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Characterization of Coal Liquids

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ABSTRACT

The objective of this investigation is to evaluate the processability of the primary products of coal liquefaction generated by three ERDA sponsored processes: Synthoil, Solvent Refined Coal (SRC), and H-Coal. The study entails actual bench scale processing of coal liquids and an in-depth analytical characterization of charge and product streams. The results are intended to indicate the nature and degree of possible upgrading of primary coal liquids using technology now available in the petroleum refining industry.

Six primary coal liquids were filtered and hydrotreated under commercial conditions, using a fixed bed of commercial catalyst. These included Synthoil, H-Coal hydroclone underflow, and four SRC process streams - SRC filter feed, SRC filtrate and solvent refined coal itself, both neat and cutback with process solvent.

In all cases catalytic hydrotreating was able to substantially eliminate sulfur and benzene insoluble matter. A 90% reduction of heptane insoluble matter and 80% reduction in nitrogen content could be achieved with SRC and H-Coal liquids.

Catalyst stability was affected by metals and particulates in the feed. None of the products, as received can be considered an acceptable feedstock to a conventional fixed bed hydrotreating unit. The ash remaining will agglomerate with the solid catalyst pellets and shorten catalyst life.

Two of the hydrotreated coal oils, Synthoil and SRC, were further processed under commercial conditions over a fixed bed of commercial hydrocracking catalyst. Catalyst stability was unsatisfactory when the total upgraded products were processed. An asphaltene-free vacuum gas oil derived from hydrotreated Synthoil responded satisfactorily to hydrocracking.

Analytical characterization of primary coal liquids and of the corresponding hydrotreated products was based on an extensive solvent and chromatographic separation scheme known as SARA (Saturates-Aromatics-Resins-Asphaltenes). Selected fractions from this separation were inspected by advanced instrumental techniques including nuclear magnetic resonance (NMR), electron spin resonance (ESR), mass spectroscopy (MS), and thermogravimetric analysis (TGA). In addition, membrane filtration was used to characterize the particulates and metals present. Ultimate objective of this phase of the study is to correlate analytical properties of coal liquids with their response to hydrotreating and their effect on catalyst stability.

I. INTRODUCTION

1.1. Technical Objectives

The objective of this work is to evaluate the processability of the primary products of coal liquefaction generated by three ERDA sponsored processes: Synthoil, Solvent Refined Coal (SRC), and H-Coal. The study entails (1) actual bench scale processing of eight coal liquids derived from these three processes, and (2) an in-depth analytical characterization of charge and product streams. The results are intended to indicate the nature and degree of upgrading of primary coal liquids possible using technology now available in the petroleum refining industry.

1.2. Background

Primary coal liquids are high viscosity black oils or pitches. Compared to petroleum crudes, they are deficient in hydrogen, only partially soluble in benzene, and contain relatively high levels of oxygen and nitrogen. They contain a variable amount of ash and unconverted coal, depending on the efficiency of the mechanical removal of solids achieved in each process.

These coal liquids were originally intended to serve as boiler fuels. Their sulfur content may be sufficiently low to qualify them as replacement for high sulfur coal, and bring sulfur dioxide emissions within acceptable limits. However, for large boilers, such as major base load power plants, pollution control via coal hydroliquefaction is probably not competitive with stack gas scrubbing.

In other fuel markets, coal liquids can be more competitive. Industrial boilers are not presently amenable to stack gas scrubbing. The same is true of smaller utility plants. In particular, peak load units require a clean, storable liquid fuel as an alternative to natural gas. However, the high viscosity of primary coal liquefaction products is undesirable for many of these applications. Also, their residual sulfur and nitrogen contents may be excessive as emission standards become more stringent.

Down the road, under conditions of short supply of petroleum, lies the problem of providing a portion of the demand for transportation fuels from coal. Transportation fuels - jet fuel, diesel fuel, and gasoline - are distillates boiling below 650°F. The quantity of such distillates in primary coal liquids is, however, small.

In order for primary coal liquids to serve these markets, they must be upgraded. A logical route is to employ current black oil conversion technology as practiced in the petroleum industry. An applicable UOP process is RCD Unibon. This comprises the direct processing of petroleum residues to reduce the sulfur content of heavy fuel oil, or to combine desulfurization with converion of residue to lighter, more valuable products. Commercially proven in several large installations around the world, the economic and technical feasibility of the process has been well established.

Successful upgrading of primary coal liquids by such processes will provide a low viscosity, non-polluting boiler fuel for industrial use. Alternatively, it will provide a syncrude more closely resembling petroleum crudes for downstream refinery processing to transportation fuels. Sulfur, nitrogen, and oxygen contents will be substantially reduced. The extensive conversion of asphaltic materials, benzene and heptane insolubles, which is evidenced in this report, is also highly significant. It implies a high yield of deasphalted charge stock for subsequent hydrocracking, considerably greater than could be obtained by vacuum distillation.

1.3. Approach

1.3.1. Process Studies

The principal process considered for upgrading was fixed bed catalytic hydrotreating, a major black oil conversion process. Processing was carried out in bench scale pilot plants operated continuously on a 24 hour basis. These units are customarily employed in petroleum research to evaluate charge stocks and catalysts. Typically, they process 25-1000 ml/hr charge stock over 10-1000 ml catalyst in a fixed bed with hydrogen recycle. They yield commercially significant data on product yields, distribution, and degree of upgrading at specified reaction conditions. The cost of operating is a fraction of that of a full scale pilot plant.

The commercial black oil conversion catalyst used was a composite of Group VI and Group VIII metals dispersed on a high surface area refractory support. The process conditions employed were generally in a range of commercially practiced conditions which may be categorized as "severe".

Temperature	375-450°C
Pressure	2000-3000 psig
Space Velocity	0.25-1.0 hr^{-1}

At the request of ERDA, two of the eight coal liquids were not primary hydroliquefaction products, but upgraded material produced in the hydrotreating program. These were hydrocracked to determine yield of distillate fuels obtainable over a commercial catalyst at commercially practicable conditions.

Ancillary to these process studies were physical operations, such as filtration, distillation, and blending, where necessary as pretreatment steps.

1.3.2. Analytical Studies

In addition to process studies, an in-depth analytical characterization of primary and upgraded coal liquids was undertaken. In the case of petroleum distillates and to some degree petroleum crudes, correlations between analytical properties and processability have served as a basis for prediction of product quality and yield structure in various refining processes. In the case of petroleum residuum, the correlations are not so advanced. However, considerable effort has been devoted, for example at the Laramie Energy Research Center (LERC), in characterizing asphaltic materials. The basis of this characterization is the SARA (Saturates-Aromatics-Resins-Asphaltenes) separation. The quantitative analytical data generated by the separation scheme are supplemented by inspection of individual fractions by instrumental techniques - mass spectroscopy (MS), electron spin resonance spectroscopy (ESR), nuclear magnetic resonance spectroscopy (NMR), thermogravimetric analysis (TGA), differential thermal analysis (DTA), and osmometric molecular weight determination. In addition, analysis for metals and particulates in the total feed should correlate with catalyst stability.

Objective of the extension of these procedures to coal liquids was to determine which of the several analytical determinations, or which of the various instrumental techniques would show promise of correlating with and predicting processability. As in the case of petroleum residuum, the study is still in an exploratory stage, and the conclusions reached must be regarded as tentative.

2. PROCESS STUDIES

2.1. General

2.1.1. Equipment

Two bench scale pilot plants were used in these studies, UOP Corporate Research Plants 505 and 638H. Plant 505 has a maximum catalyst capacity of 200 ml in a 62 cm bed. Hydrogen and coal liquid are passed concurrently downflow over the catalyst. Figure 1 illustrates the plant at the beginning of this work, and Figure 2 shows the flow scheme.

The original feed system of Plant 505 was found inadequate to handle some of the high viscosity primary coal liquefaction products. The feed system was rebuilt as shown in Figure 3 to provide high temperature tracing on all lines, and positive pressure on the feed pump suction.

Plant 638H has essentially the same flow scheme, but a maximum catalyst capacity of 800 ml in the same bed length as Plant 505. It also was provided with a special hot feed system to handle the more viscous stocks.

2.1.2. Product Workup

Products from the bench scale plants included gas, stripper overhead, and stripper bottoms. In the case of hydrotreating runs, the last usually comprised over 90% of the exit streams. It was the only portion analyzed in detail, and is referred to as "product". For hydrocracking runs, the last two were combined to provide samples for analysis and vacuum distillation, and the composite is referred to as "liquid product" in these cases. Analytical procedures were standard ASTM and UOP methods, and are specified in Appendix A.4.

2.1.3. Process Conditions

For the most part, bench scale studies were made in the range of conditions cited above as commercially practiced. For reporting purposes a set of base conditions was selected within these ranges. The experimental conditions employed in each test period are referred to these base values:

Temperature	T-T (base), °C
Pressure	P-P (base), psig
Space Velocity	WHSV/WHSV (base)

2.1.4. Tabulation of Data

The data secured in the bench scale units, both process conditions and product properties, are grouped under numbered runs, each of which corresponds to a series of experiments performed with a single catalyst loading. The runs are then divided into periods, each of which represents lined out operation at a particular set of conditions.

2.2. Hydrotreating Synthoil(1)

Two drums of centrifuged Synthoil were received from the ERDA Pittsburgh Energy Research Center. Inspections are given in Table 1 (3296-109). The sample contained 1.4% ash, necessitating a preliminary filtration. It later developed that the sample contained over 0.1% ammonium chloride which plugged the hydrotreating reactor. This necessitated further pretreatment of the filtrate by water washing.

2.2.1. Pretreatment

Filtration. One drum of Synthoil (about 160 kg) was filtered conventionally at 160°C, feeding 350 g oil/hr through a 20 cm diameter 10 μm pore Teflon filter element. The filter element was changed twice daily due to pressure buildup to as high as 60 psig. Prior to changing filter elements, the cake was nitrogen blown two hours at 5 SCF/hr.

During the first 12 days of operation, the filter cake was hard with a plastic or rubbery texture. This was probably associated with the fine particle size of the ash not removed by centrifugation. The filtrate contained 0.1% ash, considered excessive for subsequent processing in a fixed bed catalyst system. Thereafter the filter element was precoated with 100 g Celite filter aid, applied as a 10% suspension in toluene. This improved the quality of the filtrate to 0.02% ash.

The high ash filtrates were reprocessed using precoated filter elements. The filtrate quality was generally poorer, partly due to attempts to increase the filtration rate. Average ash content of the reprocessed filtrates was 0.05%.

Table 2 gives a material and component balance representative of precoat filtration with fresh feed. The Celite precoat interfered with direct measurement of ash and DMF/xylene insoluble organic matter on the cake. These were estimated, in combination, by difference. Inspections of the filtrate (3296-143) are given in Table 1.

Water Washing for NH_4Cl Removal. During the first hydrotreating run on Plant 505 with filtered Synthoil, a plug developed in the lower part of the reactor. This was immediately determined to be a high chloride material. Chloride analyses (sodium biphenyl reagent) of the filter feed showed 361 ppm Cl. A sample from the second, unopened, drum of Synthoil analyzed 438 ppm Cl. This demonstrated that chloride was present in the material as shipped, and was not introduced during transfer from the shipping drum to the filtration plant.

Since appearance of chloride in feedstocks is often associated with contamination by chlorinated solvents used for cleaning drums and cans, a sample of filtered Synthoil was vacuum distilled into five fractions and a bottoms as shown in Table 3. Each of the overhead cuts was analyzed for chloride. The chloride content peaked at 4,820 ppm in the 340-380°C cut. The summed chloride contents of the overhead cuts was 672 ppm - almost twice the analyzed level in the total feed (361 ppm), even with the chloride in the 414°C$^+$ bottoms not included. The heavy ends in the total sample apparently interfered with complete chloride assay by the sodium biphenyl method.

The 340-380°C cut was water washed. The chloride was completely water soluble. Coextracted with the 0.48% chloride was 0.60% ammonia. This indicated that the chloride contaminant was ammonium chloride. Analysis of the material which plugged the reactor confirmed the presence of ammonium chloride.

To provide chloride-free feedstock for the process variable study on Plant 505, about 17 kg of Synthoil filtrate was water washed in the laboratory. Five extractions were carried out at 90°C, a water/oil ratio of 1 to 1.5, with a mixing time of 15 minutes, settling time of 30 minutes. Water was decanted, and finally removed by centrifugation. The washed Synthoil filtrate contained <10 ppm chloride, while the nitrogen content dropped from 1.46% to 1.31%. The minimum chloride level in the unwashed Synthoil computed from analyses of distillate fractions (672 ppm), corresponds to 0.1% ammonium chloride. The drop in nitrogen content on washing (0.15%) corresponds to 0.57% ammonium chloride.

The remainder of the filtered Synthoil, principally the reprocessed filtrate, about 117 kg (28 gallons), was water washed in the pilot plants, using a 10-gallon glass lined Pfaudler kettle. Seven batches were required. Conditions were similar to those of the laboratory runs, except that centrifuging was omitted.

Inspections of the washed Synthoil filtrate (3296-147) are given in Table 1.

The increase in heptane insolubles after washing, from 15.2% to 18.8%, was verified by replicate analyses and must be regarded as real. It is probably due to prolonged exposure to air at 90°C. Other changes in physical properties, for example, increases in viscosity and average molecular weight, also indicate a slight degradation incurred by the hot washing.

2.2.2. Hydrotreating

Three bench scale hydrotreating runs were made on pretreated Synthoil. Plant 505 was used for the first two, which were process variable studies. Charge stock to Run 816 was filtered Synthoil centrifugate (3296-143). Charge stock to Run 818 was water washed Synthoil filtrate (3296-147). A 436 hour run was made with washed filtrate in Plant 638H (Run 3) at a single condition to prepare hydrocracking charge stock.

Plant 505, Run 816. Three sets of conditions were completed before plugging near the bottom of the reactor necessitated shutdown at 90 hours. Plugging was due to a deposit of ammonium chloride. Results are summarized in Table 4.

At base conditions (Periods 3 and 4), the residual heptane insoluble was 3.44%, corresponding to 77% conversion. Residual nitrogen was 0.447%, corresponding to 69% conversion. No catalyst activity check was run, due to premature shutdown.

Plant 505, Run 818. The process variable matrix run on the washed Synthoil comprised two space velocities and two pressures, at a single temperature 10°C above base. A catalyst activity check was made at the end of the run. Results are given in Table 5.

For the first 156 hours of the run, the lower part of the catalyst bed was underheated, although the catalyst peak temperature, near the inlet, was maintained at the specified value. The situation was rectified by correcting an improperly connected block thermocouple. The net effect was that the process variable study was started with a catalyst which had accumulate more service than normal in these studies.

The effect of lowering pressure 800 psig was pronounced.

	Residual, Wt-%		Conversion, Wt-%	
	Heptane Insol.	N	Heptane Insol.	N
Base Pressure, Periods 14, 15	4.31	.414	77.1	68.4
Low Pressure, Periods 20, 21	8.62	.763	54.1	41.8

The effect of pressure on heptane insoluble conversion is further illustrated in Figure 4.

The above conversions in Periods 14 and 15 are the same as obtained at base conditions in Run 816, noted above, in the presence of ammonium chloride. This suggests that ammonium chloride did not interfere with hydrotreatment. In fact, one could speculate that since Periods 14 and 15 were run 10°C above base, some benefits accrued from presence of ammonium chloride. On the other hand, catalyst service was quite different in the two cases.

There appeared to be a small activity decline between Periods 14 and 15 (156-168 hours on stream), and Periods 22 and 23 (260-272 hours on stream):

	Heptane Insoluble	
	Residual, Wt-%	Conversion, Wt-%
156-168 hours	4.31	77.1
260-272 hours	5.46	71.0

Plant 638H, Run 3. This run of 436 hours duration was made at a single set of conditions - base pressure, 5°C below base temperature, and one-half base space velocity. Object was to prepare 15 gallons of hydrotreated Synthoil containing 3.5% heptane insolubles for use as feedstock in hydrocracking studies. After 138 hours, the catalyst showed reasonable stability:

On Stream Time, Hrs	Residual Heptane Insoluble, Wt-%
42	3.46
114	3.67
138	3.84
186	4.03
282	4.05
354	4.02
425	3.94

The daily analyses are logged in Figure 5. A 5°C increase in block temperature was required over the duration of the run to maintain the specified catalyst peak temperature.

The used catalyst was removed in five sections. Each was extracted with chloroform and analyzed for carbon and some typical ash components.

Bed Location	Top	Top Middle	Middle	Bottom Middle	Bottom
Analysis, Wt-%					
C	13.9	16.6	15.7	15.2	13.0
Ti	0.81	0.39	0.05	0.02	0.01
Ca	0.022	0.034	0.023	0.016	0.013
Fe	0.22	0.23	0.12	0.06	0.04

Product Distribution. Product distributions were calculated for Plant 505, Run 818, Period 23, and for Plant 638H, Run 3, Period 5. The distributions, listed in Table 6, were remarkably similar. The preparative run in Plant 638H was made at half the space velocity and 16°C lower maximum catalyst temperature than Period 23 in the process variable study. This illustrates a trade-off of temperature for space velocity to achieve identical hydrocracking severity. However, heptane insolubles conversion was favored by low temperature and low space velocity.

Hydrogen Consumption. A hydrogen balance was made for each of the above periods for the purpose of obtaining distribution of hydrogen consumed. Results are summarized in Table 7. As might be expected from consideration of aromatic/naphthene equilibria the higher temperature operation consumed less hydrogen.

2.3. Hydrocracking Upgraded Synthoil(2)

2.3.1. Charge Stocks

The upgraded Synthoil prepared in Plant 638H, Run 3, was employed for hydrocracking studies.

Total Upgraded Synthoil. Inspection of the stripper bottoms from Plant 638H, Run 3, (3392-53) are given in Table 8. Table 9 is a summary of a selected overall material balance in Run 3 made for the purpose of obtaining product distribution data. It shows that the upgraded Synthoil constituted 85.1 wt-% of the Synthoil filtrate, corresponding to 79.2 wt-% of the Synthoil centrifugate.

Upgraded Synthoil Vacuum Distillate. The upgraded Synthoil was used to prepare a vacuum distillate. About 12.5 gallons of upgraded Synthoil was vacuum flashed to yield 7.5 gallons of 600°-950°F overhead product (Table 10). This distillate represented 59.4 wt-% of the upgraded Synthoil, corresponding to 47.0 wt-% of the Synthoil centrifugate. Inspections of the upgraded Synthoil distillate (3392-63) are given in Table 8. The table shows that the contents of nitrogen in the vacuum distillate as well as of oxygen and sulfur were the same as those in the total upgraded Synthoil.

2.3.2. Hydrocracking

Hydrocracking studies were carried out in Plant 505. Three bench scale runs were made. The first (Run 820) used the total upgraded Synthoil as feed. The second (Run 821) was a thermal hydrocracking test made at comparable conditions with the same feedstock. The third (Run 824) was carried out with the middle distillate of the upgraded Synthoil at two sets of hydrocracking conditions, including a short catalyst stability study and a final catalyst activity check at startup conditions. Commercial hydrocracking conditions, which may be categorized as "relatively severe", were used.

In Runs 820 and 824, the reactor was loaded with 150 ml of a commercial hydrocracking catalyst comprising Groups VI and VIII metals on silica-alumina. For the thermal hydrocracking run (Run 821) the reactor was loaded with 150 ml of α-Al_2O_3 spheres.

Plant 505, Run 820. Charge stock for this run was the total upgraded Synthoil (3392-53, Table 8). Hydrocracking experiments were conducted at three sets of conditions. Results are summarized in Tables 11 and 12. Table 11 shows that at base space velocity, 25°C above base temperature, and 200 psig above base pressure (Period 1) conversion, defined as volume percentage disappearance of 650°F$^+$ bottoms was 15.2%. Heptane insolubles were reduced to 2.11% from 3.68% in the feed. When the temperature was raised by 10°C (Period 5) at otherwise identical conditions, conversion increased to 25.8% while the heptane insolubles decreased to 1.63%. At the latter conditions, lowering the space velocity to 0.8 x base velocity (Period 6) increased conversion to 35.6%, and reduced the heptane insolubles to 1.54%. Although Period 6 showed a higher conversion to 650°F$^-$ distillate than Period 5, the API gravity of the liquid product remained practically unchanged.

Product distributions and hydrogen consumption data are shown in Table 12. Totals over 100% represent hydrogen added to the feedstock. Hydrogen consumption for Period 6 was slightly lower than that for Period 5, but was much higher than Period 1. Since hydrogen content of the liquid product, as shown in Table 11, was essentially the same for all these periods, the variation in hydrogen consumption was directly related to the amount of hydrogen that went to gaseous products.

Data obtained from Run 820 clearly indicate that the conversion to 650°F$^-$ distillate was very low even at conditions considered to be severe. In view of these results, it was decided necessary to prepare a Synthoil distillate for another hydrocracking run to determine if removal of the heptane insolubles would substantially increase the yield of 650°F$^-$ distillate. In addition, it was thought worthwhile to make a short thermal hydrocracking run to determine the amount of 650°F$^-$ distillate produced non-catalytically.

Plant 505, Run 821. Charge stock to this run was again the total upgraded Synthoil. The run was conducted in the absence of a catalyst. Experiments were carried out at two sets of conditions. Tables 13 and 14 summarize the results. The first experiment (Period 2) was performed at base space velocity, 12°C above base temperature, and 200 psig above base pressure. At these conditions conversion to 650°F$^-$ distillate was only 8.1%. As the temperature was increased by 25°C while other variables remained constant, conversion to 650°F$^-$ distillate increased to 18.9% (Period 4). At the latter conditions, due to high temperature treatment, the heptane insolubles in the liquid product were actually higher than that in the feedstock, 4.68% vs. 3.88%. Hydrogen content in the liquid product from both experiments was slightly lower than that of the feedstock. Hydrogen consumption (Table 14) was practically zero for the first set of conditions, indicating that the small amount of gaseous products was derived from cracking saturated short side chains. At the more severe conditions (Period 4) hydrogen consumption was 127 SCF/B. This value is in fair agreement with plant hydrogen consumption value obtained from taking the difference between measured hydrogen feed to the plant and the amount of elemental hydrogen appeared in exiting gas streams. Evidently this amount of hydrogen went to gaseous products.

Plant 505, Run 824. Charge stock for this run was the vacuum distillate of the upgraded Synthoil, (3392-63, Table 8). The objective of this run was to investigate whether removal of heptane insolubles would significantly increase production of 650°F$^-$ distillate. Conditions less severe than those used in Run 820 were selected. These conditions and the data obtained are summarized in Tables 15 and 16. Feed rate and hydrogen pressure were essentially constant over the run, base space velocity and 200 psig above base pressure. The run was started at 10°C above base temperature. Table 15 shows that from Period 1 to Period 8, while all variables stayed practically constant, there was a gradual decline in product hydrogen content from 11.50% to 11.10%, and a concomitant decrease in conversion to 650°F$^-$ distillate from 59.8% to 50.2%. When the temperature was increased by 10°C (Period 9) conversion to 650°F$^-$ distillate increased to 66.9%. During Period 11, while at identical conditions, the conversion value was unchanged. The run was then concluded with a return to the initial conditions (Period 12). This final catalyst activity check showed that after 126 hours of processing, the conversion to 650°F$^-$ distillate decreased from 59.8% to 49.7%, the product hydrogen content dropped from 11.50% to 10.99%, and the API gravity decreased from 21.9 to 17.6. It should be noted that while from Period 1 to Period 8 there was a significant loss in catalyst activity, the change in activity from Period 8 to Period 12 was very small. This seems to indicate that after an initial decline, the catalyst activity lined out.

