0.9	1.2
Oxygen ^a	4.5	3.3	4.3
Hydrogen-to-Carbon Atomic Ratio			
	1.41	1.49	1.11
Viscosity, cP, 100°F	3.1	53.6	39,700
Specific Gravity, 60°F	0.9478	1.0158	0.9871
Molecular Weight	180	240	310

^a Oxygen determined directly, elemental composition then normalized to 100 wt %.

Table 7. Results of Simulated Distillation Analysis of the Raffinates from the Acid-Base Extraction of Distillates from a Coal-Derived Liquid, vol %

Boiling Range, °F	Middle Distillate	Atmospheric Gas Oil	Vacuum Gas Oil ^a
IBP-350	0	0	0
350-550	91.5	7.8	0.5
550-800	8.5	86.9	52.6
800-1000	0	5.3	34.9
Residue	0	0	12.0

^a Data reported as weight percent as determined by the method.

Table 8. Results^a of Chromatographic Separation of the Raffinates from the Acid-Base Extraction of Distillates from a Coal-Derived Liquid, wt %

Chromatographic Fraction	Middle Distillate	Atmospheric Gas Oil	Vacuum Gas Oil
Saturates	32.3	23.0	9.5
Aromatics	37.1	35.0	33.6
Polar Aromatics	30.6	37.5	18.2
Asphaltenes	0	4.5	38.7
Preasphaltenes	0	0	0

^a Chromatographic data corrected using mass spectral results.

Table 9. Results of Hydrocarbon-Group-Type Analysis of the Raffinates from the Acid-Base Extraction of Distillates from a Coal-Derived Liquid, wt %

Hydrocarbon Type	Middle Distillate	Atmospheric Gas Oil	Vacuum Gas Oil
Alkanes	16.5	16.2	0.2
Alkenes	13.7	6.8	-
Monocyclic Alkanes	0.1	0	0
Dicyclic Alkanes	0.8	0	0
Tricyclic Alkanes	1.2	0	1.5
Tetracyclic Alkanes	0	0	5.3
Pentacyclic Alkanes	0	0	2.2
Hexacyclic Alkanes	<u>0</u>	<u>0</u>	<u>0.3</u>
Total Saturate Hydrocarbons	32.3	23.0	9.5
Monoaromatics	30.1	0.5	13.0
Diaromatics	6.9	18.0	6.5
Triaromatics	0.1	16.5	3.4
Tetraaromatics	0	0	3.6
Pentaaromatics	0	0	1.4
Thiopheno Aromatics	ND	ND	1.6
Unidentified Aromatics	<u>ND</u>	<u>ND</u>	<u>4.1</u>
Total Aromatic Hydrocarbons	37.1	35.0	33.6
Total Hydrocarbons	69.4	58.0	43.1

ND = not determined

Table 10. Chemical and Physical Properties of the Dewaxed Products of the Distillates from a Coal-Derived Liquid

Property	Atmospheric Gas Oil	Vacuum Gas Oil
Elemental Composition, wt %		
Carbon	84.5	84.5
Hydrogen	9.3	8.8
Nitrogen	0.9	1.2
Sulfur	1.1	0.8
Oxygen ^a	4.2	4.7
Hydrogen-to-Carbon Atomic Ratio	1.31	1.24
Viscosity, cP, 100°F	136	317,000
Specific Gravity,		
60°F	1.0417	-
100°F	1.0283	1.1024
Pour Point, °F	25	93

^a Oxygen determined directly, elemental composition then normalized to 100 wt %.

Table 11. Results of Simulated Distillation Analysis of the Dewaxed Products of the Distillates from a Coal-Derived Liquid, vol %

Boiling Range, °F	Atmospheric Gas Oil	Vacuum Gas Oil ^a
IBP-350	0	0
350-550	9.4	2.2
550-800	86.2	54.2
800-1000	4.4	34.5
Residue	0	8.9

^a Data reported as weight percent as determined by the method.

Table 12. Results^a of Chromatographic Separation of the Dewaxed Products of the Distillates from a Coal-Derived Liquid, wt %

Chromatographic Fraction	Atmospheric Gas Oil	Vacuum Gas Oil
Saturates	18.3	4.8
Aromatics	34.5	30.2
Polar Aromatics	34.7	18.7
Asphaltenes	11.0	44.1
Preasphaltenes	1.5	2.2

^a Chromatographic data corrected using mass spectral results.