Product distribution and hydrogen consumption data are listed in Table 16. Hydrogen consumption during Period 1 was 1413 SCF/B. This dropped to 1074 SCF/B during the final catalyst activity check period (Period 12).

The results showed that the removal of heptane insolubles increased the yield of 650°F$^-$ distillate significantly at less severe hydrocracking conditions.

As shown in Table 8, the levels of nitrogen as well as of oxygen and sulfur in the Synthoil distillate are practically the same as the total upgraded Synthoil. A comparison of results from Run 820 (Table 11) with those from Run 824 (Table 15) showed that the highest conversion of nitrogen in the upgraded Synthoil was 79.8%, while conversion of nitrogen in the distillate was 97.3% at even less severe conditions. This indicates the difficulty in converting the nitrogen present in the heptane insolubles.

2.4. Hydrotreating SRC Process Streams

Of the eight ERDA coal liquids studied, five were derived from the SRC process. This was largely due to the ready availability of samples from the large SRC plant at Ft. Lewis, Washington. The feeds processed by hydrotreating included (1) SRC filter feed, (2) SRC filtrate, (3) SRC cutback with process solvent and (4) SRC processed without addition of extraneous solvent. The fifth SRC stock was upgraded SRC, and served as a hydrocracker feed. This is covered in a separate section.

2.4.1. SRC Filter Feed.(3)

SRC filter feed was received from the Pittsburgh and Midway Coal Co., Ft. Lewis, Washington. Inspections are given in Table 17 (3296-1A). It contained 4.0% ash, which necessitated filtration prior to processing in fixed bed operation. It also contained 65 vol-% process solvent (850°F⁻ distillate). It was desirable to remove at least a part of this process solvent, and four different batch distillations were included in the pretreatment procedures.

Pretreatment

Filtration. Approximately 17 kg of SRC filter feed was filtered. Overall mass balance showed 78.2% of the feed recovered as filtrate, 19.7% as cake, and 2.1% loss. Detailed component balances are given in Table 18. Inspections of the SRC/UOP filtrate (3296-19) are given in Table 17. It is evident that the UOP filtration, in addition to removing solids, upgraded the liquid. Also, there appears to have been a slight loss of SRC, defined as 100 minus vol-% 850°F⁻ distillate by D-1160 vacuum Engler distillation:

	Filter Feed	Filtrate
Ash, wt-%	4.0	0.01
Heptane insoluble oil, wt-%	29.7	27.5
Benzene insoluble oil, wt-%	16.7	9.6
SRC, Vol-%	30.3	29.0

Distillation. The target set for distillation was a bottoms containing 80% SRC, 20% process solvent. However, the charge pump of Plant 505 requires a feed having a softening point under 350°F for dependable operation. The softening point of vacuum bottoms will depend not only on the amount of distillate taken overhead, but on the amount of degradation incurred by exposure to high temperature and atmospheric oxygen.

Four distillations were made, aimed at producing a pumpable bottoms material containing 80% SRC. They are summarized in Table 19 which includes inspection of the bottoms recovered. The first two were batch vacuum fractionations using a 3" Oldershaw column. The last two were simply batch vacuum flashes from a short necked 22 liter flask. The flash, conducted at lower temperature and shorter residence time than the fractionation, clearly risks far less thermal degradation. The fractionator bottoms containing 80% SRC was not pumpable in the hydrorefining unit, while the flash bottoms containing 77% SRC could be pumped.

Hydrotreating. Five hydrotreating runs were made using the total filtrate and the various bottoms. Conditions and results are summarized in Tables 20-23.

Plant 505, Run 801. Charge stock for this run was total filtrate 3296-19. Results are given in Table 20. Upgrading (Periods 3 and 4) was dramatic:

	Feed	Product
Benzene insoluble, wt-%	9.4	0.1
Heptane insoluble, wt-%	26.9	0.3
Sulfur, wt-%	0.72	<0.02
Nitrogen, wt-%	1.28	0.05

In view of these results, the next run was made at milder conditions.

Plant 505, Run 802. Charge stock was again total filtrate. Even under milder conditions, sulfur and benzene insolubles were reduced to negligible values (Table 20). Conversion of nitrogen and heptane insolubles responded in a normal fashion, increasing with increasing temperature, pressure, and residence time.

P-P (base) psig	T-T (base) °C	WHSV/WHSV (base)	Nitrogen, wt-%	Heptane Insol. wt-%
-800	0	1.1	0.20	1.2
-800	0	2.3	0.60	3.6
-800	-19	1.1	0.44	2.7
-1300	-21	2.3	0.61	4.1

At this point, interest developed in hydrorefining the SRC/UOP filtrate from which a substantial amount of solvent had been removed.

Plant 505, Run 805. Feed stock to this run was the 52.3 wt-% bottoms from vacuum fractionation, 3296-41. Results are given in Table 21. Space velocity and temperature were substantially constant over the run. Two pressure levels were employed. Sulfur and benzene insolubles were reduced to satisfactorily low levels. However, residual nitrogen and heptane insolubles, even at the highest pressure, were considerably higher than the values obtained in Run 801 at comparable conditions:

	Total Filtrate (Run 801 Per. 1)	52.3 Wt-% Bottoms (Run 805 Per. 10)
Nitrogen in product, wt-%	0.14	0.68
Conversion, wt-%	89	62
Heptane insolubles in product, wt-%	0.52	7.58
Conversion , wt-%	98	85

Explanations offered for the difference in response included:

(1) The SRC was downgraded by overheating in the vacuum fractionator.

(2) The solvent plays an important role in the kinetics of hydrotreating.

(3) Results should properly be compared at the same feed rate of C_7-insolubles or of organic nitrogen.

Plant 505, Run 809. Run 809 (Table 22) was started up with SRC/UOP filtrate 3296-19, to establish a base line (Periods 1-5). Then a 56.2 wt-% vacuum flash bottoms 3296-63 was processed (Periods 6-7). A reconstituted filtrate was prepared (3296-71) by blending back vacuum flash bottoms and overhead. This was processed in Periods 8 and 9. Finally the original filtrate was recharged (Periods 10-12).

Catalyst peak temperature and pressure was constant throughout. Space velocity was reduced by one half for processing the bottoms product.

The following observations can be made regarding the data from Table 22.

(1) The reconstituted filtrate responded essentially the same as the original filtrate. Hence, no substantial downgrading of bottoms material occurred in vacuum flashing.

(2) Catalyst deactivation over the course of the 144 hour run was small:

Feed: Total Filtrate	58 hrs	144 hrs
Nitrogen in product, wt-%	0.42	0.43
Heptane-insoluble in product, wt-%	3.2	3.4

(3) To obtain the same high conversion of heptane insolubles in the 56.2 wt-% bottoms as was obtained with the total filtrate the space velocity had to be reduced in half:

	Heptane Insol., wt-%		Conversion,
	Feed	Product	Wt-%
Filtrate (Period 12)	26.9	3.4	87
56.2 wt-% bottoms (Period 7)	44.3	5.0	89

This indicates that the capacity of the catalyst bed to convert asphaltene reached a limiting rate at high conversions, suggestive of a zero order reaction. On the other hand, results from Runs 801, 802, and 809 for conversion of C_7-insolubles in filtrate, plotted in Figure 4, fit first order kinetics up to at least 90% conversion. Overall, a form of Langmuir kinetics may be operating.

Pilot Plant 505, Run 810. Objective of this run was to process the heaviest pumpable SRC liquid at high severity conditions. Feed was a 41.2 wt-% vacuum flash bottoms (3296-85) containing 77% SRC. Catalyst loading was increased to 200 ml, and space velocity lowered.

The feed was marginally pumpable. At the high temperature required in the feed system, its viscosity rose, and feed rate dropped erratically in Periods 3 and 4. The run was then terminated involuntarily.

Results are given in Table 23. At 0.6 x base WHSV hydrorefining converted 94% of the heptane insolubles and 88% of the nitrogen. At least 50% of the SRC was converted to 850°F⁻ distillate. The calculation does not include light ends recovered in the stripper overhead. Inclusion of this product would increase the SRC conversion.

An estimate of product slate obtained under the high severity conditions of Run 810 is given in Table 24.

Hydrogen Consumption. Calculations at hydrogen consumption for four selected periods are given in Table 25. They range from 1800 to 3300 SCF/B. These values are in fair agreement with the measured hydrogen feed to the plant, less elemental hydrogen appearing in exit gas streams. About 80% of the hydrogen consumed was retained in the liquid product.

2.4.2. SRC Filtrate(4)

SRC process filtrate was received from the Pittsburgh and Midway Coal Company, Ft. Lewis, Washington. Inspections of the sample (3296-95) are given in Table 26. It contained over 80 wt-% process solvent (850°F⁻ distillate) as compared to 71 vol-% process solvent contained in the filtrate prepared by UOP (3296-19, Table 17).

Feedstock Preparation. One drum of sample was topped in laboratory vacuum flash equipment to yield a 30 wt-% bottoms containing 46% SRC, 38.4% heptane insolubles, and 0.04% ash. Inspections of these bottoms (3296-155) are given in Table 26.

Hydrotreating. One hydrotreating run was made with the bottoms, Plant 505, Run 819. Three sets of conditions were used. Results are given in Table 27. Periods 1, 2, 9, and 10 were made at base conditions. In Periods 3 and 4 the space velocity was cut in half. In Periods 5 and 6 the temperature was raised 10°C. In Periods 7 and 8 the space velocity was returned to base. Periods 11 and 12 were run to provide an additional catalyst activity check in comparison with Periods 3 and 4.

As severity of hydrotreatment was increased, from Period 1 to Period 6, conversion of heptane insolubles and nitrogen increased. Best results were achieved at the most severe conditions (Periods 5 and 6): 93% C_7-insoluble conversion, 89% nitrogen conversion. However, the check test made by returning to earlier conditions indicated a decline in catalyst activity.

Product Distribution. A preliminary estimate of product slate was obtained from measurement and inspection of all effluent stream recovered in Periods 2 and 4. Period 2 was run at base conditions, Period 4 at one-half base velocity. Product distributions for these periods are given in Table 28.

Hydrogen Consumption. Hydrogen consumption in Period 2 was 2540 SCF/B, and in Period 4 was 2940 SCF/B. Distribution of hydrogen consumed is listed in Table 29.

2.4.3. Cutback SRC(5)

Ten gallons of SRC granules were received from Pittsburgh and Midway

Coal Company, Ft. Lewis, Washington. Inspections of the material (3296-73) are given in Table 30. Unlike the previous SRC samples, this had been subjected to severe thermal treatment in the SRC vacuum flash tower.

Feedstock Preparation. The material as received could not be pumped in the bench scale equipment. To reduce its viscosity, it was cut back with process solvent, a 500°-850°F cut distilled from SRC filter feed 3296-1A (Table 17). The solvent was heated to 175°C under nitrogen blanket. The SRC was added in increments, permitting each increment to dissolve before adding more SRC. The final mixture represented, by makeup, 82 wt-% (80 vol-%) SRC. The SRC itself contained 7.5 vol-% solvent ($850°F^-$ distillate). The final feedstock analyzed 73.5 vol-% SRC. Inspections of solvent (1396-89) and blend (3296-93) are given in Table 30.

Hydrotreating. One hydrotreating run was made in Plant 505, Run 815. Four sets of conditions were used. Results are given in Table 31. Periods 4, 5, 13, and 14 were made at base pressure, one half base space velocity, and 5°C below base temperature. In periods 6-9, the temperature was raised 15°C. In periods 8-12, the space velocity was approximately doubled.

At the initial conditions, the conversion of heptane insolubles was 92.2%, and conversion of nitrogen was 80.0%. Raising the temperature 15°C (Periods 6 and 7) did not improve conversions. This was the first indication of catalyst activity decline. This decline was confirmed by a return to initial conditions in Periods 13 and 14. C_7-insolubles and nitrogen conversions were 82.5% and 60.0%, respectively.

Product Distribution. A preliminary estimate of product slate at base conditions was obtained from measurement and inspection of all effluent streams from Run 815, Period 5 (Table 32). It compares closely with the distribution estimated in processing 41.2% vacuum flash bottoms (3296-75) of UOP filtered SRC filter feed (Run 810, Period 2, Table 24). To the extent that both feeds contained substantial amounts of process solvent, the product slates are ambiguous with respect to conversion of the $850°F^+$ SRC itself.

Hydrogen Consumption. Hydrogen consumption in this period was 3080 SCF/B calculated from elemental analyses of feed and product. Table 33 gives distribution of hydrogen consumed.

2.4.4. SRC (Recycle Operation)(6)

The ambiguity in product distribution from SRC incurred by addition of extraneous solvent can be eliminated by recycle operation. Hydrotreated SRC is combined with fresh SRC to provide a pumpable mixture. It is necessary to provide a startup solvent, and this is done by batch hydrotreatment of SRC in an autoclave.

Feedstock

Pulverized SRC. A second shipment of SRC granules was received from the Pittsburgh and Midway Coal Company, Ft. Lewis, Washington. Inspections of this material (3392-1) are given in Table 34.

These inspections are in reasonable agreement with the previous shipment (3296-73, Table 30) used for work on cutback SRC. For recycle operation, the feed was pulverized in a Weber Bros. Laboratory Pulverizing Mill fitted with No. 50 U.S. Standard Sieve. It delivered a product 91% in the No. 30-No. 200 sieve range, with 9% passing No. 200 sieve.

The oxygen content of the SRC (3.7%)was not increased by pulverizing. The benzene insoluble content did increase from 34.7% to 42.2%. This increase is larger than might be expected from the apparently neglible oxidation incurred during pulverization, but does not appear to be critical.

Startup Solvent. A supply of startup solvent was prepared by hydrotreating SRC 3392-1 in 21 autoclave runs. The autoclave used for preparation of startup solvent was 1780 cc Aminco Shaking Reaction Vessel, Model 41-14450. No liner was used. Hydrogen pressure was provided from a cylinder, and maintained by a downstream pressure regulator. Charge to the autoclave was 500 g SRC, 50 g catalyst, and 5 g sulfur. The autoclave was sealed and pressured with hydrogen to 1800 psig at ambient temperature. The temperature was raised to 300°C and held for two hours to complete liquefaction of the SRC. Temperature was raised to 385°C and maintained for 16 hours. Hydrogen pressure was maintained at 2300 psig.

After cooling and venting the autoclave, the contents were removed and filtered with suction through a 4.0-5.5 μm sintered glass filter to separate the catalyst. The used catalyst was washed with benzene to recover absorbed oil. The benzene was flashed in a rotary evaporator at 90°C, 20 torr. The extracted oil was combined with filtered liquid product. A total of 7,959 g of liquid (3392-45) was recovered. Inspections are listed in Table 34.

Hydrotreating. Three bench scale hydrotreating runs were made in recycle mode with SRC. Plant 505 was used for the first two (Runs 822 and 823) which were process variable studies. A 456-hour run was made in Plant 638H (Run 4) at a single condition to prepare hydrocracking charge stock. Recycle operation was manual. Stripper bottoms product was added to the feed reservoir and recirculated to bring to temperature. An appropriate amount of pulverized SRC was then slowly added with stirring, to minimize possibility of undissolved particles being drawn into the plant feed pump suction.

Plant 505, Run 822. Three temperature levels were run before reactor plugging necessitated shutdown at 176 hours. Results are summarized in Table 35.

At startup, the feed reservoir was charged with 3.7 kg of 50 wt-% solution of SRC 3392-1 in startup solvent 3392-45. Thereafter the reservoir was replenished with hydrotreated product, adding an equal weight of fresh pulverized SRC. This represents a combined feed ratio of 2.0. During the course of the run, the feed recycle loop flow stopped several times, and a pressure drop developed at the reactor inlet. At 144 hours on stream time, undissolved solids were found on the bottom of the feed reservoir. It was concluded that the pulverized SRC had been added too rapidly, and that many of the operating difficulties could be due to the presence of these undissolved solids in the feed line.

Table 33 shows that the first 10°C temperature increase over base (Periods 3-6 vs. Periods 1 and 2) increased the conversion of SRC heptane insolubles, but had no effect on benzene insolubles or C/H ratio. An additional 10°C (Periods 7,8) had no further effect on heptane insoluble content, but the conversion of SRC and of nitrogen continued to respond.

Plant 505, Run 823. Plant 505 was restarted with a fresh loading of catalyst. No startup solvent was required, since feed and recycle remained from Run 822. The combined feed rate of 2.0 was maintained. Care was taken by slow addition of pulverized SRC to the feed beaker to insure that solution was complete. This eliminated operating problems, and the run was terminated voluntarily at 197 hours.

Results are summarized in Table 36. Space velocities ranged from 1/2 to 3/4 of that used in Run 822. This raised the quality of the recycle solvent, and contributed to trouble-free operation. It should be noted, however, that at the lower space velocities the amount of ash fed to the reactor was proportionately lower.

Conversion of asphaltenes was consistently over 90% in Run 823. Nitrogen conversion was substantially better than in Run 822. A concomitant increase in space velocity and temperature (Periods 7 and 8 vs. Periods 1-3) decreased the asphaltene conversion and hydrogen content of the product; the SRC conversion, however, held steady. This supports the hypothesis that in this situation hydrogenation reactions are equilibrium limited; but cracking reactions are kinetically limited and respond to temperature.

Plant 638H, Run 4. This run of 456 hours was made to provide a feedstock for subsequent hydrocracking containing a minimum amount of heptane insolubles. One set of conditions was used. Pressure was base. Catalyst peak temperature was 10°C above base. Fresh feed space velocity was 0.2 times base and combined feed ratio was 2.5.

The run was commenced with 3.8 kg of a 50 wt-% solution of SRC-3392-1 in startup solvent 3392-45 in the feed reservoir. The intention was to commence with product from Plant 505 as solvent. However, the supply of the latter material had been exhausted by sampling and by abortive startups of the Plant 638H hot feed system.

The run was scheduled for 480 hours. However, by 456 hours a pressure drop of 300 psig had built up across the reactor, and the run was terminated.

Block temperature was not changed over the course of the run. Catalyst peak temperature and location of the peak remained stable. However, the heptane insoluble analysis of the product drifted upward with time.

On Stream Time, Hrs	Heptane Insol. in Product, Wt-%
36	5.47
108	7.37
132	7.53
180	9.03
276	9.32
348	9.81
396	11.3
444	12.4

The daily analyses are logged in Figure 6.

The used catalyst was removed in five sections. Each was extracted with chloroform and analyzed for carbon and some typical ash components.

Bed Location	Top	Top-Middle	Middle	Bottom-Middle	Bottom
Analysis, Wt-%					
C	11.7	12.8	17.0	18.3	-
Ti	0.97	0.82	0.34	0.25	0.16
Ca	0.15	0.10	0.07	0.07	0.06
Fe	1.74	0.55	0.18	0.15	0.11

Product Distribution. Product distributions were calculated for Plant 505, Run 822, Periods 2, 4 and 8; for Plant 505, Run 823, Periods 2 and 8; and for Plant 638H, Run 4, Period 7. They are listed in Table 37. The weight yield of fuel products, liquid and gases, from SRC is close to 100% since the loss of heterocyclic atoms is partially compensated for by addition of hydrogen to the fuel. These distributions are undistorted since no extraneous solvent was added to the SRC.

Hydrogen Consumption. Distribution of hydrogen consumption in the three tests for which complete material balances were run is given in Table 38.

2.5. Hydrocracking SRC(7)

The upgraded SRC prepared in Plant 638H, Run 4, was employed for hydrocracking studies. One bench scale run was made under commercial conditions which may be categorized as "relatively severe". Catalyst was the same as used for hydrocracking upgraded Synthoil (2.3.2.).

2.5.1. Charge Stock

Inspections of the stripper bottoms from Plant 638H, Run 4 (3392-69) are given in Table 39. Table 40 is a summary of a selected overall material balance in Run 4 made for the purpose of obtaining product distribution data. It shows that the upgraded SRC used as hydrocracker feed constituted 77.5 wt-% of the original SRC.

2.5.2. Hydrocracking

Hydrocracking experiments were conducted in Plant 505 (Run 827) at four sets of conditions. Results are summarized in Table 41. At base space velocity, 10°C above base temperature, and 200 psig above base pressure (Period 2) conversion to $650°F^-$ distillate was 11.8 wt-% and heptane insolubles were reduced to 5.36% from 9.76% in the feed. Raising the temperature 10°C (Period 4) at otherwise identical conditions did not improve conversion or lower the heptane insoluble content in the liquid product. This was the first indication of catalyst deactivation. At the latter conditions lowering the space velocity to 0.66 x base space velocity (Period 6) resulted in increasing the conversion slightly to 10.9 vol-% and decreasing the heptane insolubles to 5.86%. When the temperature was lowered to 10°C above base temperature (Period 8) while other processing variables remained unchanged, conversion decreased to 6.0 vol-%

while heptane insolubles content increased to 6.47%. The run was then concluded with a catalyst activity check (Period 10) at the initial conditions. Results showed that after 119 hours of processing the conversion to 650°F$^-$ distillate decreased from 11.8 vol-% to 2.0 vol-%, the product hydrogen content dropped from 9.32% to 8.83%, the product nitrogen content increased from 0.153% to 0.377%, and the API gravity decreased from 5.0 to 3.2.

Product distribution and hydrogen consumption are given in Table 42. Hydrogen consumption during Period 2 was 519 SCF/B. It dropped to 248 SCF/B during the final catalyst activity check (Period 10)

Data obtained from this study show that, as in hydrocracking upgraded Synthoil, high molecular weight asphaltic materials interfered with the conversion of high boiling feed.

2.6. Hydrotreating H-Coal Hydroclone Underflow(8)

H-Coal hydroclone underflow was received from Hydrocarbon Research, Inc., Trenton, New Jersey. Inspections are given in Table 43 (3296-87). It contained 9.09% ash, which necessitated filtration prior to processing in fixed bed operation.

2.6.1. Filtration

The high viscosity of the feedstock precluded use of continuous filtration equipment. It was necessary to resort to a series of slow batch filtrations using the high pressure filtration apparatus shown in Figure 7. Filtrations were carried out at 200°C and 500 psig. The average filtration rate was 25 g oil/hr. Seven filtrations were run yielding 5 gallons (about 24 kg) of filtrate (3296-153). Inspections of the filtrate are given in Table 43. Mass balance is given in Table 44. Some loss of light ends occurred when the hot filtrate depressurized into the receiver.

In a typical filtration, the autoclave was loaded with 1700 g of hydroclone underflow solids. It was sealed, flushed with nitrogen and heated to 175°C with stirring. The fluid contents were transferred to the 200°C filter by nitrogen pressure. The transfer valve was closed, and pressure on the filter was raised to 500 psig. While the filtration proceeded, a second charge of solids was added to the autoclave. This was transferred to the filter when filtration of the first charge was complete. Three charges were normally added per filtration before the filter cake was removed.

The filter cake consisted of hard dry compacted solids of 50 mm thickness. The filter cake was not treated further to recover occluded oil. A representative sample was extracted with toluene in a vapor phase Soxhlet extractor. Table 45 gives the mass balance of the extraction. The insoluble fraction of the filter cake calculates to 16.6% of the H-Coal hydroclone underflow. This is slightly higher than the DMF-xylene insolubles (15.1%) in the original sample.

The thermal and/or oxidative degradation of the sample during filtration is apparent from the increase in heptane and benzene insolubles in the filtrate compared with those in the feed, calculated on a DMF/xylene insolubles free basis. The decrease in sulfur can be accounted for by the removal of ash which is probably high in pyrites. The carbon/hydrogen ratio was unaffected. The 0.12% ash contained in the filtrate was very finely divided, being higher than the particulates measured as DMF/xylene insolubles (0.03%).

2.6.2. Hydrotreating

One bench scale hydrotreating run was made on the laboratory filtered hydroclone underflow in Plant 505 (Run 826). The run was terminated voluntarily at 178 hours. However, toward the end of the run incipient bed plugging was evidenced by pressure surges. The residual ash in the filtrate was probably to some degree responsible.

Results are given in Table 46. Following initial periods at base conditions, space velocity was dropped to one-half base, and the heptane insoluble conversion rose to 93%. Response to a 10°C temperature increase was minor, and it is evident that by 136 hours catalyst deactivation was appreciable. In the final activity check periods at base conditions, heptane insoluble conversion had dropped to 76.7% vs. 84.8% initial. Also, the benzene insolubles were relatively high (3.24% vs. 0.93% initial).

Product distributions and hydrogen consumption are given in Tables 47 and 48. The hydrogen distribution data illustrate the tendency for more hydrogen to enter light ends (C_6-) as severity of hydrotreatment and conversion of heavy ends are increased.

2.7. Discussion

Over all, the hydrotreating of primary coal liquefaction products has resulted in remarkably high conversions of heptane insolubles and nitrogen. Admittedly, process conditions are severe, but not beyond present day commercial practice.

Reduction of heptane insolubles to, say, 3% could facilitate a yield of 90% hydrocracker feedstock by deasphalting. This is probably higher than could be obtained by vacuum flash. Furthermore, the rejected asphalt would be a higher grade than the vacuum flash bottoms, and would be amenable to recycle. Reduction of nitrogen to the parts per million level is an inherent requirement of hydrocracking systems. This is a primary function of the first stage hydrocracking. Obviously, the more that can be removed in upgrading the primary coal liquids, the lower the burden on down stream units.

2.7.1. Comparison of SRC With Synthoil

A comparison of the response of Synthoil and SRC to upgrading is made in Figure 4. Three pairs of hydrotreating runs in Plant 505 were selected for comparison.(1) The pairs represented as closely as possible, identical hydrotreating conditions:

SRC	Synthoil
Run 801, Per. 1 and 2	Run 816, Per. 3 and 4
Run 809, Per. 10-12	Run 816, Per. 1 and 2
Run 802, Per. 2	Run 818, Per. 20 and 21

The percentage of residual heptane insolubles (100-% conversion) is plotted in Figure 4 against reciprocal reduced space velocity [WHSV(base)/WHSV]. In addition to data from the above periods, two others are included: For SRC, Run 802, Period 4; and for Synthoil, Run 818, Periods 18 and 19.

The following observations are made with reference to Figure 4:

The heptane insolubles in UOP filtered SRC filter feed are more easily converted than those in Synthoil; their removal is first order up to 98% conversion; and the effect of pressure is relatively small.

The heptane insolubles in Synthoil are more refractory; their removal is not first order; and low pressure operation is disadvantageous. These observations extend for the most part to organic nitrogen also.

A further comparison of Synthoil and SRC is provided by the preparative Runs 3 and 4 in Plant 638H (Figures 5 and 6):

	Heptane Insol. in Feed, %	$\frac{\text{WHSV}}{\text{WHSV(base)}}$	Heptane Insol. Conversion, Wt-%
Synthoil	18.8	0.5	80
SRC	89.4	0.2	86-94

Although the SRC heptane insolubles were processed over the catalyst at twice the rate compared to the Synthoil heptane insolubles, the conversion was higher. As the figures show, however, the conversion was more stable in case of Synthoil.

Quite possibly the variation in sources of coal used to prepare Synthoil and SRC samples can account for the difference in their response to hydrotreating.

2.7.2. Bed Poisoning and Plugging

Ash. The ash content of primary coal liquids is critical with respect to conventional fixed bed hydrotreating. None of the feedstocks processed, with possible exception of the UOP filtered SRC filter feed, could be considered an acceptable feedstock from this standpoint.

If the ash is particulate, it is filtered out at the inlet of the bed, and eventually plugs the reactor. If it is colloidal or arises from organically bound metals, it causes pore mouth plugging and deactivation of the catalyst. An interesting demonstration of the two effects is provided by a material balance of metal components in the two runs in Plant 638H:

	Ti	Ca	Fe
Plant 638H, Run 3 (Synthoil)			
Charged, g	1.41	1.58	1.49
Recovered on Catalyst, g	1.46	0.16	0.59
Recovery, %	104	10	40
Plant 638H, Run 4 (SRC)			
Charged, g	3.87	3.41	6.85
Recovered on Catalyst, g	2.81	0.54	2.21
Recovery, %	73	16	32

The analyses suggest that iron and calcium entered the bed as particulates, and did not distribute through the catalyst bed. Titanium, on the other hand, is organically complexed and distributed throughout the bed. An alternate explanation is that all metals are organically complexed; but the calcium and iron complexes are unstable, and decompose before entering the bed.

Contrary to expectation, there was no consistent relationship between total ash charged, either per gram of catalyst, or per square centimeter of bed cross section, with plugging:

Plant and Run No.	Grams Ash Charged Per g Catalyst	Grams Ash Charged Per cm^2 Bed	Plugging
505-809	0.02	0.35	No
815	0.19	5.91	No
818	0.10	3.14	No
819	0.05	1.41	No
822	0.08	2.52	Yes
823	0.05	1.47	No
826	0.12	3.81	Yes
638H-3	0.09	2.30	No
4	0.08	2.00	Yes

Organic Matter. Carbonaceous matter, which does not report analytically as ash, can also contribute to bed poisoning and plugging. Fusinites, the low hydrogen, insoluble macerals of coal, can conceivably be filtered out at the bed inlet. More significant would be high molecular weight colloidally dispersed asphaltenes which enter the bed and plug catalyst pore mouths. It has been difficult to assess the relative contribution of ash and asphaltenes to hydrotreating catalyst deactivation in the present studies. It is a plausible suggestion that the upgrading of SRC filter feed by UOP filtration selectively removed very heavy asphaltenes, and contributed to the stable catalyst activity observed in Plant 505, Run 809 (Table 22). In the case of hydrocracking runs, the contribution of ash to the catalyst deactivation was negligible, compared to that of asphaltenes. In commercial petroleum hydrocracking practice, these are removed from feedstocks by distillation or deasphalting.

3. ANALYTICAL CHARACTERIZATION OF COAL LIQUIDS

Primary coal liquefaction products are generally not end products in themselves, and will require further downstream processing. A knowledge of their analytical characteristics and properties will aid in determining response to processes required for upgrading.

3.1. General

The complexity of coal oils requires extensive separation to give well-defined fractions amenable to compositional studies. A separation scheme is used which includes distillation, solvent extraction, and chromatography to separate the coal oils into seven fractions. This separation permits isolation of discrete classes of compounds for further characterization and study. Detailed analysis is obtained in selected fractions using a variety of instrumental and chemical techniques. The pentane insoluble fractions (asphaltenes) are especially emphasized because of their great effect on downstream processing. Instrumental techniques include nuclear magnetic resonance spectroscopy, mass spectroscopy, electron spin resonance spectroscopy, thermal analysis, and molecular weight by vapor pressure osmometry. Chemical techniques include elemental analysis of carbon, hydrogen, sulfur, oxygen, nitrogen, and the principal metals.

In addition, many of the synthetic liquid oils contain submicron particulate matter (inorganic mineral matter and unconverted coal) which makes catalytic fixed-bed processing virtually impossible. They may also contain soluble organo-metallic compounds which may have an adverse effect on catalyst life. A membrane filtration technique is employed to separate the particulate matter containing the insoluble metals from the coal oil containing the soluble metals. The principal metals of each fraction are analyzed by atomic absorption spectroscopy.

Selected feedstocks and upgraded products from the hydrorefining process studies were analyzed in depth by these procedures. The data obtained are discussed separately for each method. Agreements and interrelations from different methods are pointed out.

3.2. Modified SARA Separation

The method of separation of coal oils is a modification of the SARA (Saturates, Aromatics, Resins, and Asphaltenes) separation first developed by the API Project 60 under the joint sponsorship of the Bureau of Mines and the American Petroleum Institute and extended by Gulf Research and Development Company (9,10).

3.2.1. Separation Procedure

The procedure is illustrated in Figures 8 and 9. Details are provided in Appendix A.1. Seven fractions are normally obtained in the separation. For samples containing no material boiling below 243°C, the initial distillation is omitted, and only six fractions are obtained. Distillation of the sample is necessary with samples containing materials boiling below 243°C. This gives the light ends fraction, IBP-243°C. This fraction must be removed since it would be lost during subsequent steps in which the solvents used in the separation scheme are evaporated.

The material boiling above 243°C is separated into saturates, aromatics, bases, acids, neutral nitrogen,and pentane insolubles. The composite group of bases, acid,and neutral nitrogen is designated as resins. The pentane insolubles are designated as asphaltenes. The aromatics are separated into monoaromatics, di- and triaromatics and polyaromatics, including polar compounds. The bases are separated into very weak bases, weak bases, and strong bases. The acids are separated into very weak acids, weak acids, and strong acids. The neutral nitrogens are separated into two fractions. The pentane insolubles are solvent fractionated to give three asphaltene fractions.

To effect the above separation, the material boiling above 243°C is coated on Fluoropak 80(11) and Soxhlet extracted with n-pentane. The pentane insolubles are extracted with benzene, chloroform, and dimethylformamide (DMF) to separate the pentane insolubles (asphaltenes) into three fractions, a, b, and c, respectively.

Bases present in the pentane soluble extract are collected on Amberlyst 15, a cation exchange resin(12).

Acids present in the base-free pentane soluble extract are collected on Amberlite IRA 904, an anion exchange resin(12).

Neutral nitrogens are removed by passing the acid- and base-free pentane soluble extract over a packing of ferric chloride in chromosorb W-Kaolin(12).

The pentane effluent from the ferric chloride column is separated on a dry alumina column into saturates, monoaromatics, di-and triaromatics, and polyaromatics along with polar compounds not previously separated, using a gradient elution system(13). n-Hexane elutes the saturates, cyclohexane the monoaromatics, chloroform the di- and triaromatics, and methyl alcohol finally elutes the polyaromatics along with polar compounds.

3.2.2. Characterization of Fractions

In depth characterization is obtained on selected fractions, the light ends, saturates, aromatics, and pentane insolubles (asphaltenes).

The pentane insolubles are characterized by nuclear magnetic (NMR) and electron spin (ESR) resonance spectroscopy, thermal gravimetric analysis (TGA),and molecular weight by vapor pressure osmometry. In addition, elemental analysis, carbon, hydrogen, sulfur, oxygen and nitrogen, are obtained.

The light ends, IBP-243°C and saturates are characterized by mass spectroscopy (MS).

The aromatics are characterized by nuclear magnetic resonance (NMR) spectroscopy.

3.2.3. Samples

Seven coal liquid feedstocks and the associated refined products from six of these were selected for characterization. Inspections of these coal oils are given in Table 49.

Three of the feedstocks and two of the associated refined products were derived from filter feed from the Solvent Refined Coal (SRC) Process (Section 2.4.1.).

Feedstock 3296-19 is UOP filtered SRC filter feed. Its associated refined product 3296-43 was selected from Run 802 (Table 20).

Feedstock 3296-41 is 52.3% bottoms from vacuum fractionation of UOP filtered SRC filter feed. Its associated refined product 3296-57 was selected from Run 805 (Table 21).

Feedstock 3296-55 is 43.5% bottoms from vacuum fractionation of UOP filtered SRC filter feed. An associated refined product was not obtained for this feedstock. It was not run in the hydrorefining unit because it was not pumpable at 350°F. This feedstock was analytically characterized to determine the effect of exposure to high temperature during fractionation.

Feedstock 3296-93, cutback SRC, was also derived from the SRC Process (Section 2.4.3.). It was prepared by cutting back SRC with a minimum amount of process solvent needed to give a pumpable feedstock. Its associated refined product 3296-141 was selected from Run 815 (Table 31).

Feedstock 3296-147 was derived from the Synthoil process. The Synthoil as received was filtered and water washed to prepare the feedstock (Section 2.2.1.). Its associated refined product 3296-65 was selected from Run 818 (Table 5).

The remaining two feedstocks were derived from the H-Coal process. Feedstock 3296-153 is UOP filtered H-Coal hydroclone underflow (Section 2.6.1.). Its associated refined product 3392-67 was selected from Run 826 (Table 46). Feedstock 3296-81 is H-Coal vacuum bottoms. This feedstock contains 30.2% mineral matter and unconverted coal, 94.4% heptane insolubles, 63.3% benzene insolubles and 2% distillables. Its softening point is 402°F. Its pour point is too high for determination by the modified ASTM method D97, "Pour Point of Petroleum Oils".

These properties precluded pretreatment to provide a homogeneous feedstock suitable for subsequent continuous hydrorefining. To prepare the refined product 3392-57, the feedstock as received was hydrorefined in an autoclave in a batch separation. The conditions and procedure are described in Section 2.4.4.

3.2.4. Discussion of Results

The results obtained from the modified SARA separation of coal oils are given in Table 50.

Overall Composition. The overall SARA analyses of the feedstocks are generally similar. The feedstocks comprise in most frequent order of decreasing amounts, pentane insolubles, aromatics, bases, acids, neutral nitrogen, and saturates. The pentane insolubles, aromatics, and bases make up from 75 to 90 wt-% of the feedstocks.

The pentane insolubles comprise in most frequent order of decreasing amounts, Fraction a, b, and c. Fraction a makes up from 46 to 90 wt-% of the pentane insolubles.

The main fraction of the aromatics is the di- and triaromatics. It makes up from 60 to 96 wt-% of the aromatics.

The bases comprise, in most frequent order of decreasing amounts very weak bases, strong bases and weak bases. The very weak bases make up from 48 to 66 wt-% of the bases.

The overall compositions of the hydrotreated products are generally similar. They comprise, in most frequent order of decreasing amounts, aromatics, bases, pentane insolubles, acids, neutral nitrogen,and saturates. The aromatics, bases, and pentane insolubles make up from 70 to 80 wt-% of the products. The distribution within the fractions is generally similar to that of the feedstocks.

In the hydrotreatment of the feedstocks, the following pattern emerges. The pentane insolubles decrease with all feedstocks. The highest percentage conversion of pentane insolubles is obtained in fraction c. The aromatic fractions increase, mainly the di- and triaromatics. The saturate fraction shows a small increase. The behavior of the other fractions, the bases, acids, and neutral nitrogen, is inconsistent.

Changes taking place as a result of hydrotreatment are as follows. The pentane insolubles decrease forming aromatics, bases, acids, neutral nitrogen, and saturates. The aromatic fraction increases from conversion of pentane insolubles and removal of heteroatoms from bases, acids, and neutral nitrogens. Very little, if any, saturation of aromatics takes place.

Analysis of Pentane Insolubles in Feedstocks. The analytical data obtained for the SARA separated pentane insolubles are summarized in Table 51.

Properties of Separated Fractions. The various fractions of pentane insolubles from the feedstocks are similar. The molecular weight of Fraction a ranges from 430-600 and H/C atomic ratio from 0.814-0.895. For Fraction b, the molecular weight is 780-1330 and the H/C atomic ratio range is 0.723-0.826. For Fraction c, the molecular weight is range 1200-2430, and the atomic ratio is 0.732-0.779.

The molecular weight of Fractions a, b, and c increase in that order, and H/C atomic ratio decreases. High molecular weight and low H/C atomic ratios reflects high aromaticity and more highly condensed ring systems. Pentane insolubles of this type would be much more difficult to process than lower molecular weight, less hydrogen deficient pentane insolubles.

There does not appear to be any difference in the properties of various fractions of the pentane insolubles among the several feedstocks which would indicate differences in processability. However, differences in relative amounts of each type may be significant.

Effect of Thermal Exposure. The pentane insoluble analyses of the three feedstocks derived from UOP filtered SRC filter feed (3296-19, 3296-41, and 3296-55) may be compared on a common basis by recalculating them on the basis of the SRC content of each stock:

Feedstock No.	% SRC	Pentane Insolubles, % of SRC			
		a	b	c	Total
3296-19	29.0	58.6	15.9	15.5	90.0
3296-41	72.0	47.8	15.7	15.4	78.9
3296-55	80.0	40.6	15.5	19.0	75.1
3296-93	73.5	53.7	21.5	15.5	90.8

If the asphaltene content or distribution incurred no change by thermal exposure during distillation, the recalculated analyses should be identical. This was indeed true for Fraction b. However, with increasing depth of fractionation, the total pentane insolubles in the SRC dropped, and the drop was principally in Fraction a, the lowest molecular weight and least hydrogen deficient of the fractions. A suggested explanation is that mild thermal exposure dissociates Fraction a materials, so that a portion reports analytically to resins rather than to Fraction a pentane insolubles.

Some evidence of polymerization can be seen in 3296-55, where the distribution is shifted to the highest molecular weight Fraction c. A similar shift is seen in 3296-93, the cutback SRC. The total pentane insoluble, based on SRC, is identical to that of the UOP/SRC filtrate. However, the Fraction b is higher and the Fraction a lower. This may reflect thermal exposure in the SRC vacuum tower.

Analysis of Pentane Insolubles in Products. The fractions of pentane insolubles from the various hydrotreated products are similar. The molecular weight of Fraction a ranges from 750-1220 and the H/C atomic ratio from 0.779-0.829. The molecular weight of Fraction b ranges from 2010-2820 and the H/C atomic ratio from 0.729-0.816. No molecular weights were obtained for Fraction c.

There is a significant change in properties of the pentane insolubles fractions of the products from those of the corresponding fractions in the feedstocks.

The pentane insolubles Fraction a from the hydrotreated products is similar in molecular weight and H/C atomic ratio to the pentane insolubles Fraction b from the feedstocks. The content of the heteroatoms is reduced in the hydrotreated product. Likewise, the pentane insolubles Fraction b from the hydrotreated products are similar in molecular weight and H/C atomic ratio to the pentane insolubles of Fraction c from the feedstocks. Content of the heteroatoms is also reduced in the hydrotreated product. These shifts are explained as follows. The solvent fractionation of pentane insolubles is based on both polarity and molecular weight. As polarity of the asphaltenes is reduced by removal of heteroatoms, the higher molecular weight species become more soluble in the less polar solvents and report analytically to, for example, Fraction a rather than Fraction b.

In the hydrotreatment of the feedstocks, the highest conversion of the pentane insolubles is obtained in Fraction c followed by b, then a. From the analysis of the fractions, one would expect Fraction a (lowest molecular weight and highest hydrogen content) to be the most readily convertible. It appears, therefore, that the reactions which convert pentane insolubles to pentane soluble material take place stepwise. The pentane insolubles in Fraction c are converted to material reporting in Fraction b. Those in Fraction b are converted to material reporting in Fraction a. Those in Fraction a are converted to pentane soluble material. The net conversion observed in such a cascade will be least for Fraction a and greatest for Fraction c.

3.3. Nuclear Magnetic Resonance Studies

This section covers nuclear magnetic resonance (NMR) studies of the pentane insoluble and aromatic fractions from the SARA separation. All NMR analyses were run on a JEOL MH-100 spectrometer. The pentane soluble fractions were dissolved in an appropriate solvent and filtered when necessary. Their poor solubility was a source of a great deal of difficulty. In the case of DMF extracts (Fraction c) the spectra were frequently not run because of this solubility problem. Deuterated chloroform, dimethylsulfoxide, and pyridine were used as solvents with a majority of the samples being run in d-chloroform. All aromatic fractions were run in d-chloroform.

3.3.1. NMR of Pentane Insoluble Fractions

The NMR of various pentane insoluble fractions of both starting materials and finished products are given in Table 52. The results have been presented on a straightforward basis in terms of the proton resonances of the various regions of the spectra. The spectra were divided into four regions on the basis of chemical shift. This has been done by others, using basically the same criteria for division(14). The region extending from 0.50 δ to 1.00 δ is called H_γ. This region includes all of the aliphatic methyl group protons. The next region is called H_β and extends from 1.00 δ to 2.00 δ The region includes the methylene and naphthenic protons. The region from 2.00 δ to 4.00 δ is called H_α. The resonances of protons adjacent to aromatic rings, heteroalkyl protons, and certain methine protons fall into this region. All of the aromatic ring protons are included in the region from 6.00 δ -9.00 δ.

The spectra have been analyzed in terms of the ratio of the aromatic protons to the aliphatic protons. This approximates the aromaticity, but does not include those carbon atoms that do not have protons attached to them. Nevertheless, it is a good semi-quantitative estimate, and gives a reasonable idea of the effects of hydrotreatment. The spectra will be discussed by comparing the results obtained before and after the treatment of various feedstocks.

SRC. The data for the SARA separated pentane insoluble fraction of SRC/UOP filtrate shows the following. With all fractions, the aromatic ratio decreased upon hydrogenation. The greatest percentage increase among the various groups of protons occurred in the H_β region, where the increase on hydrogenation was twofold. This fact, along with the corresponding decrease in aromatic integral, suggests that the aromatic portions of the original asphaltenes are being hydrogenated. The relatively large increase in the H_β region shows that the hydrotreatment leads to an increase in the naphthenic structures of the pentane insolubles.

The 52.3 wt-% bottoms of SRC/UOP filtrate showed a similar pattern after hydrotreatment. There was a large increase in both H_β and H_α integrals. The aromatic ratio was much diminished with the chloroform (b) and DMF (c) fractions showing no aromatic protons whatsoever.

The cutback SRC feedstock gave the expected pattern upon hydrogenation, with a considerable decrease in the aromatic ratio and also an increase in the naphthenic proton content represented by the increased integral. There was a decrease in the integrals of the H_α protons, probably because of the scission reactions that cleave H_α protons from the pentane insolubles. Whenever hydrogenolysis occurs, an aromatic proton site is created. This tends to increase the number of aromatic protons, but this increase is more than balanced by the ring hydrogenation that is taking place.

In general, the findings for this group of runs may be summarized as follows. There is a decrease in the aromatic ratio for all fractions. This is always accompanied by an increase in the naphthenic proton content and usually a small increase in the integral for the H_β protons. The H_α region shows no consistent pattern, and probably reflects the nature and amount of scission that is taking place.

Synthoil. For the Synthoil samples, there was very little difference in the values obtained for the feedstock pentane insolubles as compared to the products. There was actually a slight increase in aromatic ratio in both the benzene (a) and chloroform (b) fractions. There could be at least two explanations for this. First, it is possible that there has been produced a hard core of highly aromatic material that is rather resistant to further treatment. Another possible explanation is that the asphaltenic material has reached a steady state, and is simply functioning as a catalytic hydrogen transfer agent in the medium.

H-Coal. In the case of the H-Coal samples, the H-Coal hydroclone underflow filtrate and vacuum bottoms, there was the expected decrease in aromatic ratio upon hydrogenation. As usual, the decrease in aromatic ratio was reflected in an increase in the absorption in the naphthenic region of the spectrum. The behavior of the vacuum bottoms was inconsistent in that there is an increase in the aromatic ratio of the benzene extracted pentane insolubles, Fraction a. The chloroform Fraction b showed the expected decrease. There is no comparison for the DMF extract, Fraction c. The original was not run for reasons of solubility.

3.3.2. NMR of Aromatic Fractions

The data for the aromatic fractions were treated in the same way as described for the pentane insoluble fractions. The data for both the feedstocks and hydrotreated products are given in Table 53.

SRC. There was a relatively large increase in the H_α protons in the monoaromatic fraction of the hydrotreated SRC/UOP filtrate, approximately double the integral of the untreated filtrate. At the same time, there was a relative decrease in the integral of the H_β protons. There are at least three plausible processes for the formation of monoaromatics in this system. They are,

(1) hydrogenation of di- and polyaromatics,
(2) hydrogenolysis of di- and polyaromatics,
(3) dehydrogenation of naphthenes.