Table 13. Results of Hydrocarbon-Group-Type Analysis of the Dewaxed Products of the Distillates from a Coal-Derived Liquid, wt %

Hydrocarbon Type	Atmospheric Gas Oil	Vacuum Gas Oil
Alkanes	11.6	1.7
Alkenes	6.7	-
Monocyclic Alkanes	0	0.2
Dicyclic Alkanes	0	0.5
Tricyclic Alkanes	0	1.0
Tetracyclic Alkanes	0	0.7
Pentacyclic Alkanes	0	0.6
Hexacyclic Alkanes	<u>0</u>	<u>0.1</u>
Total Saturate Hydrocarbons	18.3	4.0
Monoaromatics	0.5	10.6
Diaromatics	14.5	5.3
Triaromatics	19.5	4.1
Tetraaromatics	0	3.1
Pentaaromatics	0	1.1
Thiopheno Aromatics	ND	0.7
Unidentified Aromatics	<u>ND</u>	<u>5.3</u>
Total Aromatic Hydrocarbons	34.5	30.2
Total Hydrocarbons	52.8	35.0

ND = not determined

Table 14. Chemical and Physical Properties of Fuel Candidates Prepared from a Coal-Derived Liquid

Property	High-Density Fuel	Test Fuel #1	Test Fuel #2
Elemental Composition, wt %			
Carbon	-	83.1	83.9
Hydrogen	13.0 min	9.7	9.9
Nitrogen	-	0.2	0.2
Sulfur	0.4 max	0.6	0.6
Oxygen ^a	-	6.4	5.4
Specific Gravity, 60°F	0.85 min	0.9638	0.9518
Freeze Point, °F	-53 max	-	-
Pour Point, °F	-	-	-24
Heat of Combustion (net), Btu/gal	130,000 min	128,650	129,110

^a Oxygen determined directly, elemental composition then normalized to 100 wt %.

Table 15. Results of Simulated Distillation Analysis of Fuel Candidates Prepared from a Coal-Derived Liquid, °F

Boiling Range, vol %	High-Density Fuel	Test Fuel #1	Test Fuel #2
IBP	300	334	343
10%	-	387	394
20%	-	406	417
50%	-	458	472
90%	-	534	546
FBP	550	615	700

Table 16. Results^a of Hydrocarbon-Group-Type Analysis of the Hydrocarbon Fraction from Test Fuel #2 Prepared from a Coal-Derived Liquid, wt %

Saturate Hydrocarbons		Aromatic Hydrocarbons	
Alkanes	15.1	Alkylbenzenes	3.0
Alkenes	6.6	Indanes/Tetralins	55.0
Monocyclic Alkanes	0	Naphthalenes	19.4
Dicyclic Alkanes	0.1	Fluorenes	0.4
Tricyclic Alkanes	<u>0.4</u>	Anthracenes	<u>0</u>
Total Saturate Hydrocarbons	22.2	Total Aromatic Hydrocarbons	77.8

^a 62.2 wt % of sample not analyzed by GC/MS.

Table 17. Conditions Used, Yields, and Properties of Coker Distillate Obtained from the Vacuum Gas Oil from a Coal-Derived Liquid

Process Conditions		Coker Distillate Properties	
Pressure, psig	100	Elemental Composition, wt %	
Reactor Volume, mL	721	Carbon	85.1
Reactor Temperature, °F	900	Hydrogen	8.4
Outlet Temperature, °F	800	Nitrogen	1.2
Oil Flow Rate, mL/hr	200	Sulfur	0.9
		Oxygen ^a	4.4
Yield		H/C Ratio	1.18
		Specific Gravity, 60°F	1.0408
Material In, g		Boiling Range, vol %	
Feed to the Reactor	356	IBP-350°F	9.0
Material Out, g		350-550°F	19.2
Coker Distillate	205	550-800°F	62.7
Coke	104	800-1000°F	9.1
Gas	23	Residue	0
Water + Loss	24		
Recovery, %	93.3		

^a Oxygen determined directly, elemental composition then normalized to 100 wt %.

Table 18. Results^a of Hydrocarbon-Group-Type Analysis of the Hydrocarbon Fraction from Coker Distillate Obtained from the Vacuum Gas Oil from a Coal-Derived Liquid, wt %

Saturate Hydrocarbons		Aromatic Hydrocarbons	
Alkanes	7.5	Monoaromatics	17.7
Alkenes	0.3	Diaromatics	9.3
Monocyclic Alkanes	0	Triaromatics	12.7
Dicyclic Alkanes	0	Tetraaromatics	0
Tricyclic Alkanes	0	Pentaaromatics	0
Total Saturate Hydrocarbons	7.8	Total Aromatic Hydrocarbons	39.7

^a 52.5 wt % of sample not analyzed by GC/MS.