All of these processes would lead to a relative increase in the α-hydrogen content. Since the β-hydrogen integral decreases, it suggests that Processes 2 and 3 are probably more important than Process 1 under the conditions of this hydrotreatment.

There was no monoaromatic fraction isolated from the feedstock of the 52.3 wt-% bottoms of the SRC/UOP filtrate. The cyclohexane eluate that should contain monoaromatics contained only alkyl resonances. The hydrotreatment process led to the formation of a considerable amount of monoaromatics. The only direct comparison that is of importance for this run is that for the di-aromatics. The amount of polyaromatics is so small as to be insignificant. There is an increase in the H_β integral of the di-aromatic fraction. This leads to a decrease of about 70% in the aromatic ratio for the di-aromatic fraction.

The behavior of these fractions from the cutback SRC feedstock on hydrogenation was consistent with that obtained for the previously discussed SRC fractions. There were no monoaromatics in the cyclohexane fraction. The mono- and di-aromatic fractions showed a large increase in the product. In the case of the di-aromatics, this was the largest increase both on a percentage and also on an absolute basis for all of the runs. There was a decrease in the aromatic ratio of the di-aromatic fraction and, of course, what has to be called an increase in aromatic ratio of the monoaromatic fraction. The ratio in the polyaromatic fraction remained essentially the same.

To summarize, the NMR on the SRC aromatic fractions showed that the aromatic ratio usually decreased with hydrotreatment. The total amount of all aromatic species increased.

Synthoil. The NMR data for the aromatic fractions derived from Synthoil show the following. There was very little change in any of the values upon hydrotreatment. The di-aromatic and the polyaromatic fractions decreased in aromatic ratio as expected, while there was a small increase in the monoaromatic fraction.

H-Coal. The H-Coal vacuum bottoms feedstock was different from all others in this series in the relative lack of aromatics in the feedstock. The cyclohexane fraction which normally contains monoaromatics was very small and contained no aromatics whatsoever. The di-aromatic fraction was also relatively small, and had a very low aromatic ratio. The polyaromatic fraction showed no aromatic protons at all although it was probably aromatic in nature. With the aromatic ratio being so low to begin with, it is reasonable to expect that hydrotreatment would lead to an increase in the aromatic content. The increase did in fact occur with by far the greatest increase taking place in the di-aromatic fraction.

In contrast to the vacuum bottoms, the hydroclone underflow filtrate feedstock was normal in its constitution. The response to hydrogenation is as expected with a decrease in the aromatic ratio and an increase in the naphthenic proton content.

To summarize, we find that these three materials are quite different as feedstocks in their aromatic content and the aromatic ratio. The Synthoil shows relatively little change upon hydrotreatment. The H-Coal vacuum bottoms which originally contained very little aromatic materials shows an increase in aromatics with hydrotreatment. The H-Coal hydroclone underflow filtrate, which has a normal or average distribution of aromatic material as a feedstock, shows increased aromatic content upon hydrotreatment and a decrease in the aromatic ratio.

3.4. Mass Spectroscopy Analyses

This section covers mass spectroscopy (MS) analyses for two selected fractions included in the analytical scheme, the IBP-243°C fraction, and the saturate fraction from the SARA separation. All MS data were obtained on an AEl MS-30 spectrometer. The aromatic compound types determination and carbon number distribution in the gasoline range samples were made on the total sample using high resolution - low voltage ($\sim$ 10 ev) mass spectrometry. Saturates, paraffins, and naphthenes were analyzed according to ASTM D-2786-71. The saturates were removed quantitatively from the total sample using liquid-liquid chromatography, ASTM D-2002-72, "Isolation of representative saturate fractions from low olefinic petroleum naphthas".

3.4.1. IBP-243°C Fraction

In Table 54 are listed analyses for all the saturate fractions of the feedstock light ends, as well as those in the hydrotreated products. In Table 55 is given the breakdown of the aromatic compounds according to type.

In some instances there were no light ends in the feedstocks. This was true in the case of bottoms materials such as the SRC, 52.3 wt-% bottoms of SRC/UOP filtrate, H-Coal hydroclone underflow filtrate and H-Coal vacuum bottoms. In one instance, the SRC/UOP filtrate, the amount of light ends doubled as a result of hydrotreatment, 4.8 wt-% vs. 9.6 wt-%. In the case of Synthoil, the product had less light ends than the feedstock.

Saturated Material. In all instances, there were substantial changes in the distribution of saturate material upon hydrotreatment. For the SRC/UOP filtrate feedstock, the percentage of paraffins decreased from 42.5 wt-% to 5.7 wt-% (Table 54). In Synthoil, the percentage of paraffins decreased from 28.4 wt-% before hydrotreatment to 7.7 wt-% after hydrotreatment. This result is undoubtedly indicative of the hydrogenation of aromatic rings as well as the hydrogenolysis of napththenic material from asphaltenes. There is substantially no source of potential paraffins because coal asphaltenes do not have long paraffinic chains. Thus, the concentration of paraffins remains relatively constant while the naphthenes content increases.

Aromatic Material. The aromatic distributions of the light ends, corresponding to the saturates discussed above are included in Table 55. Direct comparisons are available for the SRC/UOP filtrate feedstock and product. The hydrotreatment increased the concentration of benzenes and tetralins. The percentage of benzenes increased from 1.2% in the untreated SRC filtrate to 5% in the hydrotreated sample. Likewise, in the case of Synthoil, the increase was from 1.5% to 6%. According to one theory of hydrogenation, various cyclohexyl derivatives become dehydrogenated by transferring hydrogen to other less readily reducible species in the coal.

The heteroaromatics were reduced considerably by hydrogenation. Phenols constituted a relatively high percentage of those compounds, comprising 28% of the total aromatic sample. Hydrotreatment reduced their concentration to less than 5%. The pyridines were hardly affected at all by the treatment, presumably because the pyridine ring is very stable and relatively resistant to hydrogenation and hydrogenolysis.

A direct comparison is also available for Synthoil feedstock and hydrotreated product. Just as with the SRC/UOP filtrate, there was an increase of benzene and tetralins, a decrease in the phenol content from ca. 30% to ca. 2% and a slight decrease in the pyridine content. It is interesting to note that the naphthenopyridines were decreased to a much greater extent than was pyridine itself, the concentration decreasing from 2.6% to 0.4% in the hydrotreated product.

3.4.2. Heavier Saturate Fractions

The MS analyses for the heavier saturate fractions that were obtained by hexane elution as part of the SARA separation are given in Table 56. In some cases, the amount obtained was vanishingly small, and no analysis was run. Direct comparison of feed and product saturate compositions may be made in the case of the SRC/UOP filtrate, Synthoil, H-Coal hydroclone underflow filtrate, and H-Coal vacuum bottoms. Usually the total saturates content increased with the naphthenic portion being responsible for most of the increase.

3.4.3. Summary

In summary, the data from mass spectral analyses show the changes that occur with hydrotreatment for the overhead fractions and the saturate fraction from SARA separation. These changes are (1) an increase in naphthenic content for both light ends saturates as well as saturates isolated from the SARA, (2) a substantial decrease in heteroatom compounds in the light ends aromatic fraction, and (3) an increase in the monoaromatic content. The increase in naphthene content is consistent with the findings of NMR. The increase in concentration of monoaromatics upon hydrogenation accords with the findings of other investigators(15). Generally, the increase has been attributed to the dehydrogenation of naphthenes which behave as hydrogen transfer agents during the hydrogenation process.

3.5. Electron Spin Resonance Studies

This section covers the study of electron spin resonance (ESR) of the material boiling above 243°C from the feedstocks and hydrotreated products and the pentane insoluble fraction from the SARA separation.

The Varian 4300-10A spectrometer with dual cavity was used for all measurements. The asphaltene samples from the SRC filtrate and 52.3% bottoms material were run homogeneously by melting and pouring them into the sample tube. When the bottoms samples were too heavy, they were run by mixing a weighed amount with a coal derived solvent. All asphaltenes except those derived from SRC filtrate and 52.3% bottoms were run in this fashion by removing an aliquot of the extract and concentrating the aliquot in the coal solvent. This allowed variable temperature runs to be carried out on these fractions from ambient to 300°C. The results were expressed by measuring the peak height of the ESR response and then normalizing it in terms of peak height/gram or peak height/0.1 gram.

3.5.1. ESR of Pentane Insoluble Fractions

The ESR analyses of the pentane insolbles fractions are given in Tables 57 and 58.

The pentane insolubles obtained from the SRC/UOP filtrate feedstock and the hydrotreated product were run in the solvent used for their extraction during the SARA separation. The corresponding samples from the 52.3 wt-% bottoms of SRC/UOP filtrate were treated likewise. This technique has the disadvantage of giving information for ambient temperature only. At ambient temperatures, the pentane insolubles are known to be associated, and one does not usually get a good evaluation of the free radical content by a single measurement at ambient probe temperature. In order to better characterize the materials, the pentane insoluble samples obtained after work was completed on the SRC/UOP filtrate were run in coal derived solvent.

Ambient Temperature ESR of Pentane Insolubles. In Table 57 are listed ESR data for the pentane insolubles derived from the feedstock and hydrotreated product of SRC/UOP filtrate and the 52.3 wt-% bottoms of SRC/UOP filtrate. All of these samples were run in the extraction solvent as they were extracted by the SARA separation. In the case of the SRC/UOP filtrate feedstock and the hydrotreated product, there was no consistent variation of the ESR values in terms of peak height/gram, proceeding with the extraction from less polar to more polar solvents. Fraction b, the chloroform extract, shows a higher response than the other fractions for both the untreated as well as the treated materials. It is not possible from this information to arrive at any definite conclusions regarding the nature of the pentane insolubles in each separate fraction that give rise to these differences in behavior.

For the 52.3 wt-% bottoms of the SRC/UOP filtrate, the ESR response in general was similar to that described above for the SRC/UOP filtrate materials. For the feedstock, Fraction c, the DMF extract, showed the highest response among the product pentane insolubles.

ESR of Pentane Insolubles as a Function of Temperature. In Table 58 are listed ESR data of the pentane insolubles as a function of temperature for the feedstock and hydrotreated product of 52.3 wt-% bottoms of the SRC/UOP filtrate, Synthoil, H-Coal hydroclone underflow filtrate, and H-Coal vacuum bottoms. These samples were run in the coal derived solvent. In this table and all subsequent tables where variable temperature ESR data are shown, the maximum ESR value reached is underlined. The final column gives the average value over the full range of temperature. The maximum was usually reached at 200-250°C.

A comparison of the ESR signals from the various feedstock pentane insolubles shows a wide range of values. Synthoil asphaltene gave the most intense signal, and SRC/UOP filtrate the least. These differences may be associated with differences in processability between Synthoil and SRC discussed in Section 2.7.1.

ESR response of asphaltene from upgraded products give variable results. For the 52.3 wt-% bottoms of the SRC/UOP filtrate the maximum ESR signal increased with hydrogenation for Fractions b and c, and decreased for Fraction a. The average value decreased in all cases except that of Fraction b, which showed an increase with hydrotreatment.

In the case of Synthoil, Fraction a showed an average 30% increase, Fraction b remained about the same, while Fraction c decreased by about 50%. For both H-Coal samples, the maximum ESR value increased with hydrogenation for all pentane insoluble fractions. It also increased as the extraction proceeded from less polar to more polar solvents.

3.5.2. ESR of Coal Oils

In Tables 59 and 60 are listed ESR data for the coal oils and associated upgraded products as a function of temperature. Data for the SRC/UOP filtrate feedstock and products and 52.3 wt-% bottoms of SRC/UOP filtrate feedstock and products are found in Table 59. The determinations were made in the neat sample. Data for the feedstocks and products of cutback SRC, Synthoil and H-Coal samples are found in Table 60. The determinations were made on samples dissolved in a coal derived solvent.

The effect of hydrotreatment is clear, both with regards to the maximum and the average ESR value. The free radical content was substantially reduced by the hydrotreatment in all cases.

3.6. Thermal Analysis

This section covers the thermal analysis of the materials boiling above 243°C from the feedstocks and hydrotreated products and the pentane insoluble fractions from the SARA separation.

3.6.1. Procedure

All samples were run on a Mettler Thermoanalyzer II fitted with a corrosive gas furnace. The samples to be analyzed were placed on a 8 mm flat platinum crucible and heated in the thermoanalyzer, with an empty platinum crucible as reference for differential thermal analysis (DTA). The samples were heated to ∿750°C at 8°C/min. at a constant nitrogen flow of 10 ℓ/hr through the balance and furnace and 7.3 ℓ/hr as back flush.

For samples smaller than 10 mg, the sensitivity of the thermogravimetric analysis (TGA) remained at 1.0 mg/in., the differential thermogravimetric analysis (DTG) at 0.05 mg/min./in., and the DTA at 10 μ/in. For samples larger than 10 mg, the TGA was set at 10.0 mg/in., the DTG at 0.5 mg/min./in. and the DTA remained the same.

After reaching ca. 750°C and maintaining a constant weight, the sample was cooled to room temperature while still under a nitrogen atmosphere. The samples were then heated to ca. 1000°C in an air/nitrogen mixture with a flow of 10 ℓ/hr of nitrogen through the balance and 3.4 ℓ/hr air through the side inlet. All other conditions remained the same.

The percent coke formed was equal to the percent weight loss in air. The dry ash was calculated from the original weight minus the total weight loss.

3.6.2. Thermal Analysis of Coal Oils and Pentane Insoluble Fractions.

The thermal analysis of the coal oils and pentane insoluble fractions are given in Tables 61-63. Weight loss in nitrogen and air, coke formed, and ash present in the sample were determined. The most useful information obtained from the thermal analysis method is the amount of coke formation. The portion of a feedstock that goes to form coke is probably deficient in hydrogen and very graphitic in nature.

SRC. The thermal analysis of the various SRC feedstocks and products and SARA separated pentane insolubles are given in Table 61. The hydrotreated products always gave less coke than the feedstocks. This is true also with regard to the pentane insoluble fractions that are separated from the corresponding feedstocks and products. Although the percentage of coke from a given pentane insoluble fraction may be relatively high, the total amount of the pentane insoluble fraction is always lower in the product than in the feedstock.

Analysis of the dry ash content shows the ash to be concentrated in the pentane insoluble fraction. As the extraction of the pentane insolubles proceeds from less polar to more polar solvents, the ash content increases. The high ash content in the pentane insolubles implies that metals forming the ash are either complexed or associated to the pentane insolubles, or else of very small particle size finely dispersed in the pentane insolubles.

Synthoil and H-Coal. In Table 62 and 63 are given the thermal analyses of Synthoil and H-Coal feedstocks and products and of SARA separated pentane insolubles. The pattern that was seen for the SRC material was continued for Synthoil and H-Coal. That is, the coke formation was often higher on a percentage basis in the product than in the feedstock.

3.6.3. Comparative ESR and Coke Formation Data

The fact that one obtains a higher percentage of coke from a product pentane insoluble fraction is also suggested by the ESR information. As mentioned in the discussion of the ESR data on this point, it may be explained by assuming that the hydrotreatment process reduces the pentane insoluble fractions through hydrogenolysis to give a core of relatively intractable, graphitic material. This material is probably very good at stabilizing free radicals and also leads to a considerable amount of coke formation.

Table 64 lists the comparative ESR and coke formation data for all of the various coal oils, both feedstocks and products. The greater the ESR response, the higher the percent coke formed. The relationship is far from linear, and one would not expect it to be, given the complexity of the materials and system under consideration.

3.7. Membrane Filtration

Primary coal liquefaction products generally contain submicron particulate matter (insoluble mineral matter and unconverted coal). This interferes with analysis of the soluble metal compounds in these coal oils. The submicron particulate matters can be removed from the coal oils by filtration through filters of very small openings. The heavy viscous nature of coal oil precludes filtration neat, making dilutions necessary. Solvents for dilution must be completely miscible with the coal oil.

The membrane filtration technique employed uses a 0.2 μm Fluoropore filter. Material retained on this filter designated particulate matter. Material passing through the filter is considered soluble in the coal liquid. These definitions may not be exact, since it is conceivable to encounter particulate matter of sufficiently small size to pass through the filter. As operational definitions, they serve as a starting point to gain some insight as to the nature of the particulate matter and soluble metals contained in the coal oils.

3.7.1. Procedure

The detailed procedure for membrane filtration is outlined in Appendix A.2. Filters of smaller pore size, on the order of 50 to 250 Å, would have been preferable, but none were found that were chemically resistant to the solvent. The solvent used was 2 parts by weight dimethylformamide (DMF) to 1 part of weight xylenes. The coal sample is dissolved in the solvent and filtered with pressure through the 0.2 μm Fluoropore filters, and the total particulate matter in the coal oils determined.

The filter cake containing the insoluble metals and the filtrate containing the soluble metals are analyzed for the principal metals found in coal oils (Fe, Ti, Al, Ca, Mg, Na and Si).

The insoluble metals are determined by wet digestion of the filter cake with sulfuric acid and nitric acid and analysis of the digested sample by atomic absorption spectroscopy(16). The procedure is outlined in the Appendix A.3.

The soluble metals are determined by analysis of the filtrate by atomic absorption spectroscopy using ASTM Method D-2788-72.

3.7.2. Samples

Six coal liquids feedstock and four refined products were selected for characterization by membrane filtration. Three of the feedstocks and one product were derived from the Solvent Refined Coal Process.

Feedstock 3296-19 and Product 3296-141 are described in Section 3.2.3.

Feedstock 3296-155 is 30 wt-% bottoms of SRC filtrate. It was prepared by vacuum flash of SRC filtrate (Section 2.4.2.).

Feedstock 3392-1 is SRC (Section 2.4.4.).

The three remaining feedstocks - 3296-147, 3296-153, 3296-81 and associated refined Products 3392-65, 3392-67, 3392-57 are described in Section 3.2.3.

3.7.3. Discussion of Results

The analyses of particulates and the principal metals contained in the particulates and filtered coal oil are summarized in Tables 65-67.

Particulate Analysis. The particulates in the feedstocks ranged from 0.01 wt-% for the SRC/UOP filtrate to 0.16 wt-% for Synthoil. H-Coal vacuum bottoms contained 30.2 wt-%, but this feedstock had not undergone any solid-liquid separation. The particulates in the products analyzed 0.02 wt-% or less with the exception of Synthoil which contained 0.17 wt-%.

SRC Feedstocks. Table 65 provides a comparison of particulates in feedstocks filtered at UOP and at the SRC plant. The SRC/UOP filtrate 3296-19 contained the least particulate matter, 0.01%. Even when adjusted for process solvent, the particulates were only a quarter of those in the SRC filtrate 3296-155. Moreover, the particulates in the UOP/SRC filtrate were predominantly inorganic, while the reverse appears to hold for SRC filtered materials 3296-155 and 3392-1.

The upgraded SRC 3296-141 produced by hydrotreating 20% cutback SRC 3296-93 in Run 815 (Table 31) contained only 0.02% particulates as compared to 0.15% in the SRC itself. These product particulates appear to be mostly inorganic.

Synthoil. Particulates in upgraded Synthoil 3392-65 (Table 66) were unexpectedly high, practically unchanged from the filtered feedstock value of 0.16%. These particulates were very low in metal. The unusual appearance of the filter cake obtained in filtering Synthoil was noted in Section 2.2.1.

H-Coal. Particulates in filtered H-Coal hydroclone underflow were predominantly organic. They were reduced by hydrotreating (Table 67).

Analysis of Soluble Metals. The metals present in the membrane filtrate (soluble metals) varied with the coal oil. The H-Coal feedstocks had the highest metal content and Synthoil the lowest. The soluble metals were generally appreciably higher than the insoluble metals present in the particulates. This implies that most of the metals remaining after process filtration are in the form of oganometallic compounds or complexes. The soluble metals were appreciably reduced by hydrotreating, even to a greater extent than the metals contained in the particulates. This indicates that the soluble metals will be deposited in the catalyst or in the reactor. If the metals exist as a complex and if the complex is relatively stable, deposition of the metal would occur inside the catalyst in the catalyst pores. This appears to be the case for titanium. Analysis of the used catalyst for metals (Section 2.7.2.) indicates high recovery on the catalyst of the feed titanium charged. This was not the case for the calcium or iron.

In the previous discussion it was suggested that calcium and iron were present as particulates. If so, they would have to be extremely fine to pass the membrane filter. An alternate hypothesis is that they are present as labile organic complexes which decompose before they can be transported through the catalyst bed.

3.7.4. Conclusions

SRC/UOP filtrate caused much less catalyst deactivation than the other feedstocks. It contained 0.01 wt-% particulates, 34 ppm Ti and other metals accounting for 16 ppm.

Severe catalyst deactivation resulted from processing the 30 wt-% bottoms of SRC filtrate. It contained 0.07 wt-% particulates, 103 ppm Ti and the other metals accounting for 133 ppm. Severe catalyst deactivation also resulted from recycle processing SRC. It contained 0.15 wt-% particulates, 118 ppm Ti and other metals accounting for 162 ppm. Catalyst deactivation resulted from processing Synthoil, although in the preparative run (Figure 5) the catalyst activity stabilized. Synthoil contained 0.16 wt-% particulates, 16 ppm Ti, and the other metals accounting for only 5 ppm.

From the processing of the various SRC feedstocks, one can conclude that the increased catalyst deactivation results in part from particulates and in part from metals. In the case of Synthoil, one rules out deactivation resulting from the metals, and concludes that the particulates were responsible for initial catalyst deactivation. Possibly only the small pores were affected, which would account for the stabilization observed.

3.8. Summary

Quantitative correlations exist which permit accurate prediction of properties and yields of products derived from hydrorefining petroleum distillate stocks. Experience at UOP indicates that these correlations hold also for distillates derived from coal.

In the case of petroleum residuum such correlations are less sophisticated, and tend to be qualitative. This is in part due to the increased complexity of the analytical problem, and in part because hydroprocessing of residuum does not give a very broad product slate. Nevertheless there is ongoing research in the petroleum industry to improve the analytical characterization of residuum and determine which properties are most closely related to processability.

From the preceding studies it may be concluded that the status of the correlation of analytical properties of residuum from coal liquefaction with processability is comparable to that for petroleum residuum. The techniques which show the most promise for further emphasis are electron spin resonance studies, thermal analysis, and the characterization of asphaltenes, particulates, and metals. Specifically, a comparison of processability of Synthoil and SRC liquefaction products indicates that the electron spin resonance of their respective asphaltene fractions may correlate well with the ease of conversion of heptane insolubles. Likewise, the nature and amount of particulates and metals appear to be related to the nature and degree of catalyst deactivation. As more coal liquids are processed and analyzed using these techniques, correlations with asphaltene and heteroatom conversion and catalyst life, the important parameters which define processability, will be derived.

4. OVERALL ENGINEERING EVALUATION

Soft coals can be converted to liquid hydrocarbon products having properties equivalent to those of present day petroleum refinery fuels. The technology for this conversion process requires 3 steps:

Step I consists of liquefaction of the coal wherein the coal is mixed with a recycle solvent and passed through a reactor under hydrogen atmosphere at elevated temperatures and pressures to produce a high melting point liquid which can be subjected to an appropriate liquid/solid separation to remove a major part of the ash.

Step II consists of further hydrogenation in contact with a solid catalyst to force more hydrogen into the molecules giving products which contain a major part of distillable liquids (boiling below 1050°F-565°C).

Step III consists of the following:

A. Fractionation, producing the following cuts:

  (1) Light Naphtha
  (2) Heavy Naphtha
  (3) Middle Distillates
  (4) Vacuum Gas Oils
  (5) Vacuum Bottoms

B. Refining Processes

  (1) Reforming of the heavy naphtha and mixing with the light naphtha to produce a marketable gasoline; or alternatively, to produce aromatics for the petrochemical industry.

  (2) Hydrogenating the middle distillate to produce home heating oil and diesel fuel; or alternatively, hydrocracking the middle distillates to naphthas.

  (3) Hydrocracking the vacuum gas oils to middle distillates and gasoline; or alternatively, the vacuum gas oils can be hydrogenated and converted to gasoline directly in a Fluid Catalytic Cracking unit.

  (4) The vacuum bottoms after dilution with a cutter stock can be sold as a low sulfur residual fuel.

The Step II products can be processed directly in the fractionation and conversion facilities in many present day refineries. The primary requirement of Step II products to substitute for the present day petroleum crude is that 80% of this Step II products boil below about 1050°F.

The Step I and Step II processes require equipment which is not present in present day refineries. Both Step I and Step II require more expensive processing procedures than the Step III processing. Step II requires conversion over a solid catalyst. Catalyst consumption will be high and, therefore, catalyst costs will be high. The ash remaining in the Step I product will agglomerate with the solid catalyst pellets and shorten catalyst life. Even with the boiling catalyst bed technique, the Step I product particulates still present a problem.

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Table 1

Inspection of Synthoil Samples

Sample Designation	Synthoil Centrifugate	Filtrate	Washed Filtrate
Sample No.	3296-109	3296-143	3296-147
°API @ 60°F	-5.7	-3.5	-4.3
Sp. Gr. @ 60°F	1.1248	1.1055	1.1124
Distillation (ASTM D-1160)			
IBP, °F	395	407	455
5%	470	480	519
10%	510	515	552
20%	579	518	606
30%	642	635	665
40%	700	697	730
50%	762	760	795
60%	845	842	865
70%	945	951	970
% Over	70.0	70.0	70.0
% Bottoms	30.0	30.0	30.0
Heptane Insoluble, Wt-%	19.0	15.2	18.4
Benzene Insoluble, Wt-%	6.3	5.0	4.4
DMF/Xylene Insoluble, Wt-%	3.0	-	0.16
Ash (ASTM), Wt-%	1.40	0.02	0.015 (a)
Molecular Weight, average		280	308
Pour Point, °F		70	75
Viscosity, cSt			
175°F	135		
210°F	43.65	34.25	56.20
250°F	16.84	14.08	18.73
Ultimate, Wt-%			
H		7.58	7.42
C		89.70	88.28
S		0.55	0.56
N		1.46	1.31
O		2.18	2.27
Cl (ppm)		>670	< 10

(a) Hydrotreating studies were made on material containing 0.05 Wt-% ash.

Table 2

Filtration of Centrifuged Synthoil

Material and Component Balance, Wt-%

	Centrifuged Synthoil	H_2O Trap	Filtrate	Cake	Total
Light Oil	0.20	0.20			0.20
C_7-Soluble Oil	81.10		78.95	3.56	82.51
Benzene Sol, C_7-Insol. Oil	12.41		9.53	0.66	10.19
DMF/Xylene Sol, Benzene Insol. Oil	3.32		4.60	0.10	4.70
DMF/Xylene Insoluble Oil	1.57				
Ash (ASTM)	1.40		0.02	2.38	2.40
Total	100.00	0.20	93.10	6.70	100.00

Table 3

Fractionation and Chloride Analysis of Synthoil

Cut	Boiling Range °C	Wt-%	Cl,ppm
1	188-254	9.38	27
2	254-298	9.43	32
3	298-340	9.65	376
4	340-380	10.0	4,820
5	380-414	8.34	1,779
Botts.	414°C+	47.56	-

Total Synthoil	361 ppm Cl
Summation, Cuts 1-5	672 ppm Cl
Cut 4, Water Soluble Cl	0.48 Wt-%

Table 4

Hydrotreating Filtered Synthoil Centrifugate

Trickle Bed Operation, 200 ml Catalyst

Plant 505, Run 816

Period No.	Feed	1,2	3,4	5,6
Hours on Stream	3296-143	20-28	42-54	62-74
WHSV/WHSV (base)		2.0	1.1	1.0
T-T (base), °C		0	0	0
P-P (base), psig		0	0	0
Heptane Insol., Wt-%	15.2	5.01	3.44	3.46
Heptane Insol., Conv., Wt-%		67.0	77.4	77.2
Benzene Insol., Wt-%	4.96	0.05	0.03	0.09
Ash (ASTM), Wt-%	0.02	0.002	0.002	<0.001
Viscosity, cSt, @ 100°F		132.2	105.6	88.2
Sp. Gr. @ 60°F	1.1055	1.0291	1.0261	1.0291
850°F+ Bottoms, Vol-%	39.3	32.8	32.4	32.2
Conversion to 850°F-, Vol-%		16.5	17.6	18.1
Ultimate, Wt-%				
H	7.58	-	9.28	-
C	87.70	-	89.68	-
S	0.55	-	0.05	-
N	1.46	0.544	0.447	0.404
O	2.18	-	0.42	-
Cl (ppm)	>670	<0.1	66	60
N in 850°F- Distillate, Wt-%		0.395	0.291	0.298

Table 5

Hydrotreating Filtered Synthoil Centrifugate

Trickle Bed Operation, 200 ml Catalyst

Plant 505, Run 818

Period No. Hours on Stream	Feed 3296-147	14,15 156-168	16,17 189-200	18,19 215-232	20,21 240-246	22,23 260-272
WHSV/WHSV (base)		1.1	0.51	0.49	1.1	0.98
T-T (base), °C		9	9	9	9	9
P-P (base), psig		0	0	-800	-800	0
Heptane Insol., Wt-%	18.8	4.31	3.02	6.00	8.62	5.46
Heptane Insol. Conv., Wt-%		77.1	83.9	68.1	54.1	71.0
Benzene Insol., Wt-%	4.40	-	-	-	-	0.17
Ash (ASTM), Wt-%	0.05	-	-	-	-	-
Viscosity, cSt, @ 100°F		113.9	53.0	93.2	280.9	156.4
Sp. Gr. @ 60°F	1.1124	1.0246	1.0143	1.0397	1.0568	1.0397
850°F$^+$ Bottoms, Vol-%	42.1	32.0	26.5	30.0	38.0	34.6
Conversion to 850°F$^-$, Vol-%		24.0	37.1	28.7	9.7	17.8
Ultimate, Wt-%						
H	7.42	-	-	-	-	9.11
C	88.28	-	-	-	-	90.61
S	0.56	-	-	-	-	0.02
N	1.31	0.414	0.252	0.393	0.763	0.544
O	2.27	-	-	-	-	0.46
N in 850°F$^-$ Distillate, Wt-%		0.228	0.123	0.303	0.517	0.376

Table 6

Fuel Product Distribution

Hydrotreating Synthoil

	Plant 505 Run 818 Period 23	Plant 638H Run 3 Period 5
Catalyst Bed Volume, ml	200	800
Hours on Stream	266-272	102-126
WHSV/WHSV (base)	1.0	0.5
T-T (base), °C	10	-6
P-P (base), psig	0	0
Heptane Insol. Conv., Wt-%	71.0	80.5
Fuel Product, Wt-%	98.5	99.0
Distribution, Wt-%		
Gas (C_1-C_4)	1.8	1.7
Gasoline (C_5-400°F)	8.3	9.0
Kerosine (400-527°F)	11.4	11.3
Light Gas Oil (527-752°F)	37.9	37.5
Heavy Gas Oil (752-850°F)	10.7	10.6
Bottoms	29.9	29.9
Total	100.0	100.0
Hydrogen Consumption, SCF/B	1840	2000

Table 7

Distribution of Hydrogen Consumption

	Plant 505 Run 818 Period 23	Plant 638H Run 3 Period 5
Hydrogen Consumption, Wt-%		
Liquid Products (Strip. Botts. and Lt. Prod.)	69.4	71.5
C_5 and C_6 in Gas	2.1	4.2
Gas (C_1 - C_4)	9.5	7.6
H_2O	9.9	8.5
H_2S	1.2	1.2
NH_3	7.9	7.0
Total	100.0	100.0
Total Hydrogen Consumption, SCF/B	1840	2000

Table 8

Inspection of Upgraded Synthoil Samples

Sample Designation	Upgraded Synthoil	Upgraded Synthoil Distillate
Sample No.	3392-53	3392-63
°API @ 60°F	7.2	9.5
Sp. Gr. @ 60°F	1.0202	1.0035
Distillation (ASTM D-1160)		
IBP, of	380	463
5%	462	543
10%	495	565
20%	547	603
30%	592	638
40%	642	670
50%	700	701
60%	762	735
70%	850	774
80%	990	812
90%		863
95%		901
EP		950
Heptane Insoluble, Wt-%	3.88	-
Benzene Insoluble, Wt-%	0.43	-
Conradson Carbon, Wt-%	10.77	0.06
Aromatics, Wt-%	89.8	87.0
Ultimate, Wt-%		
H	9.47	9.77
C	89.08	89.17
S	0.02	0.02
N	0.376	0.377
O	0.35	0.33

Table 9

Upgrading Synthoil

Product Distribution

Plant 638H, Run 3

Period 5

Product Distribution, Wt-% of Synthoil Feed	
Stripper Bottoms[(a)]	85.1
Light Product	11.2
C_5 and C_6 in Plant Gas	1.3
Gas (C_1 - C_4)	1.6
H_2O	2.2
H_2S	0.6
NH_3	0.9
Total	102.9
H_2 Consumption, Wt-% of Feed	2.9
H_2 Consumption, SCF/B	2000

(a) Designated as Upgraded Synthoil

Table 10

Vacuum Flash Distillation of Upgraded Synthoil (3392-53)

Cut No.	Pressure mm	Temperature, OH Corr. °F	Wt. Grams	Wt-%
Trap			562	1.2
1	0.55	IBP-600°	6,723	14.0
2[a]	0.48	600-950°	28,591	59.4
Botts.		950°+	12,224	25.4
			48,100	100.0

[a] Hydrocracking feedstock designated 3392-63.

Table 11

Hydrocracking Upgraded Synthoil

Trickle Bed Operation, 150 ml Catalyst

Plant 505, Run 820

	Feed	Liquid Product		
Period No.	3392-53	1	5	6
Hours on Stream		12-18	48-54	69-77
LHSV/LHSV (base)		1.0	1.0	0.8
T-T (base), °C		25	35	35
P-P (base), psig		200	200	200
Heptane Insoluble, Wt-%	3.88	2.11	1.63	1.54
Sp. Gr. @ 60°F	1.0202	0.9893	0.9786	0.9779
°API @ 60°F	7.2	11.5	13.1	13.2
650° F+ Bottoms, Vol-%	59.3	50.3	44.0	38.2
Conversion to 650°F-, Vol-%		15.2	25.8	35.6
Ultimate, Wt-%				
H	9.47	9.83	9.82	9.82
C	89.08	89.62	89.33	89.17
S	0.02	-	-	-
N	0.376	0.076	0.100	0.084
O	0.35	-	-	-

Table 12

Product Distribution

Hydrocracking Upgraded Synthoil

Plant 505, Run 820

Period No.	1		5		6	
Hours on Stream	12-18		48-54		49-77	
LHSV/LHSV (base)	1.0		1.0		0.8	
T-T (base), °C	25		35		35	
P-P (base), psig	200		200		200	
Product Distribution	Wt-%	Vol-%	Wt-%	Vol-%	Wt-%	Vol-%
C_1-C_4 Fraction	0.6		1.9		1.7	
C_5-C_6 Fraction	0.4	0.6	1.1	1.7	0.8	1.2
C_7-390°F Fraction	4.5	5.5	6.2	7.6	6.4	7.7
390°-650°F Fraction	42.9	47.3	44.9	49.2	50.4	54.8
650°F Bottoms	52.2	50.3	46.6	44.0	41.5	38.2
Total	100.6	103.7	100.7	102.5	100.8	101.9
Hydrogen Consumption, SCF/B		347		446		426

Table 13

Thermal Hydrocracking Upgraded Synthoil

Trickle Bed Operation, 150 ml Al_2O_3

Plant 505, Run 821

	Feed	Liquid Product	
Period No.	3392-53	2	3
Hours on Stream		20-32	50-56
LHSV/LHSV (base)		1.0	1.0
T-T (base), °C		12	37
P-P (base), psig		200	200
Heptane Insoluble, Wt-%	3.88	3.79	4.68
Sp. Gr. @ 60°F	1.0202	1.0239	1.0209
°API @ 60°F	7.2	6.7	7.1
650° F + Bottoms, Vol-%	59.3	54.5	48.1
Conversion to 650°F -,Vol-%		8.1	18.9
Ultimate, Wt-%			
H	9.47	9.40	9.36
C	89.08	89.20	89.85
S	0.02	-	-
N	0.376	0.428	0.437
O	0.35	-	-

Table 14

Product Distribution

Hydrocracking Upgraded Synthoil

Plant 505, Run 821

Period No.	2		4	
Hours on Stream	26-32		50-56	
LHSV/LHSV (base)	1.0		1.0	
T-T (base), °C	12		37	
P-P (base), psig	200		200	
Product Distribution	Wt-%	Vol-%	Wt-%	Vol-%
C_1-C_4 Fraction	0.7		2.6	
C_5-C_6 Fraction	0.2	0.3	0.6	0.9
C_7 -390°F Fraction	1.8	2.3	3.2	4.1
390°-650°F Fraction	39.3	42.5	42.0	45.3
650°F+ Bottoms	58.1	54.5	51.8	48.1
Total	100.1	99.6	100.2	98.4
Hydrogen Consumption, SCF/B	0		127	

Table 15

Hydrocracking Distillate of Upgraded Synthoil

Trickle Bed Operation, 150 ml Catalyst

Plant 505, Run 824

	Feed	Liquid Product					
Period No.	3392-63	1	2	8	9	11	12
Hours on Stream		12-20	20-28	68-76	88-96	116-124	136-146
LHSV/LHSV (base)		1.0	1.0	1.0	1.0	1.0	1.0
T-T (base), °C		10	10	10	20	20	10
P-P (base), psig		200	200	200	200	200	200
°API @ 60°F	13.7	21.9	21.0	18.3	21.0	21.8	17.6
Sp. Gr. @ 60°F	1.0035	0.9224	0.9279	0.9446	0.9279	0.9230	0.9490
650°F+ Bottoms, Vol-%	66.2	26.6	26.9	33.0	21.9	22.9	33.3
Conversion to 650°F-, Vol-%		59.8	59.4	50.2	66.9	65.4	49.7
Ultimate, Wt-%							
H	9.77	11.50	11.45	11.10	11.15	11.19	10.99
C	89.17	87.72	88.69	88.70	88.18	88.15	89.21
S	0.02	-	-	-	-	-	-
N	0.377	< 0.01	< 0.01	0.01	< 0.01	< 0.01	0.01
O	0.33	0.02	-	-	0.02	-	0.02

Table 16

Product Distribution

Hydrocracking Distillate of Upgraded Synthoil

Plant 505, Run 824

Period No.	1		2		8		9		11		12	
Hours on Stream	12-20		20-28		68-76		88-96		116-124		136-146	
LHSV/LHSV (base)	1.0		1.0		1.0		1.0		1.0		1.0	
T-T (base), °C	10		10		10		20		20		10	
P-P (base), psig	200		200		200		200		200		200	
Product Distribution	Wt-%	Vol-%	Wt-%	Vol-%	Wt-%	Vol-%	Wt-%	Vol-%	Wt-%	Vol-%	Wt-%	Vol-%
C_1-C_4 Fraction	2.6		2.7		2.9		3.4		3.7		2.8	
C_5-C_6 Fraction	1.9	3.0	2.8	4.4	1.0	1.6	3.3	5.2	1.6	2.5	1.2	1.9
C_7-390°F Fraction	10.1	12.4	12.3	15.0	7.4	8.9	10.9	13.5	12.5	15.3	7.0	8.5
390°-650°F Fraction	61.5	67.3	57.6	62.7	57.5	62.2	62.3	67.5	61.3	66.4	57.1	61.5
650°F+ Bottoms	26.2	26.6	26.7	26.9	33.1	33.0	22.2	21.9	23.0	22.9	33.7	33.3
Total	102.3	109.3	102.1	109.0	101.9	105.7	102.1	108.1	102.03	107.1	101.8	105.2
Hydrogen Consumption, SCF/B	1413		1396		1280		1261		1260		1074	

Table 17

Inspection of SRC Samples

Sample Designation	Filter Feed	UOP Filtrate
Sample No.	3296-1A	3296-19
°API @ 60°F	-11.8	-5.8
Sp. Gr. @ 60°F	1.1813	1.1257
Distillation (ASTM D-1160)		
IBP, °F	400	400
5%	540	520
10%	579	550
20%	620	585
30%	654	620
40%	699	652
50%	729	685
60%	793	740
70%	925	825
80%	-	1020
% Over	70.0	80.0
% Bottoms	30.0	20.0
SRC (850°F+), Vol-%	35.0(30.3)(a)	29.0
H_2O, Wt-%	0.35	~0.0
Heptane Insoluble, Wt-%	34.4(29.7)(a)	26.9
Benzene Insoluble, Wt-%	22.3(16.7)(a)	9.4
DMF/Xylene Insoluble, Wt-%(b)	6.7	-
Ash (ASTM), Wt-%	4.0	0.01
Molecular Weight, average		273
Pour Point, °F		50
Viscosity, SFS at 100°F		884
cSt at 210°F		20.45
Ultimate, Wt-%		
H		6.90
C		86.77
S		0.72
N		1.28
O		3.81

(a) Corrected to "ash plus unconverted coal" free basis
(b) Assumed to be "ash plus unconverted coal"

Table 18

Mass and Component Balance in Filtration of SRC Filter Feed

(467 g/hr at 103°C, 17-23 psig)

	SRC Filter Feed	Filtrate		Cake		Loss
Light Oil	2.1	-		-		2.1
C_7-soluble Oil	63.5	56.8	(72.5)	6.9	(35.1)	-
Benzene Sol., C_7-insol. Oil	12.1	14.0	(17.9)	1.7	(8.6)	-
Benzene, Insol. Oil	15.6	7.4	(9.6)	4.4	(22.3)	-
Unconverted Coal	2.7		-	2.7	(13.7)	-
Ash (ASTM)	4.0		-	4.0	(20.3)	-
	100.0	78.2	(100.0)	19.7	(100.0)	2.1

Table 19

Batch Distillation of SRC Filtrate 3296-19

Bottoms Product No. 3296-	41	55	63	75
Column	Oldershaw		Flash	
Duration, hrs.	17.5	13.5	6.0	9.5
Temperature, max.,pot, °C	288	318	153	175
Temperature, max.,skin, °C	-	-	258	280
Pressure, mm Hg	1.0-2.3	1.1-2.6	0.2	0.2
Bottoms product, Wt-%	52.3	43.5	56.2	41.2
Pumpability	good	poor	good	fair
Inspection of Bottoms Product				
°API,@ 60°F	-13.7	-16.3	-13.6	-15.8
Sp. Gr., @ 60°F	1.2005	1.2283	1.1966	1.2225
Distillation (ASTM D-1160)				
IBP, °F	720	752	605	732
5%	790	787	670	769
10%	820	805	698	790
20%	850	835	735	836
30%	880	871	770	907
40%	910	950	819	995
50%	940	1020(46%)	892	1019(45%)
60%	950(52%)		960(56%)	
% Over	52.0	46.0	56.0	45.0
% Bottoms	48.0	54.0	44.0	55.0
SRC (850°F+), Vol-%	72.0	80.0	57.4	77.1
Heptane Insoluble, Wt-%	51.93	77.00	44.26	68.54
Benzene Insoluble, Wt-%	22.05	32.26	20.47	28.27
Ash (ASTM), Wt-%	0.04	0.02	<0.1	0.011
Pour Point, °F	220	300	210	365
Ultimate, Wt-%				
H	6.33	6.17	6.59	6.18
C	87.01	87.64	87.93	87.05
S	0.77	0.82	0.80	0.79
N	1.79	1.82	1.73	1.86
O	3.94	3.55	3.78	4.83

Table 20

Hydrotreating SRC Filtrate 3296-19

Trickle Bed Operation, 150 ml Catalyst

Plant 505

Run No.	Feed	801		802				
Period No.	3296-19	1,2	3,4	1,2	7,8	3,4	5,6	9,10
Hours on Stream		22-34	44-56	22-34	88-100	44-56	66-72	110-122
WHSV/WHSV (base)		1.10	0.70	1.10	1.10	2.30	2.30	1.10
T-T (base), °C		0	0	0	-19	0	-19	-21
P-P (base), psig		0	0	-800	-800	-800	-800	-1300
Heptane Insol., Wt-%	26.9	0.52	0.34	1.19	2.70	3.60	6.90	4.12
Heptane Insol. Conv., Wt-%		98.1	98.7	95.6	90.0	86.6	74.3	84.7
Benzene Insol., Wt-%	9.4	0.03	0.01	<0.01	<0.01	0.02	0.26	0.04
Viscosity, cSt, @ 100°F		-	30.30	-	-	-	-	-
Sp. Gr. @ 60°F	1.1257	-	-	-	-	1.0328	-	-
SRC (850°F+), Vol-%	29.0	-	-	-	-	18.0	-	-
SRC Conversion, Vol-%		-	-	-	-	37.9	-	-
Ultimate, Wt-%								
H	6.90	10.33	10.59	9.59	9.26	8.83	8.60	8.83
C	86.77	88.50	88.20	89.79	90.22	89.80	89.48	88.66
S	0.72	<0.02	<0.02	<0.02	-	<0.02	0.14	0.04
N	1.28	0.141	0.052	0.196	0.435	0.601	0.725	0.609
O	3.81	0.25	0.12	0.14	-	1.01	1.06	-
N in 850°F - Distillate, Wt-%		0.034	0.014	0.13	-	-	-	-

Table 21

Hydrotreating 52.3 Wt-% Vacuum Distillation Bottoms 3296-41

Trickle Bed Operation, 100 ml Catalyst

Plant 505, Run 805

Period No.	Feed	2	4	6	8	10
Hours on Stream	3296-41	44/50	55/61	67/73	79/85	91/97
WHSV/WHSV (base)		1.20	1.70	1.20	1.70	1.40
T-T (base), °C		-	-2	-2	0	-1
P-P (base), psig		-800	-200	-800	-800	-800
Heptane Insol.,Wt-%	51.93	9.04	12.10	8.63	9.84	7.58
Heptane Insol. Conv., Wt-%		82.6	76.7	83.4	81.1	85.4
Benzene Insol., Wt-%	22.05	0.21	0.48	0.15	0.33	0.13
Sp. Gr. @ 60°F	1.2005	1.0679	-	-	-	1.0591
SRC (850°F+), Vol-%	80.0	43.8	-	-	-	42.1
SRC Conversion, Vol-%		45.3	-	-	-	47.4
Ultimate, Wt-%						
H	6.33	8.91	8.75	9.10	8.97	9.13
C	87.01	90.12	89.95	89.93	89.96	89.83
S	0.77	0.04	0.06	0.04	0.04	0.04
N	1.79	0.751	-	-	0.763	0.681
O	3.94	0.640	-	-	0.620	0.700

Table 22

Hydrotreating SRC Liquids

Trickle Bed Operation, 100 ml Catalyst

Plant 505, Run 809

T-T (base), °C: 2-4;   P-P (base), psig: 0

Periods 1-5, 10-12: Filtrate 3296-19
Periods 6-7: 56.2 Wt-% vacuum flash bottoms 3296-63
Periods 8-9: Reconstituted filtrate 3296-71