Table 19. Conditions Used and Properties of Process Intermediates from the Hydrogenation of Distillates from a Coal-Derived Liquid

	Middle Distillate		Atmospheric Gas Oil	
<u>Process Conditions</u>				
Pressure, psig	1750	1750	2000	2000
Liquid Hourly Space				
Velocity, V_o/V_c /hr	1	1	1	1
Hydrogen Feed, scfb	8000	8000	8000	8000
Temperature, °F	635	650	700	715
Hydrogen Consumption, scfb	2681	2835	2269	2559
<u>Product Properties</u>				
Elemental Composition,				
Carbon, wt %	86.0	85.9	87.8	87.6
Hydrogen, wt %	14.0	14.1	12.2	12.4
Nitrogen, ppm	<20	<20	270	59
Sulfur, ppm	<20	27	97	35
Specific Gravity, 60°F	0.9208	0.9178	0.9598	0.9558
Boiling Range, vol %				
IBP-350°F	49.8	51.9	7.6	8.9
350-550°F	46.2	44.0	34.8	36.7
550-800°F	4.0	4.1	54.6	51.7
800-1000°F	0	0	3.0	2.7
Residue	0	0	0	0
Hydrocarbon Type, wt %				
Alkanes	4.2	3.8	8.8	13.7
Alkenes	34.2	35.1	17.5	17.4
Monocyclic Alkanes	34.2	36.2	18.5	17.8
Dicyclic Alkanes	0.6	1.4	1.8	1.1
Tricyclic Alkanes	<u>0.5</u>	<u>0</u>	<u>0.2</u>	<u>0</u>
Total Saturate				
Hydrocarbons	73.7	76.5	46.8	50.0
Alkylbenzenes	8.1	8.7	6.8	7.0
Indanes/Tetralins	18.0	14.7	42.8	40.7
Naphthalenes	0.2	0.1	0.8	0.8
Fluorenes	0	0	2.0	1.0
Anthracenes/Phenanthrenes	<u>0</u>	<u>0</u>	<u>0.8</u>	<u>0.5</u>
Total Aromatic				
Hydrocarbons	26.3	23.5	53.2	50.0

Table 20. Results of Hydrocarbon-Group-Type Analysis of FCC Light Cycle Oil and a Prototype High-Density Aviation Turbine Fuel, wt %

Hydrocarbon Type	FCC Light Cycle Oil ^a	Prototype High-Density Fuel ^b
Alkanes	4.4	4.6
Alkenes	0	0
Monocyclic Alkanes	0	12.2
Dicyclic Alkanes	0	54.6
Tricyclic Alkanes	<u>0</u>	<u>12.3</u>
Total Saturate Hydrocarbons	4.4	83.7
Alkylbenzenes	7.9	8.2
Indanes/Tetralins	4.9	6.8
Hexahydrofluorenes	2.4	1.1
Naphthalenes	38.9	0
Hexahydrophenanthrenes	2.0	0
Dihydrofluorenes	17.6	0.1
Fluorenes	15.4	0
Anthracenes/Phenanthrenes	6.4	0
Dihdropyrenes	<u>0.2</u>	<u>0</u>
Total Aromatic Hydrocarbons	95.7	16.2

^a Cha et al. 1988

^b Smith et al. 1986

CONCLUSIONS

In this study, we evaluated five processes for their ability to produce intermediates from suitable distillates for the production of high-density aviation turbine fuel. These processes include acid-base extraction, solvent dewaxing, Attapulugus clay treatment, coking, and hydrogenation. Acid-base extraction decreased the heteroatom content of the distillates (middle distillate, atmospheric gas oil, and vacuum gas oil), in particular, nitrogen in all of them and oxygen in the middle distillate. Because of their low paraffin content, solvent dewaxing did not have a significant affect on the chemical properties of the gas oils. The only meaningful changes were increases in the viscosity and specific gravity and decreases in the pour point. However, the products were still not suitable for evaluation as fuel candidates because their heteroatom contents were still too high.

Attapulugus clay treatment of the middle distillate reduced the heteroatom content, but not to the level required for a high-density aviation turbine fuel. In addition, the hydrogen content was low, and the aromatic content was high. The distillate range and the specific gravity of the vacuum gas oil were reduced through coking. In addition, the H/C ratio was slightly increased due to the conversion of aromatic compounds to coke. However, the heteroatom content was not significantly affected by the process. Consequently, we decided that further evaluation of this product was not warranted. Because acid-base extraction and Attapulugus clay treatment did not reduce the heteroatom content of the distillates to the levels appropriate for a fuel candidate, hydrogenation was evaluated as a process to not only reduce the heteroatom content but also saturate the aromatic rings present in the middle distillate and atmospheric gas oil. The heteroatom content of the process intermediates was reduced to the part-per-million level. However, the saturation of aromatics and olefins was not accomplished during the application of the single-stage hydrogenation process. Consequently, evaluation of the process intermediates as fuel candidates was not conducted. In summary, the processes evaluated did not result in the production of materials that satisfied all of the requirements of a high-density aviation turbine fuel.

In spite of our difficulties in preparing fuel candidates suitable for evaluation as high-density aviation turbine fuels, we believe that a two-stage hydrogenation process can be employed to produce a high-density turbine fuel that meets the requirements of the U.S. Air Force. This premise is based on the observation that the process intermediates from hydrogenation contain high concentrations of dicyclic alkanes and indanes/tetralins; compounds that are necessary for the production of a high-density aviation turbine fuel.

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DISCLAIMER

Mention of specific brand names or models of equipment is for information only and does not imply endorsement by Western Research Institute or the United States Department of Energy.

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