Period No.	Feed	1-5	10-12	Feed	6-7	Feed	8-9
Hours on Stream	3296-19	22-58	120-144	3296-63	68-84	3296-71	94-110
WHSV/WHSV (base)		2.0	2.0		1.2		2.0
Heptane Insol., Wt-%	26.9	3.15	3.40	44.3	4.97	23.9	3.24
Heptane Insol. Conv., Wt-%	-	88.3	87.4	-	88.8	-	86.4
Benzene Insol., Wt-%	9.4	0.08	0.04	20.4	0.03	9.8	0.02
Sp. Gr. @ 60°F	1.1257	1.0122	1.0283	1.1973	1.0458	1.1212	1.0259
SRC (850°F+), Vol-%	29.0	18.0	20.0	57.4	33.0	31.5	21.0
SRC Conversion, Vol-%	-	37.9	31.0	-	42.5	-	33.3
Ultimate, Wt-%							
H	6.90	9.46	9.15	6.59	9.32	6.75	9.30
C	86.77	88.11	89.34	87.93	90.01	87.28	89.07
S	0.72	0.06	0.05	0.80	0.04	-	0.05
N	1.28	0.42	0.43	1.73	0.50	1.22	0.44
O	3.81	1.88	0.83	3.78	0.67	-	1.31
N in 850°F - Distillate, Wt-%		0.26	0.29		0.31		0.28

Table 23

Hydrotreating 41.2 Wt-% Vacuum Flash Bottoms 3296-75

Trickle Bed Operation, 200 ml Catelyst

P-P (base), psig: 0

Plant 505, Run 810

Period No. Hours on Stream	Feed 3296-75	1,2 22-34	3,4 40-52
WHSV/WHSV (base)		0.73	0.25
T-T (base), °C		18	28
Heptane Insol., Wt-%	68.5	2.5	1.7
Heptane Insol. Conv., Wt-%		96.4	97.5
Benzene Insol., Wt-%	28.3	<0.01	<0.01
Sp. Gr. @ 60°F	1.2225	1.0336	-
SRC (850°F+), Vol-%	77.1	38.0	-
SRC Conversion, Vol-%		50.7	-
Ultimate, Wt-%			
H	6.18	9.50	9.92
C	87.05	89.92	89.03
S	0.79	0.02	<0.03
N	1.86	0.23	0.12
O	4.83	0.32	0.17
N in 850°F - Distillate, Wt-%		0.15	-

Table 24

Fuel Product Distribution

Hydrotreating 41.2 Wt-% Vacuum Flash SRC Bottoms 3296-75

Plant 505, Run 810

	Period 2
WHSV/WHSV (base)	0.73
T-T (base), °C	18
P-P (base), psig	0
Fuel Product, Wt-%	96.1
Distribution, Wt-%	
Gas (C_1-C_4)	2.2
Gasoline (C_5-400°F)	7.0
Kerosine (400-527°F)	8.6
Light Gas Oil (527-752°F)	36.0
Heavy Gas Oil (752-850°F)	13.9
Bottoms	32.3
Total	100.0
Hydrogen Consumption, SCF/B	3540

Table 25

Distribution of Hydrogen Consumption

Plant 505

Run No.	801	802	805	809	810
Period No.	3	4	2	7	2
Hydrogen Consumption, Wt-%					
Liquid Products (Strip. Botts. and Lt. Prod.)	77.3	70.4	74.7	73.2	67.6
C_5 and C_6 in Gas	3.3	2.2	2.0	3.4	2.8
Gas (C_1-C_4)	3.5	6.1	3.6	4.3	6.8
H_2O	9.5	13.8	12.0	10.6	13.3
H_2S	0.9	1.8	1.3	1.3	1.1
NH_3	5.5	5.7	6.4	7.2	8.4
Total	100.0	100.0	100.0	100.0	100.0
Total Hydrogen Consumption, SCF/B	3270	1830	2490	2670	3540

Table 26

Inspection of SRC Samples

Sample Designation	SRC Filtrate (as received)	30 Wt-% Botts. of SRC Filtrate
Sample No.	3296-95	3296-155
°API @ 60°F	2.5	-12.2
Sp. Gr. @ 60°F	1.0560	1.1858
Distillation (ASTM D-1160)		
IBP, °F	385	572
5%	428	647
10%	435	680
20%	450	723
30%	462	750
40%	475	780
50%	498	825
60%	535	850 (54%)
70%	600	
80%	700	
89%	875	
% Over	59.0	54.0
% Bottoms	11.0	46.0
SRC (850°F+), Vol-%	12.3	46.0
Heptane Insoluble, Wt-%		38.4
Benzene Insoluble, Wt-%		20.6
Ash (ASTM), Wt-%	0.02	0.04
Conradson Carbon, Wt-%		29.27
Molecular Weight, average		327
Pour Point, °F		180
Viscosity, SFS, @ 250°F		172.2
SFS, @ 300°F		30.3
Ultimate, Wt-%		
H		6.55
C		87.65
S		0.73
N		1.69
O		3.63

Table 27

Hydrotreating SRC Filtrate, 30 Wt-% Bottoms

Trickle Bed Operation, 200 ml Catalyst

Plant 505, Run 819

Period No. Hours on Stream	Feed 3296-155	1,2 48-64	3,4 80-100	5,6 116-136	7,8 144-160	9,10 158-184	11,12 200-220
WHSV/WHSV (base)		0.98	0.54	0.54	1.04	1.02	0.50
T-T (base), °C		0	0	10	10	0	0
P-P (base), psig		0	0	0	0	0	0
Heptane Insol., Wt-%	38.4	6.20	3.02	2.65	7.51	9.81	5.22
Heptane Insol. Conv., Wt-%		83.9	92.1	93.1	80.4	74.5	86.4
Benzene Insol., Wt-%	20.6	0.18	0.13	-	-	-	-
Ash (ASTM), Wt-%	0.04	-	-	-	-	-	-
Viscosity, cSt, @100°F		313.2	107.1	42.7	316.7	-	-
Sp. Gr. @ 60°F	1.1858	0.9888	0.9779	0.9659	0.9923	-	-
SRC (850°F+), Vol-%	46.0	30.0	30.0	23.0	30.0	-	-
SRC Conversion, Vol-%		34.8	34.8	50.0	34.8	-	-
Ultimate, Wt-%							
H	6.55	9.21	9.60	-	-	-	-
C	87.65	89.16	89.15	-	-	-	-
S	0.73	0.05	0.03	-	-	-	-
N	1.69	0.489	0.269	0.188	0.593	0.584	0.393
O	3.63	0.49	0.30	-	-	-	-
N in 850°F - Distillate, Wt-%	1.28	0.240	0.121	0.079	0.371	-	-

Table 28

Fuel Product Distribution

Hydrotreating SRC Filtrate, 30 Wt-% Bottoms

Plant 505, Run 819

	Period 2	Period 4
WHSV/WHSV (base)	1	0.5
T-T (base), °C	0	0
P-P (base), psig	0	0
Fuel Product, Wt-%	97.1	97.5
Distribution, Wt-%		
Gas (C_1-C_4)	0.5	0.9
Gasoline (C_5-400°F)	3.7	4.4
Kerosine (400-527°F)	7.8	9.7
Light Gas Oil (527-752°F)	46.1	44.6
Heavy Gas Oil (752-850°F)	11.5	10.5
Bottoms	30.4	29.9
Total	100.0	100.0
Hydrogen Consumption, SCF/B	2540	2900

Table 29

Distribution of Hydrogen Consumption

Plant 505, Run 819

	Period 2	Period 4
Hydrogen Consumption, Wt-%		
Liquid Products (Strip. Botts. and Lt. Prod)	74.3	75.2
C_5 and C_6 in Gas	1.5	1.6
Gas (C_1-C_4)	1.9	3.0
H_2O	12.5	11.0
H_2S	1.4	1.2
NH_3	8.4	8.0
Total	100.0	100.0
Total Hydrogen Consumption, SCF/B	2540	2900

Table 30

Inspection of Cutback SRC and Components

Sample Designation	SRC	Solvent	Cutback SRC
Sample No.	3296-73	3296-89	3296-93
°API @ 60°F	-15.6	-0.2	-14.1
Sp. Gr. @60°F	1.2210	1.0777	1.0252
Distillation (ASTM D-1160)			
IBP, °F	650	475	550
5%	796	539	610
10%	896	557	653
20%	1005	578	749
30%		593	905
50%		620	
70%		660	
90%		741	
% Over	20.0	90.0	30.0
% Bottoms	80.0	10.0	70.0
SRC (850°F$^+$), Vol-%	92.5		73.5
Heptane Insoluble,	88.5		65.7
Benzene Insoluble, Wt-%	37.1		29.1
Ash (ASTM), Wt-%			0.17
Softening Point, °F	348	-	-
Pour Point, °F			285
Viscosity, cSt, 350°F			495
Ultimate, Wt-%			
H			6.06
C			87.65
S			0.59
N			1.92
O			4.80
Cl (ppm)			57

Table 31

Hydrotreating Cutback SRC

Trickle Bed Operation, 200 ml Catalyst

Plant 505, Run 815

Period No.	Feed	4	5	6,7	8,9	10-12	13,14
Hours in Stream	3296-93	61-69	69-77	93-109	117-137	141-161	179-193
WHSV/WHSV (base)		0.58	0.58	0.50	1.0	1.0	0.52
T-T (base), °C		-5	-5	10	10	-5	-5
P-P (base), psig		0	0	0	0	0	0
Heptane Insol., Wt-%	65.7	5.1	7.0	7.3	14.9	19.3	11.5
Heptane Insol. Conv., Wt-%		92.2	89.3	88.9	77.3	70.6	82.5
Benzene Insol., Wt-%	29.1	0.01	0.03	0.17	2.14	4.49	1.84
Ash (ASTM), Wt-%	0.17	-	0.006	0.004	0.007	0.036	0.040
Sp. Gr. @ 60°F	1.2052	-	1.0568	1.0505	1.1098	1.1186	1.0893
SRC (850°F$^+$), Vol-%	73.5	-	42.0	30.0	47.0	50.0	53.1
SRC Conversion, Vol-%	-	-	42.9	59.2	36.1	32.0	27.8
Ultimate, Wt-%							
H	6.06	9.18	8.77	-	-	-	-
C	87.65	91.01	89.87	-	-	-	-
S	0.59	0.02	<0.02	-	-	-	-
N	1.92	0.38	0.49	0.43	1.42	1.50	0.77
O	4.80	0.22	0.32	-	-	-	-
N in 850°F - Distillate, Wt-%		-	0.23	0.19	0.61	0.67	-

Table 32

Fuel Product Distribution

Hydrotreating Cutback SRC

Plant 505, Run 815

Period No.	5	7	9	12	14
Hours on Stream	69-77	101-109	125-133	157-161	185-193
WHSV/WHSV (base)	0.58	0.50	1.0	1.0	0.52
T-T (base), °C	-5	10	10	-5	-5
P-P (base), psig	0	0	0	0	0
Fuel Product, Wt-%	96.3	-	-	-	-
Distribution, Wt-%					
Gas (C_1-C_4)	2.8	4.6	2.8	2.6	4.7
Gasoline (C_5-400°F)	8.0	10.6	5.6	4.2	8.2
Kerosine (400-527°F)	8.5	12.1	7.9	5.7	8.0
Light Gas Oil (527-752°F)	32.3	35.6	30.2	26.4	28.1
Heavy Gas Oil (752-850°F)	9.7	10.7	8.9	12.4	9.3
Bottoms	38.7	26.4	44.6	48.7	41.7
Total	100.0	100.0	100.0	100.0	100.0
Hydrogen Consumption, SCF/B	3080	-	-	-	-

Table 33

Distribution of Hydrogen Consumption

Plant 505, Run 815

Period 5

Hydrogen Consumption, Wt-%	
Liquid Product (Strip. Botts. and Lt. Prod.)	62.3
C_5 and C_6 in Gas	4.4
Gas (C_1-C_4)	9.8
H_2O	14.2
H_2S	0.9
NH_3	8.4
Total	100.0
Total Hydrogen Consumption, SCF/B	3080

Table 34

Inspection of SRC Samples

Sample Designation	SRC	Startup Solvent
Sample No.	3392-1	3392-45
°API @ 60°F	-13.7	-1.4
Sp. Gr. @ 60°F	1.2012	1.0876
Distillation (ASTM D-1160)		
IBP, °F	648	210
5%	834	391
10%	905	491
15%	951	-
20%		612
30%		712
40%		803
50%		888
59%		962
% Over	15.0	59.0
% Bottoms	85.0	41.0
SRC (850°F+), Vol-%	93.0	54.5
Heptane Insoluble, Wt-%	89.4	15.7
Benzene Insoluble, Wt-%	34.7	-
DMF/Xylene Insoluble, Wt-%	0.15	-
Ash (ASTM), Wt-%	0.11	-
Conradson Carbon, Wt-%	55.85	24.68
Molecular Weight, average	622	388
Viscosity, cSt, @ 210°F		89
cSt, @ 250°F		35.5
SFS, @ 450°F	944	
Ultimate, Wt-%		
H	5.63	
C	84.44	
S	0.78	
N	2.12	
O	3.71	

Table 35

Hydrotreating SRC, Recycle Mode (CFR=2.0)

Trickle Bed Operation, 200 ml Catalyst

Plant 505, Run 822

Period No. Hours on Stream	Feed 3392-1	1,2 44-68	3-6 92-140	7,8 152-176
WHSV/WHSV (base)		0.50	0.50	0.50
T-T (base),°C		0	10	20
P-P (base), psig		0	0	0
Heptane Insol., Wt-%	89.4	15.1	12.4	12.7
Heptane Insol. Conv., Wt-%	-	83.1	86.1	85.8
Benzene Insol., Wt-%	34.7	1.9	1.7	1.9
Ash (ASTM), Wt-%	0.11	-	-	-
Viscosity, cSt, @ 122°F	-			1030
cSt, @ 210°F	-	271	101	-
Sp. Gr. @ 60°F	1.2012	1.1037	1.1012	1.0986
SRC (850°F+), Vol-%	93.0	58.0	51.5	49.0
SRC Conversion, Vol-%	-	37.6	44.6	47.3
Ultimate, Wt-%				
H	5.63	8.13	8.13	8.11
C	84.44	90.06	90.84	90.59
S	0.78	-	-	<0.03
N	2.12	1.00	0.86	0.78
O	3.71	-	-	0.24
N in 850°F - Distillate, Wt-%	-	0.53	0.49	0.45

Table 36

Hydrotreating SRC Recycle Mode (CFR=2.0)

Trickle Bed Operation, 200 ml Catalyst

Plant 505, Run 823

Period No. Hours on Stream	Feed 3392-1	1-3 39-87	4 99-111	7,8 129-153	9,10 169-197
WHSV/WHSV (base)		0.26	0.35	0.35	0.25
T-T (base), °C		0	10	20	0
P-P (base), psig		0	0	0	0
Heptane Insol., Wt-%	89.4	6.9	8.0	8.7	7.9
Heptane Insol. Conv., Wt-%	-	92.3	91.1	90.3	91.2
Benzene Insol., Wt-%	34.7	0.6	-	1.3	-
Ash (ASTM), Wt-%	0.11	-	-	-	-
Viscosity, cSt, @ 122°F	-	653	-	564	-
Sp. Gr. @ 60°F	1.2012	1.0568	-	1.0703	-
SRC (850°F+), Vol-%	93.0	41.0	-	42.0	-
SRC Conversion, Vol-%	-	55.9	-	54.8	-
Ultimate, Wt-%					
H	5.63	9.02	-	8.62	-
C	84.44	90.48	-	90.77	-
S	0.78	<0.03	<0.03	<0.03	-
N	2.12	0.42	-	0.50	-
O	3.71	0.21	0.09	-	-
N in 850°F - Distillate, Wt-%	-	0.12	-	0.21	-

Table 37

Fuel Product Distribution

Hydrotreating SRC

Plant No.	505					638H
Run No.	822	822	822	823	823	4
Period No.	2	4	8	2	8	7
Catalyst Volume, ml	200	200	200	200	200	800
Hours on Stream	56-68	104-116	164-176	55-71	141-153	120-144
WHSV/WHSV (base)	0.50	0.50	0.52	0.26	0.35	0.20
T-T (base), °C	0	10	20	0	20	10
P-P (base), psig	0	0	0	0	0	0
Fuel Product, Wt-%	-	-	96.2	98.4	-	98.7
Distribution, Wt-%						
Gas (C_1-C_4)	1.9	4.6	3.4	4.0	8.2	1.5
Gasoline (C_5-400°F)	1.8	5.3	2.9	10.9	4.6	5.2
Kerosine (400-527°F)	3.8	6.5	3.9	9.0	4.5	5.6
Light Gas Oil (527-752°F)	21.4	23.0	26.2	28.7	29.2	32.7
Heavy Gas Oil (752-850°F)	13.4	13.2	15.3	13.5	14.4	14.2
Bottoms	57.7	47.4	48.3	33.9	39.1	40.8
Total	100.0	100.0	100.0	100.0	100.0	100.0
Hydrogen Consumption, SCF/B	-	-	2640	3940	-	3790

Table 38

Distribution of Hydrogen Consumption

Plant No.	505		638H
Run No.	822	823	4
Period No.	8	2	7
Hydrogen Consumption, Wt-%			
Liquid Product (Strip. Botts. and Lt.Prod.)	57.5	68.1	68.2
C_5 and C_6 in Gas	3.5	3.5	5.4
Gas (C_1-C_4)	13.7	11.5	10.5
H_2O	13.7	7.8	7.4
H_2S	1.5	1.0	0.9
NH_3	10.1	8.1	7.6
Total	100.0	100.0	100.0
Total Hydrogen Consumption, SCF/B	2640	3940	3790

Table 39

Inspection of Upgraded SRC
(Plant 638 H, Run 4)

Sample Designation	Upgraded SRC
Sample No.	3392-69
°API @ 60°F	9.6
Sp. Gr. @60°F	1.0028
Distillation (ASTM D-1160)	
IBP, °F	433
5%	555
10%	600
20%	660
30%	718
40%	780
50%	850
60%	940
65%	1000
% Over	65.0
% Bottoms	35.0
SRC (850°F+), Vol-%	50.0
Heptane Insoluble, Wt-%	9.76
Benzene Insoluble, Wt-%	1.68
Ash (ASTM), Wt-%	0.001
Conradson Carbon, Wt-%	16.31
Aromatics, Wt-%	91.7
Molecular Weight, average	360
Pour Point, °F	55
Viscosity, cSt, @ 210°F	32.69
cSt, @ 250°F	14.43
Ultimate, Wt-%	
H	8.76
C	90.85
S	0.02
N	0.548
O	0.20

Table 40

Upgrading SRC

Product Distribution

Plant 638H, Run 4

Period 7

Product Distribution, Wt-% of SRC Feed	
Stripper Bottoms(a)	77.5
Light Product	15.1
C_5 and C_6 in Plant Gas	2.9
Gas (C_1-C_4)	3.2
H_2O	3.4
H_2S	0.8
NH_3	2.1
Total	105.0
H_2 Consumption, Wt-% of Feed	5.0
H_2 Consumption, SCF/B	3791

(a) Designated as upgraded SRC

Table 41

Hydrocracking Upgraded SRC

Trickle Bed Operation, 150 ml Catalyst

Plant 505, Run 827

	Feed			Liquid Product		
Period No.	3392-69	2	4	6	8	10
Hours on Stream		20-28	48-56	85-95	161-131	141-147
LHSV/LHSV (base)		1.0	1.0	0.66	0.66	1.0
T-T (base), °C		10	20	20	10	10
P-P (base), psig		200	200	200	200	200
Heptane Insoluble, Wt-%	9.79	5.36	6.13	5.86	6.47	7.34
Sp. Gr., @ 60°F	1.0028	1.0366	1.0435	1.0382	1.0505	1.0505
°API, @ 60°F	9.6	5.0	4.1	4.8	3.2	3.2
650°F+ Bottoms, Vol-%	70.10	61.82	65.46	62.43	65.89	68.68
Conversion to 650°F^{-}, Vol-%		11.8	6.6	10.9	6.0	2.0
Ultimate, Wt-%						
H	8.76	9.32	9.11	8.99	8.99	8.83
C	90.85	90.01	89.80	89.69	90.77	90.01
S	<0.02	<0.02	<0.02	<0.02	<0.02	
N	0.548	0.153	0.304	0.269	0.349	0.377
O	0.20	0.11	0.16	0.10	0.10	0.13

Table 42

Product Distribution

Hydrocracking Upgraded SRC

Plant 505, Run 827

Period No.	2		4		6		8		10	
Hours on Stream	20-28		48-56		85-95		161-131		141-147	
LHSV/LHSV (base)	1.0		1.0		0.66		0.66		1.0	
T-T (base), °C	10		20		20		10		10	
P-P (base),psig	200		200		200		200		200	
Product Distribution	Wt-%	Vol-%	Wt-%	Vol-%	Wt-%	Vol-%	Wt-%	Vol-%	Wt-%	Vol-%
C_1-C_4 Fraction	1.1		1.4		2.4		1.8		1.4	
C_5-C_6 Fraction	0.8	1.3	0.5	0.8	1.3	2.0	1.5	2.3	0.7	1.1
C_7-390°F Fraction	3.9	4.7	1.3	1.6	4.0	4.9	2.2	2.6	2.6	2.9
390°-650°F Fraction	27.6	29.1	26.0	27.5	24.9	26.4	23.2	24.6	20.3	21.2
650°F+ Bottoms	67.5	61.8	71.5	65.5	68.1	62.4	72.0	65.9	75.4	68.7
Total	100.9	96.9	100.7	95.4	100.7	95.7	100.7	95.4	100.4	93.9
Hydrogen Consumption, SCF/B	519		440		421		402		248	

Table 43

Inspection of H-Coal Samples

Sample Designation	Hydroclone Underflow	Hydroclone Underflow Filtrate
Sample No.	3296-87	3296-153
°API @ 60°F	-16.5	-17.7
Sp. Gr. @ 60°F	1.2307	1.2433
Distillation (ASTM D-1160)		
IBP, °F	466	493
5%	533	538
10%	560	567
20%	615	621
30%	690	680
40%	770	752
50%	876	822
60%	-	910
% Over	50.0	60.0
% Bottoms	50.0	40.0
Heptane Insoluble, Wt-%	49.9 (41.0)(a)	49.0
Benzene Insolable, Wt-%	35.0 (23.4)(a)	29.0
DMF/Xylene Insoluble, Wt-%(b)	15.1	0.03
Ash (ASTM), Wt-%	9.09	0.12
Conradson Carbon, Wt-%	39.43	33.20
Molecular Weight, average	-	373
Softening Point, °F	172	-
Pour Point, °F	-	240
Viscosity, SFS		
@ 250°F	307.3	161.4
@ 300°F	-	154.1
Ultimate, Wt-%		
H	6.35	6.96
C	79.35	87.07
S	1.43	0.66
N	1.11	1.30
O	3.92	4.38

(a) Corrected to "ash plus unconverted coal" free basis.

(b) Assumed to be "ash plus unconverted coal"

Table 44

Filtration of H-Coal Hydroclone Underflow Mass Balance, Wt-%

Filtration Temperature, °C		200
Filtration Pressure, psig		500
Average Filtration Rate, g/hr.		25
Filtrate	72.7	
Filter Cake	21.5	
Loss	5.8	
Filter Feed	100.0	

Table 45

Extraction of Filter Cake
(From Filtration of H-Coal Hydroclone Underflow)

Sample	Filter Cake	Fraction Oil	Fraction Water	Fraction Insolubles
Wt-% of Filter Cake	100.0	21.6	1.0	77.4
Analysis, Wt-%				
H	3.53	-		2.09
C	48.56	-		34.84
C_7-insol.		21.8		
Benzene Insol.		0.42		
Ash (ASTM)	42.54	-		56.45

Table 46

Hydrotreating Filtered H-Coal Hydroclone Underflow

Trickle Bed Operation, 200 ml Catalyst

Plant 505, Run 826

Period No.	Feed	1-3	4,5	6-8	9,10	11,12
Hours on Stream	3296-153	20-38	54-78	92-128	136-148	166-178
WHSV/WHSV (base)		1.0	0.5	0.5	1.0	1.0
T-T (base), °C		0	0	10	9	0
P-P (base), psig		0	0	0	0	0
Heptane Insol., Wt-%	49.0	7.45	3.45	3.25	7.04	11.4
Heptane Insol. Conv., Wt-%	-	84.8	93.0	93.4	85.6	76.7
Benzene Insol,, Wt-%	29.0	0.93	0.06	0.25	2.01	3.24
Ash (ASTM), Wt-%	0.12	0.003	-	-	-	-
Viscosity, cSt, 100°F	-	484.7	107.4	66.7	406.4	100.4
Sp. Gr. @ 60°F	1.2433	1.0420	1.0158	1.0114	1.0486	1.0536
850°F+ Bottoms, Vol-%	46.8	34.0	28.0	25.0	34.0	36.0
Conversion to 850°F-,Vol-%	-	27.4	40.2	46.6	27.4	23.1
Ultimate, Wt-%						
H	6.96	9.33	9.56	9.32	8.84	8.77
C	87.07	89.87	89.48	89.59	90.20	89.70
S	0.66	<0.03	<0.02	-	-	-
N	1.30	0.47	0.17	0.22	0.33	0.59
O	4.38	0.59	0.39	-	-	-
N in 850°F - Distillate, Wt-%	-	0.17	0.05	0.09	0.22	0.21

Table 48

Distribution of Hydrogen Consumption

Plant 505, Run 826

Period No.	1-3	4,5
Hydrogen Consumption, Wt-%		
Liquid Product (Strip, Botts. and Lt. Prod.)	70.0	63.8
C_5 and C_6 in Gas	2.0	5.4
Gas (C_1-C_4)	4.7	7.2
H_2O	15.7	15.0
H_2S	1.3	1.2
NH_3	6.3	7.4
Total	100.0	100.0
Total Hydrogen Consumption, SCF/B	2520	2760

Table 47

Fuel Product Distribution

Hydrotreating Filtered H-Coal Hydroclone Underflow

Plant 505, Run 826

Period No.	1-3	4,5	6-8	9,10	11,12
WHSV/WHSV (base)	1.0	0.5	0.5	1.0	1.0
T-T (base), °C	0	0	10	9	0
P-P (base), psig	0	0	0	0	0
Fuel Product, Wt-%	96.8	96.5	-	-	-
Distribution, Wt-%					
Gas (C_1-C_4)	1.1	2.5	3.4	2.5	0.9
Gasoline (C_5-400°F)	0.7	1.9	1.6	1.1	0.3
Kerosine (400-527°F)	12.1	14.6	16.5	11.2	10.3
Light Gas Oil (527-752°F)	44.5	47.2	45.7	43.7	51.2
Heavy Gas Oil (752-850°F)	11.4	9.6	12.1	11.0	3.8
Bottoms	30.2	24.2	20.7	30.5	33.5
Total	100.0	100.0	100.0	100.0	100.0
Hydrogen Consumption, SCF/B	2524	2762	-	-	-

Table 49

Inspection of Coal Oils

Sample Designation	SRC/UOP Filtrate		52.3 Wt-% Botta. of SRC/UOP Filtrate		43.5 Wt-% Botta. of SRC/UOP Filtrate	Cutback SRC		Synthoil		H-Coal Hydroclone Underflow Filtrate		H-Coal Vacuum Bottoms	
	Feedstock	Product	Feedstock	Product	Feedstock	Feedstock	Product	Feedstock	Product	Feedstock	Product	Feedstock	Product
Sample No.	3296-19	3296-43	3296-41	3296-57	3296-55	3296-93	3296-141	3296-147	3292-65	3296-153	3392-67	3296-81	3392-57
Hydrotreating Conditions													
WHSV/WHSV (base)		2.30		1.34			0.58		0.98		1.0		
T-T (base), °C		0		-2			-5		9		0		
P-P (base), psig		-800		-800			0		0		0		
Properties of Sample													
°API @ 60°F	-5.8	5.5	-13.7	1.5	-16.3	-14.1	3.7	-4.3	4.2	-17.7	4.3	-34.2	-2.5
SP.Gr. @ 60°F	1.1257	1.0328	1.2005	1.0639	1.2283	1.2052	1.0466	1.1124	1.0427	1.2433	1.0420	1.4546	1.0969
Distillation (ASTM D-1160)													
IBP	400	400	720	455	752	550		455	388	493	425	826	315
5%	520	482	790	560	787	610		519	480	538	508	855(f)	495
10%	550	503	820	605	805	653		552	510	567	535		541
20%	585	540	850	662	835	749		606	565	621	587		599
30%	620	569	880	702	871	905		665	611	680	631		681
40%	652	593	910	745	950			730	660	752	677		758
50%	685	619	940	790	1020(c)			795	705	822	733		848
60%	740	650	950(b)	873				865	750	910	797		958
70%	825	710		1010				970	809		850(e)		
80%	1020	805							900				
90%		985(a)							982(d)				
% Over	80.0	88.0	52.0	70.0	46.0	30.0		70.0	87.0	60.0	66.0	2.0	60.0
% Bottoms	20.0	12.0	48.0	30.0	54.0	70.0		30.0	13.0	40.0	34.0	98.0	40.0
Heptane Insoluble, Wt-%	27.5	3.73	51.9	8.88	77.0	67.5	5.45	18.8	6.14	49.0	7.90	94.4	15.2
Benzene Insoluble, Wt-%	9.6	0.10	22.1	0.12	32.0	29.1	0.01	4.4	0.81	29.0	0.93	63.3	2.59
DMF/Xylene Insoluble, Wt-%	0.01						0.02	0.16	0.17	0.03	0.01	30.2	0.01
Ash (ASTM), Wt-%	0.01	<0.001	0.04	0.001	0.02	0.17	<0.001	0.015	0.001	0.12	0.003	19.6	0.015
Molecular Weight, average	273							308	282	373	320		388
Ultimate, Wt-%													
H	6.90	8.93	6.33	9.21	6.17	6.06	9.18	7.42	8.96	6.96	9.33	4.61	7.88
C	86.77	89.51	87.01	89.07	87.64	87.65	91.01	88.28	90.16	87.07	89.87	69.56	90.18
S	0.72	0.04	0.77	0.05	0.82	0.59	0.02	0.56	<0.02	0.66	<0.03	2.02	0.08
N	1.28	0.60	1.79	0.64	1.82	1.92	0.38	1.31	0.54	1.30	0.47	1.40	0.87
O	3.81	1.01	3.94	0.58	3.55	4.80	0.22	2.27	0.42	4.38	0.59	5.04	0.70

(a) 88.0%, (b) 52.0%, (c) 46.0%, (d) 87.0%, (e) 66.0%, (f) 2.0%

Table 50

Modified SARA Separation of Coal Oils

Sample Designation	SRC/UOP Filtrate		52.3 Wt-% Botts. of SRC/UOP Filtrate		43.5 Wt-% Botts. of SRC/UOP Filtrate	Cutback SRC		Synthoil		H-Coal Hydroclone Underflow Filtrate		H-Coal Vacuum Bottoms	
	Feedstock	Product	Feedstock	Product	Feedstock	Feedstock	Product	Feedstock	Product	Feedstock	Product	Feedstock	Product
Sample No.	3296-19	3296-43	3296-41	3296-57	3296-55	3296-93	3296-141	3296-147	3392-65	3296-153	3296-67	3296-81	3392-57
Separated Fraction, Wt-%													
IBP-243°C	4.8	9.6	0.0	3.6	0.0	0.0	4.8	11.6	8.7	0.0	4.4	0.0	11.0
Pentane Insoluble Fraction													
a	17.0	4.5	34.4	14.0	32.5	39.5	8.5	25.0	8.6	23.5	12.8	26.5	21.7
b	4.6	0.6	11.3	1.6	12.4	15.8	0.9	3.2	1.3	14.2	2.4	13.6	2.1
c	4.5	0.4	11.1	1.3	15.2	11.4	0.1	0.3	0.3	12.8	0.3	11.7	0.3
Total	26.1	5.5	56.8	16.9	60.1	66.7	9.5	28.5	10.2	50.5	15.5	51.8	24.1
Bases													
Very Weak Bases	11.6	6.6	11.1	8.7	10.4	9.1	6.3	10.5	8.0	10.1	6.2	4.7	6.0
Weak Bases	1.9	4.2	1.3	1.0	0.9	1.3	0.2	2.4	0.8	1.2	1.9	0.8	1.0
Strong Base Fraction a	6.3	3.8	4.2	7.1	4.0	2.7	3.2	7.0	4.4	3.2	0.2	1.6	6.5
Strong Base Fraction b	3.8	2.4	1.3	3.5	1.0	0.6	7.5	2.0	2.1	0.7	1.8	0.8	2.3
Total	23.6	17.0	17.9	20.3	16.3	13.7	17.2	21.9	15.3	15.2	10.1	7.9	15.8
Acids													
Very Weak Acids	2.5	2.8	2.7	4.9	2.6	3.3	3.6	4.4	5.3	1.4	2.4	1.0	4.4
Weak Acids	3.7	0.9	0.4	0.4	1.4	0.2	1.9	0.8	0.5	0.4	0.4	0.1	0.6
Strong Acid Fraction a	1.6	1.4	1.3	1.9	2.8	1.0	1.8	1.7	1.7	1.8	1.7	1.9	1.7
Strong Acid Fraction b	<0.1	0.1	0.2	0.1	0.5	0.2	0.1	<0.1	0.2	0.1	0.1	0.1	0.3
Total	7.8	5.2	4.6	7.3	7.3	4.7	7.4	6.9	7.7	3.7	4.6	3.1	7.0
Neutral Nitrogen Fraction													
a	2.6	2.4	2.7	5.7	4.8	3.6	4.3	5.1	5.8	2.1	2.3	3.2	3.1
b	0.1	0.1	0.4	0.1	0.9	0.4	0.3	0.4	0.3	1.5	0.3	0.7	1.2
Total	2.7	2.5	3.1	5.8	5.7	4.0	4.6	5.5	6.1	3.6	2.6	3.9	4.3
Saturates	1.7	5.1	1.0	2.7	0.5	0.3	3.1	1.1	3.1	1.9	7.3	0.1	1.3
Aromatics													
Mono	0.6	18.2	0.4	12.9	0.2	0.2	18.3	2.6	16.2	8.5	20.5	<0.01	2.9
Di-, Tri-	31.8	35.5	15.1	28.9	9.0	9.8	30.8	20.6	31.2	15.1	31.6	2.7	30.4
Poly	0.9	1.4	1.1	1.6	0.9	0.6	4.3	1.3	1.5	1.5	3.4	0.3	3.2
Total	33.3	55.1	16.6	43.4	10.1	10.6	53.4	24.5	48.9	25.1	55.5	3.0	36.5
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	69.8[a]	100.0

(a) 30.2 Wt-% of sample is insoluble mineral and unconverted coal

Table 51

Analytical Data for Modified SARA Separated Pentane Insolubles

Sample Designation	Sample No.	SARA Separated Pentane Insoluble Fraction	Molecular Weight	Ultimate, Wt-%					Atomic Ratios			
				H	C	S	N	O	H/C	S/C	N/C	O/C
SRC/UOP Filtrate Feedstock	3296-19	a	490	6.13	84.39	0.82	2.29	6.62	0.866	0.0036	0.023	0.059
		b	1330	5.47	83.38	0.97	2.27	6.13	0.782	0.0043	0.023	0.055
		c		5.83	79.30	0.83	3.19	7.39	0.876	0.0039	0.034	0.070
SRC/UOP Filtrate Product	3296-43	a	1220	6.21	89.70		1.58	2.87	0.829		0.015	0.024
		b	2010	5.38	80.40		1.69	6.64	0.797		0.018	0.062
		c										
52.3 Wt-% Botts. of SRC/UOP Filtrate Feedstock	3296-41	a	550	5.87	83.23	0.80	1.83	5.96	0.840	0.0036	0.019	0.054
		b	1050	5.63	82.86	0.90	2.47	5.50	0.810	0.0040	0.026	0.050
		c	1950	5.04	81.93	0.95	2.92	7.16	0.734	0.0043	0.031	0.060
52.3 Wt-% Botts. of SRC/UOP Filtrate Product	3296-57	a	1170	6.20	89.15	0.12	1.45	2.54	0.829	0.0005	0.014	0.021
		b		5.75	85.12	0.27	1.49	3.60	0.805	0.0010	0.015	0.032
		c		5.34	47.64	0.23	2.52	13.69	1.336	0.0018	0.045	0.216
43.5 Wt-% Botts. of SRC/UOP Filtrate Feedstock	3296-55	a	450	5.87	85.88	0.82	1.95	5.61	0.814	0.0036	0.019	0.049
		b	950	5.29	81.55	0.81	2.44	5.50	0.723	0.0037	0.026	0.046
		c	2430	5.07	82.47	0.80	2.33	5.54	0.732	0.0036	0.024	0.050
Cutback SRC Feedstock	3296-93	a	600	6.01	85.38	0.56	1.95	5.88	0.839	0.0024	0.020	0.052
		b	980	5.82	83.94	0.62	2.35	5.78	0.826	0.0027	0.024	0.052
		c	1910	5.12	80.47	0.61	3.33	6.09	0.758	0.0028	0.035	0.057
Cutback SRC Product	3296-141	a	750	6.19	91.12	0.05	1.22	1.52	0.809	0.0002	0.011	0.012
		b		5.33	87.45	0.08	1.31	2.24	0.726	0.0003	0.013	0.019
		c		7.29	60.67	0.45	2.30	11.66	1.433	0.0028	0.033	0.144
Synthoil Feedstock	3296-147	a	520	6.04	88.13	0.68	2.11	4.20	0.817	0.0029	0.021	0.036
		b	1060	5.08	86.18	0.60	2.14	4.27	0.702	0.0026	0.021	0.037
		c		6.44	70.96	0.54	3.68	9.81	1.081	0.0028	0.044	0.104
Synthoil Product	3392-65	a	930	6.07	91.36	0.06	1.21	3.47	0.792	0.0002	0.011	0.029
		b	2150	5.28	89.22	0.14	1.35	4.77	0.705	0.0006	0.013	0.040
		c		4.85	50.96	0.26	1.77	14.56	1.134	0.0019	0.030	0.214
H-Coal Hydroclone Underflow Filtrate Feedstock	3296-153	a	430	6.12	84.78	1.08	1.75	5.76	0.860	0.0048	0.018	0.051
		b	780	5.63	81.93	1.17	1.97	5.61	0.819	0.0053	0.021	0.051
		c	1200	5.17	80.90	1.05	2.61	6.94	0.761	0.0049	0.028	0.064
H-Coal Hydroclone Underflow Filtrate Product	3392-67	a	1090	6.49	89.94	0.10	1.24	3.68	0.860	0.0004	0.012	0.031
		b	2820	5.84	85.29	0.16	1.51	3.23	0.816	0.0007	0.015	0.028
		c		5.23	60.07	0.24	3.54	9.01	1.037	0.0015	0.051	0.112
H-Coal Vacuum Bottoms Feedstock	3296-81	a	520	6.47	86.10	0.86	1.35	3.96	0.895	0.0037	0.013	0.034
		b	880	5.75	55.92	1.22	2.06	4.78	0.797	0.0053	0.021	0.042
		c	1210	5.18	79.36	1.05	3.13	5.73	0.779	0.0050	0.034	0.054
H-Coal Vacuum Bottoms Product	3392-57	a	990	5.91	90.95	0.11	1.39	3.69	0.777	0.0005	0.013	0.030
		b	2400	5.40	88.30	0.17	1.70	6.49	0.729	0.0007	0.017	0.055
		c		5.66	58.83	0.09	3.30	9.51	1.146	0.0006	0.045	0.124

Table 52

NMR Data for SARA Separated Pentane Insolubles

Sample Designation	Sample No.	SARA Separated Pentane Insoluble Fractions	Wt-%	Hydrogen Types, %				
				H_γ	H_β	H_α	H_{AR}	H_{AR}/H_{ALK}
SRC/UOP Filtrate Feedstock	3296-19	a	17.0	6	15	35	44	0.79
		b	4.6	7	14	38	41	0.71
		c	4.5	9	16	53	22	0.28
SRC/UOP Filtrate Product	3296-43	a	4.5	8	28	39	35	0.54
		b	0.6	23	26	24	27	0.37
		c	0.4	37	34	26	3	0.03
52.3 Wt-% Botts. of SRC/UOP Filtrate Feedstock	3296-41	a	34.4	6	17	35	42	0.72
		b	11.3	9	18	33	40	0.67
		c	11.1	8	20	37	35	0.54
52.3 Wt-% Botts. of SRC/UOP Filtrate Product	3296-57	a	14.0	9	34	35	22	0.28
		b	1.6	21	41	38	-	-
		c	1.3	15	37	48	-	-
Cutback SRC Feedstock	3296-93	a	39.5	5	17	31	47	0.89
		b	15.8	15	41	20	24	0.32
		c						
Cutback SRC Product	3296-141	a	8.5	7	28	33	32	0.47
		b	0.9	14	48	20	18	0.22
		c	0.1	15	47	26	12	0.14
Synthoil Feedstock	3296-147	a	25.0	12	19	29	40	0.67
		b	3.2	9	45	25	21	0.27
		c	0.3	19	48	26	7	0.08
Synthoil Product	3296-65	a	8.6	5	24	21	42	0.72
		b	1.3	17	39	21	23	0.30
		c						
H-Coal Hydroclone Underflow - Filtrate Feedstock	3296-153	a	23.5	8	20	36	36	0.56
		b	14.2	11	27	31	31	0.45
		c						
H-Coal Hydroclone Underflow - Filtrate Product	3392-67	a	12.8	9	29	34	28	0.39
		b	2.4	11	40	28	21	0.27
		c						
H-Coal Vacuum Bottoms Feedstock	3296-81	a	26.5	7	21	35	37	0.59
		b	13.6	11	28	28	33	0.66
		c						
H-Coal Vacuum Bottoms Product	3392-57	a	21.7	5	20	29	46	0.85
		b	2.1	10	50	15	25	0.33
		c	0.3	19	48	19	14	0.16

Table 53

NMR Data for SARA Separated Aromatic Fractions

Sample Designation	Sample No.	SARA Separated Aromatic Fractions	Wt-%	Hydrogen Types, %				
				H_γ	H_β	H_α	H_{AR}	H_{AR}/H_{ALK}
SRC/UOP Filtrate Feedstock	3296-19	Mono-	0.6	20	56	18	6	0.06
		Di-	31.8	3	12	25	60	1.50
		Poly-	0.9	9	34	31	27	0.43
SRC/UOP Filtrate Product	3296-43	Mono-	18.2	9	45	35	11	0.11
		Di-	35.5	7	24	29	40	0.67
		Poly-	1.4	8	33	37	22	0.28
52.3 Wt-% Botts. of SRC/UOP Filtrate Feedstock	3296-41	Mono-	0.4	17	83	-	-	-
		Di-	15.1	5	16	27	52	1.10
		Poly-	1.1	11	47	27	15	0.18
52.3 Wt-% Botts. of SRC/UOP Filtrate Product	3296-57	Mono-	12.9	19	49	25	2	0.08
		Di-	28.9	7	33	36	24	0.32
		Poly-	1.6	9	36	34	21	0.27
Cutback SRC Feedstock	3296-93	Mono-	0.2	7	93	-	-	-
		Di-	9.8	6	21	23	50	1.00
		Poly-	0.6	14	38	27	21	0.27
Cutback SPC Product	3296-141	Mono-	18.3	18	48	25	9	0.10
		Di-	30.8	11	31	29	29	0.41
		Poly-	4.3	10	31	33	26	0.35
Synthoil Feedstock	3296-147	Mono-	2.6	12	59	24	5	0.05
		Di-	20.6	7	25	35	33	0.50
		Poly-	1.3	9	31	34	26	0.35
Synthoil Product	3392-65	Mono-	16.2	16	49	27	8	0.09
		Di-	31.2	9	29	35	27	0.37
		Poly-	1.5	6	30	40	24	0.32
H-Coal Hydroclone Underflow - Filtrate Feedstock	3296-153	Mono-	8.5	15	43	22	20	0.25
		Di-	15.1	6	20	32	42	0.72
		Poly-	1.5	6	26	36	32	0.47
H-Coal Hydroclone Underflow - Filtrate Product	3392-67	Mono-	20.5	17	49	26	8	0.09
		Di-	31.6	12	33	33	22	0.28
		Poly-	3.4	11	32	37	20	0.25
H-Coal Vacuum Bottoms Feedstock		Mono-	<0.1	20	80	-	-	-
		Di-	2.7	12	34	26	26	0.35
		Poly-	0.3	20	80	-	-	-
H-Coal Vacuum Bottoms Product		Mono-	2.9	15	58	21	6	0.06
		Di-	30.4	6	29	31	34	0.52
		Poly-	3.2	6	29	35	30	0.43

Table 54

High Resolution - High Ionization Voltage (70 ev) MS Saturate Types Analysis of IBP -243°C Fraction of Coal Oils

Sample Designation	SRC/UOP Filtrate		52.3 Wt-% Botts. of SRC/UOP Filtrate	Cutback SRC	Synthoil		H-Coal Hydroclone Underflow Filtrate	H-Coal Vacuum Bottoms
	Feedstock	Product	Product	Product	Feedstock	Product	Product	Product
Sample No.	3296-19	3296-43	3296-57	3296-141	3296-147	3392-65	3292-67	3392-57
IBP -243°C Fraction in Coal Oil, Wt -%	4.8	9.6	3.6	4.8	11.6	8.7	4.4	11.0
Aromatics, Wt-%	98.0	60.0	46.5	50.9	88.8	53.8	53.4	54.0
Saturates, Wt-%	2.0	40.0	53.5	49.1	11.2	46.2	46.4	46.0
Saturate Analysis, Wt-%								
Paraffins	42.5	5.7	-	4.3	28.4	7.7	7.8	13.7
Naphthene Ring								
1	25.0	62.4	63.2	57.8	25.1	50.0	51.4	58.1
2	21.4	30.5	36.0	35.3	27.0	35.2	38.0	25.0
3	8.7	1.4	0.8	2.6	14.7	7.1	2.8	3.2
4	2.4	trace			4.8			
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Table 55
High Resolution - Low Voltage (10 ev) MS Aromatic Type Analysis of IBP -243°C Fraction of Coal Oils

Sample Designation		SRC/UOP Filtrate		52.3 Wt-% Botts. of SRC/UOP Filtrate	Cut-Back SRC	Synthoil		H-Coal Hydroclone Underflow Filtrate	H-Coal Vacuum Bottoms
		Feedstock	Product	Product	Product	Feedstock	Product	Product	Product
Sample No.		3296-19	3296-43	3296-57	3296-141	3296-147	3392-65	3392-67	3392-57
IBP -243°C Fraction in Coal Oil, Wt-%		4.8	9.6	3.6	4.8	11.6	8.7	4.4	11.0
Series	Possible Types								
	Aromatics, Wt-%								
	Aromatic Hydrocarbons								
C_nH_{2n-6}	Benzenes	1.2	5.0	5.9	4.3	1.5	6.0	5.7	11.3
C_nH_{2n-8}	Tetralins & Indans	15.2	44.6	36.3	38.1	18.2	37.2	41.5	24.8
C_nH_{2n-10}	Dihydronaphthalenes	0.8	1.4	1.0	1.8	5.7	2.4	1.3	2.3
C_nH_{2n-12}	Naphthalenes	40.9	2.5	0.7	1.8	12.4	2.1	1.3	9.4
C_nH_{2n-14}	Acenaphthenes	2.6	0.2	trace	0.8	0.7	0.1		0.4
C_nH_{2n-16}	Dihydrophenapthrenes				trace				
	Total	60.7	53.7	43.9	46.8	38.5	47.8	49.8	48.2
	Oxygenated Aromatics								
$C_nH_{2n-6}O$	Phenols	28.5	4.5	1.7	0.1	29.6	1.7	0.8	1.6
$C_nH_{2n-8}O$	Naphthenophenols	1.9	<0.1	0.1		8.6			0.1
$C_nH_{2n-10}O$	Benzofurans	0.8	<0.1	trace	0.1	0.5		trace	0.1
$C_nH_{2n-12}O$	Naphthols					trace			
$C_nH_{2n-14}O$	Naphthenophthols	1.8			0.3	trace			
$C_nH_{2n-16}O$	Dibenzofuran					0.1			
	Total	33.0	4.6	1.8	0.5	38.8	1.7	0.8	1.8
	Nitrogenated Aromatics								
$C_nH_{2n-5}N$	Pyridines	1.4	1.2	0.3	0.8	1.9	1.5	0.8	1.0
$C_nH_{2n-7}N$	Naphthenopyridines	0.2		0.3	0.4	2.6	0.4	0.6	0.6
$C_nH_{2n-9}N$	Indoles	1.4	0.5	0.1	1.6	2.9	2.2	1.2	1.5
$C_nH_{2n-11}N$	Quinolines	0.7		trace	0.8	1.0	0.1	0.2	0.4
$C_nH_{2n-13}N$	Naphthenoquinolines					0.3	0.1		0.5
$C_nH_{2n-15}N$	Carbazoles					trace			
$C_nH_{2n-17}N$	Acridines					0.1			
	Total	3.8	1.7	0.7	3.6	8.8	4.3	2.8	4.0
	Sulfurated Aromatics								
$C_nH_{2n-8}S$	Dihydrobenzothiophenes	trace				1.3			
$C_nH_{2n-10}S$	Benzothiophenes	0.5				1.4			
	Total	0.5				2.7			
	TOTAL	98.0	60.0	46.5	50.9	88.8	53.8	53.4	54.0
	Summary of Averages								
	Average C number	10.1	11.3	10.9	11.2	12.4	11.4	11.4	10.8
	Average Z number (C_nH_{2n-z})	9.2	4.9	4.0	8.1	9.6	8.0	4.5	8.5
	Average Molecular weight	138.5	153.8	149.0	148.7	164	151.6	154.8	142.7

Table 56

High Resolution - High Ionization Voltage (70 ev) MS Analysis of SARA Separated Saturate Fraction

Sample Designation	SRC/UOP Filtrate		52.3 Wt-% Botts. of SRC/UOP Filtrate	43.5 Wt-% Botts. of SRC/UOP Filtrate	Cutback SRC	Synthoil		H-Coal Hydroclone Underflow, Filtrate		H-Coal Vacuum Bottoms
	Feedstock	Product	Feedstock	Feedstock	Product	Feedstock	Product	Feedstock	Product	Product
Sample No.	3296-19	3296-43	3296-41	3296-55	3296-141	3296-147	3392-65	3296-153	3392-67	3392-57
Saturate Fraction in Coal Oil, Wt-%	1.7	5.1	1.0	0.5	3.1	1.1	3.1	1.9	7.3	1.3
Saturate Analysis, Wt-%										
Paraffin	60.9	37.5	44.6	33.0	10.8	55.3	29.9	43.5	20.5	22.4
Naphthene Ring										
1	6.8	18.5	15.6	13.7	17.0	7.9	14.7	9.2	11.9	10.9
2	6.7	14.9	8.6	9.8	28.4	9.9	20.0	13.1	19.3	19.7
3	8.4	14.8	11.0	13.1	25.9	8.2	18.2	9.2	22.4	16.1
4	10.4	12.8	10.4	13.9	14.7	12.0	11.8	15.9	18.5	17.1
5	6.1	1.5	6.5	10.7	3.2	5.5	5.4	7.9	7.4	10.8
6	0.7		3.3	5.8		1.2		1.2		3.0
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Table 57

Ambient Temperature ESR Data for SARA Separated Pentone Insolubles

	SRC/UOP Filtrate						52.3 Wt -% Botts. of SRC/UOP Filtrate					
Sample Designation	Feedstock			Product			Feedstock			Product		
Sample No.	3296-19			3296-43			3296-41			3296-57		
SARA Separated Pentane Insoluble Fraction	a	b	c	a	b	c	a	b	c	a	b	c
Solvent	Benzene	$CHCl_3$	DMF	Benzene	$CHCl_3$	DMF	Benzene	$CHCl_3$	DMF	Benzene	$CHCl_3$	DMF
Wt-%	17.0	4.6	4.5	4.5	0.5	0.4	34.4	11.3	11.1	14.0	1.6	1.3
Peak Height/Gram	11.0	95.4	45.1	83.2	244	165	25.0	56.0	118	50.0	200	100

Table 58

ESR Data for SARA Separated Pentane Insolubles as a Function of Temperature (a)

Sample Designation	Sample No.	SARA Separated Pentane Insoluble Fraction	Temperature, °C 25	100	150	200	250	300	Average Peak Height per 0.1 Gram
			Peak Height per 0.1 Gram						
52.3 Wt-% Botts. of SRC/UOP Filtrate									
Feedstock	3296-41	a		40	70	105	94	55	78
		b		20	50	180	226	185	132
		c		120	340	565	555	500	416
Product	3296-57	a	5	45	40	65	70	65	48
		b	5	45	150	340	430	250	203
		c	35	65	140	370	580	576	294
Synthoil									
Feedstock	3296-147	a	565	626	1,183	1,939	2,099	1,718	1,360
		b	3,647	6,059	6,882	7,058	8,000	7,647	6,550
		c	40,000	55,500	69,000	93,000	128,000	107,000	82,300
Product	3392-65	a	810	1,584	2,095	2,000	2,548	2,405	1,900
		b	3,667	5,333	10,666	7,667	7,833	4,500	6,610
		c	36,000	42,500	48,000	46,500	52,500	37,500	43,800
H-Coal Hydroclone Underflow Filtrate									
Feedstock	3296-153	a	276	529	851	1,149	1,368	1,540	952
		b	745	1,145	1,287	2,253	3,582	3,745	2,130
		c	3,120	4,100	4,180	4,240	5,500	5,420	4,430
Product	3392-67	a	864	1,500	2,136	2,924	3,530	3,439	2,400
		b	6,692	10,000	10,846	10,846	11,538	10,846	10,100
		c	5,000	6,500	13,000	17,000	25,000	22,000	14,800
H-Coal Vacuum Bottoms									
Feedstock	3296-81	a	532	476	1,040	1,889	1,690	1,500	1,190
		b	1,086	1,571	2,743	4,800	5,771	4,314	3,381
		c	3,476	3,537	3,659	2,927	2,561	2,439	3,099
Product	3392-57	a	707	1,060	1,276	1,716	2,216	2,009	1,500
		b	2,636	4,182	5,455	8,000	10,000	9,636	6,650
		c	17,333	29,333	44,667	62,667	69,333	64,000	47,900

(a) Maximum ESR peak is underlined

Table 59

ESR Data for Coal Oils and Associated Upgraded Products as a Function of Temperature[a]

		Temperature, °C						Average Peak
		25	100	150	200	250	300	Height
Sample Designation	Sample No.	Peak Height per Sample						per Sample
SRC/UOP Filtrate								
Feedstock	3296-19	70	430	700	900	1,000	1,020	686
Product	3296-43	8	33	36	41	38	34	32
52.3 Wt-% Botts. of SRC/UOP Filtrate								
Feedstock	3296-41	250	1,120	1,650	1,620	1,430	1,120	1,175
Product	3296-57	24	64	160	360	474	530	270

(a) Maximum ESR peak is underlined

Table 60

Comparison of ESR Data for Coal Oils and Associated Upgraded Products as a Function of Temperature (a)

Sample Designation	Sample No.	Temperature, °C						Average Peak Height per 0.1 Gram
		25	100	150	200	250	300	
		Peak Height per 0.1 Gram						
Cutback SRC								
Feedstock	3296-93	441	975	1,165	1,324	1,374	1,083	1,060
Product	3296-141	220	756	150	215	220	173	189
Synthoil								
Feedstock	3296-147	265	589	719	879	713	504	612
Product	3392-65	289	130	181	223	228	205	209
H-Coal Hydroclone Underflow Filtrate								
Feedstock	3296-153	657	1,352	1,519	1,734	1,706	1,455	1,400
Product	3392-67	87	126	172	207	190	157	156
H-Coal Vacuum Bottoms								
Feedstock	3296-81	3,209	2,438	1,317	1,291	2,164	2,153	2,095
Product	3392-57	157	400	546	600	463	328	416

(a) Maximum ESR peak is underlined.

Table 61
Thermal Analysis of SRC Coal Oils and SARA Separated Pentane Insolubles

Sample Designation	Sample No.	SARA Separated Pentane Insoluble Fraction	Wt-% of Sample	Weight Loss, % in N_2	Weight Loss, % in Air	Weight Loss, % Total	Coke Formed Wt-%	Dry Ash Wt-%	Temperature Range of Weight Loss, °C in N_2	Temperature Range of Weight Loss, °C in Air
SRC/UOP Filtrate Feedstock	3296-19		95.2(a)	86.81	12.56	99.37	12.56	0.64	101-515	582-827
		a	17.0	71.59	27.14	98.73	27.14	1.27	79-714	558-774
		b	4.6	36.51	61.74	98.25	61.74	1.75	132-718	574-776
		c	4.5	35.39	61.67	97.06	61.67	2.94	121-715	364-543
SRC/UOP Filtrate Product	3296-43		90.4(a)	95.63	4.17	99.79	4.17	0.21	93-519	590-754
		a	4.5	50.52	48.38	98.90	48.38	1.10	267-526	480-671
		b	0.6	27.44	63.33	90.77	63.33	9.23	168-569	490-647
		c	0.4	52.42	18.73	71.15	18.73	28.85	184-718	346-476
52.3 Wt-% Botts of SRC/UOP Filtrate Feedstock	3296-41		100	74.37	25.10	99.47	25.10	0.53	139-567	559-814
		a	34.4	70.49	28.13	98.62	28.13	1.38	104-714	438-731
		b	11.3	37.78	60.66	98.44	60.66	1.56	161-716	462-792
		c	11.1	24.00	73.60	97.60	73.60	2.40	192-719	389-658
52.3 Wt-% Botts of SRC/UOP Filtrate Product	3296-57		96.4(a)	92.34	7.49	99.83	7.49	0.17	94-513	578-759
		a	14.0	54.15	45.61	99.76	45.61	0.24	144-713	528-763
		b	11.6	24.43	69.09	93.52	69.09	6.48	188-686	491-728
		c	1.3	70.86	14.42	85.28	14.42	14.72	110-718	378-504
43.5 Wt-% Botts of SRC/UOP Filtrate Feedstock	3296-55		100	70.54	27.85	98.39	27.85	1.61	162-712	561-848
		a	32.5	71.02	24.40	95.42	24.40	4.58	197-492	532-728
		b	12.4	38.01	61.00	99.01	61.00	0.99	78-699	536-809
		c	15.2	22.80	75.54	98.34	75.54	1.66	154-702	386-609
Cutback SRC Feedstock	3296-93		100	70.62	29.33	99.95	29.33	0.05	100-714	452-700
		a	39.5	72.90	26.88	99.78	26.88	0.22	103-722	417-654
		b	15.8	39.52	59.45	98.97	59.45	1.03	110-721	433-733
		c	11.4	22.40	73.42	95.82	73.42	4.18	167-723	332-596
Cutback SRC Product	3296-141		95.2(a)	92.95	7.05	100	7.05	<0.01	102-556	553-838
		a	8.5	50.36	48.39	98.75	48.39	1.25	137-596	577-861
		b	0.9	26.40	68.84	95.24	68.84	4.77	237-733	510-770
		c	0.1	57.54	32.79	90.33	32.79	9.67	174-735	413-533

(a) 243°C + fraction

Table 62

Thermal Analysis of Synthoil Coal Oils and SARA Separated Pentane Insolubles

Sample Designation	Sample No.	SARA Separated Pentane Insoluble Fraction	Wt-%	Weight Loss, % in N_2	Weight Loss, % in Air	Weight Loss, % Total	Coke Formed Wt-%	Dry Ash Wt-%	Temperature Range of Weight Loss, °C in N_2	Temperature Range of Weight Loss, °C in Air
Synthoil Feedstock	3296-147		88.4(a)	85.75	13.77	99.52	13.77	0.48	116-571	555-815
		a	25.0	73.82	26.07	99.89	26.07	0.11	207-547	564-753
		b	3.2	25.01	73.80	98.81	73.80	1.19	202-590	542-768
		c	0.3	57.04	28.15	85.19	28.15	14.81	222-732	418-476
Synthoil Product	3392-65		91.3(a)	93.32	6.42	99.74	6.42	0.26	75-558	553-798
		a	8.6	53.80	44.55	98.35	44.55	1.65	115-579	567-812
		b	1.3	24.11	75.50	99.61	75.50	0.39	197-709	556-757
		c	0.3	59.75	27.00	86.75	27.00	13.25	104-638	392-480

(a) 243° C + fraction

Table 63

Thermal Analysis of H-Coal Oils and SARA Separated Pentane Insolubles

Sample Designation	Sample No.	SARA Separated Pentane Insoluble Fraction	Wt-%	Weight Loss, %			Coke Formed Wt-%	Dry Ash Wt-%	Temperature Range of Weight Loss, °C	
				in N_2	in Air	Total			in N_2	in Air
H-Coal Hydroclone			100	72.67	26.55	99.22	26.55	0.78	56-636	492-769
Underflow Filtrate	3296-153	a	23.5	67.99	31.65	99.64	31.65	0.36	102-726	531-794
Feedstock		b	14.2	40.03	57.84	97.87	57.84	2.13	160-731	492-836
		c	12.8	27.94	70.18	98.12	70.18	1.88	214-729	393-647
H-Coal Hydroclone			95.6(a)	92.19	7.75	99.94	7.75	0.06	74-556	558-773
Underflow Filtrate	3392-67	a	12.8	48.34	51.17	99.51	51.17	0.49	126-732	518-795
Product		b	2.4	30.55	67.76	98.31	67.76	1.69	127-729	503-772
		c	0.3	54.31	34.74	89.05	34.74	10.95	154-603	347-476
H-Coal Vacuum Bottoms			100	39.99	40.52	80.51	40.52	19.49	222-734	464-783
Feedstock	3296-81	a	26.5	74.26	24.37	98.63	24.37	1.38	106-733	532-764
		b	13.6	43.21	54.95	98.16	54.95	1.84	102-733	522-783
		c	11.7	28.11	66.96	95.07	66.96	4.93	176-737	384-612
H-Coal Vacuum Bottoms			89.0(a)	86.88	12.32	99.20	12.32	0.80	100-560	550-754
Products	3392-57	a	21.7	56.95	41.77	98.72	41.77	1.28	121-581	571-802
		b	2.1	24.68	74.99	99.67	74.99	0.33	129-733	504-767
		c	0.3	52.62	42.87	95.49	42.87	4.51	149-736	381-530

(a) 243°C + fraction

Table 64

Comparison of Thermal Analysis and ESR Data for Coal Oils

Sample Designation	Sample No.	Wt-%	Maximum ESR Response (b)	Coke Formed Wt-%	Dry Ash Wt-%
Cutback SRC Feedstock	3296-93	100.0	1,374	29.33	0.05
Cutback SRC Product	3296-141	95.2 (a)	220	7.05	<0.01
Synthoil Feedstock	3296-147	88.4 (a)	879	13.77	0.48
Synthoil Product	3296-65	91.3 (a)	228	6.42	0.26
H-Coal Hydroclone Underflow Filtrate Feedstock	3296-153	100.0	1,734	26.55	0.78
H-Coal Hydroclone Underflow Filtrate Product	3392-67	95.6 (a)	201	7.75	0.06
H-Coal Vacuum Bottoms Feedstock	3296-81	100.0	3,209	54.95	19.49
H-Coal Vacuum Bottoms Product	3392-57	89.0 (a)	600	12.32	0.80

(a) 243°C + fraction

(b) See Tables 59 and 60

Table 65

Metal Contents of SRC Samples from Membrane Filtration

Sample Designation	SRC/UOP Filtrate Feedstock		30 Wt-% Botts. of SRC Filtrate Feedstock		SRC Feedstock		Cutback SRC Product	
Sample No.	3296-19		3296-155		3392-1		3296-141	
Fraction	Filtrate	Filter Cake	Filtrate	Filter Cake	Filtrate	Filter Cake	Filtrate	Filter Cake
Particulates(a), Wt-%		0.01		0.07		0.15		0.02
Wt-% of SRC		0.03		0.13		0.16		
Metals by AAS, Wt. ppm								
Fe	1.8	13.5	66	10	93	116	4.8	12
Ti	34	<5	103	≤1	118	<2	16	<0.5
Al	5	2	10	3	25	23	≤2	23
Ca	0.5	1.3	14	1.4	32	72	≤0.1	18
Mg	0.4	0.8	8	0.3	1.7	2.9	≤0.08	1.7
Na	0.08	<0.03	10	5.4	6.9	7.6	0.6	1.2
Si	8.8	≤23	25	2.6	3.6	≤15	<0.2	≤5
SiO_2(b)	--	--	--	--	--	72	--	≤100

(a) Insoluble mineral matter and unconverted coal

(b) Silica which was not dissolved by wet digestion, estimated gravimatrically

Table 66

Metal Contents of Synthoil Samples from Membrane Filtration

Sample Designation	Synthoil Feedstock		Synthoil Product	
Sample No.	3296-147		3392-65	
Fraction	Filtrate	Filter Cake	Filtrate	Filter Cake
Particulates [(a)], Wt-%		0.16		0.17
Metals by AAS, Wt. ppm				
Fe	4.8	12	0.5	<0.1
Ti	16	<0.5	<2	0.5
Al	≤2	23	≤2	0.3
Ca	<0.1	18	<0.7	0.02
Mg	<0.08	1.7	0.04	<0.005
Na	0.6	1.2	0.9	0.4
Si	≤0.2	≤5	≤1	6
SiO_2 [(b)]	---	≤100	---	---

(a) Insoluble mineral matter and unconverted coal

(b) Silica which was not dissolved by wet digestion, estimeated gravimetrically

Table 67

Metal Contents of H-Coal Samples from Membrane Filtration

	H-Coal Hydroclone Underflow Filtrate				H-Coal Vacuum Bottoms			
	Feedstock		Product		Feedstock		Product	
Sample No.	3296-153		3392-67		3296-81		3392-57	
Fraction	Filtrate	Filter Cake	Filtrate	Filter Cake	Filtrate	Filter Cake	Filtrate	Filter Cake
Particulates (a), Wt-%		0.03		0.01		30.2		0.01
Metals by AAS, Wt. ppm								
Fe	208	6	0.4	4.1	279	2.2Wt-%	20	1.3
Ti	164	2	6	1	147	390	≤2	≤0.5
Al	52	2.8	≤2	2.4	87	1.13Wt-%	≤2	≤0.5
Ca	40	2.2	0.8	0.6	216	>900	<0.08	0.5
Mg	14	0.2	0.2	<0.005	16	900	<0.02	<0.005
Na	4	0.6	0.1	<0.1	51	79	0.5	<0.1
Si	24	6.4	≤1	12	19	1770	7	≤0.5
SiO_2(b)	---	---	---	---	---	10.47Wt-%	---	---

(a) Insoluble mineral matter and unconverted coal

(b) Silica which was not dissolved by wet digestion, estimated gravimetrically

FIGURE 1

UOP CORPORATE RESEARCH PLANT 505 SHOWING FEED SYSTEM AND FURNACE

FIGURE 2

HYDROTREATING PLANT

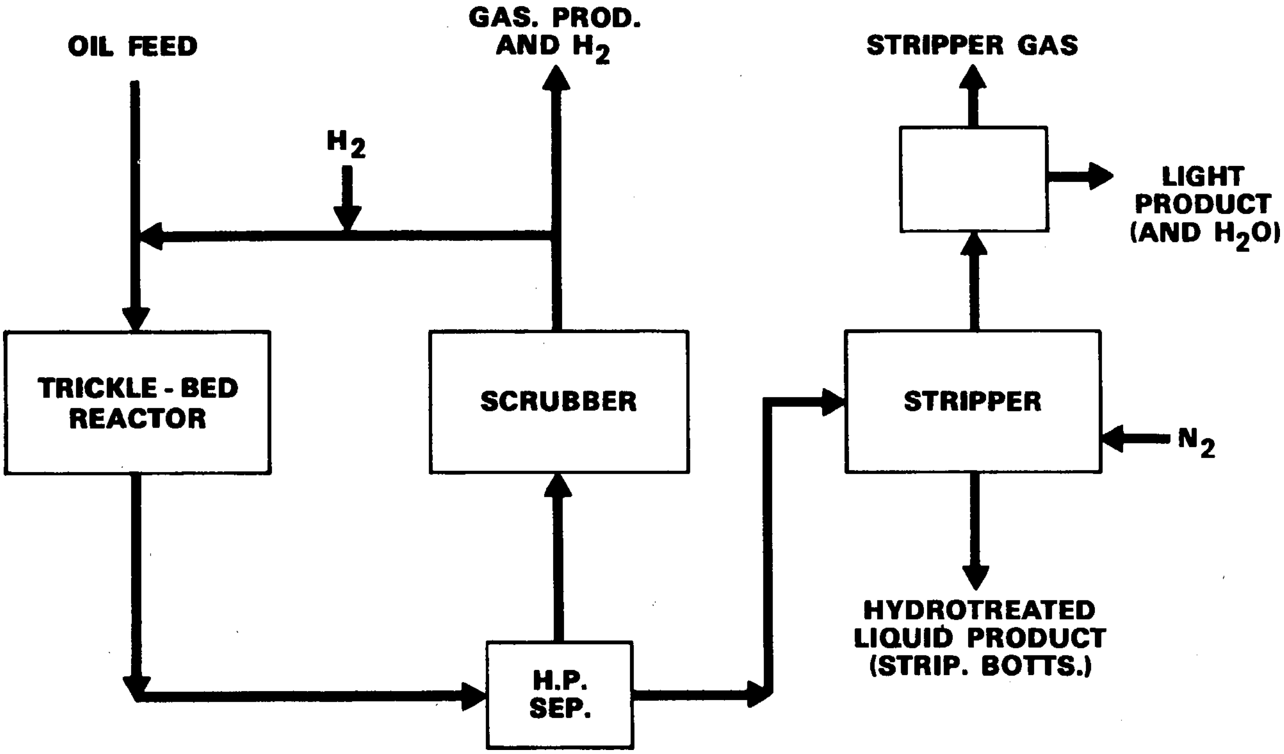


FIGURE 3

PLANT 505 REVISED FEED SYSTEM

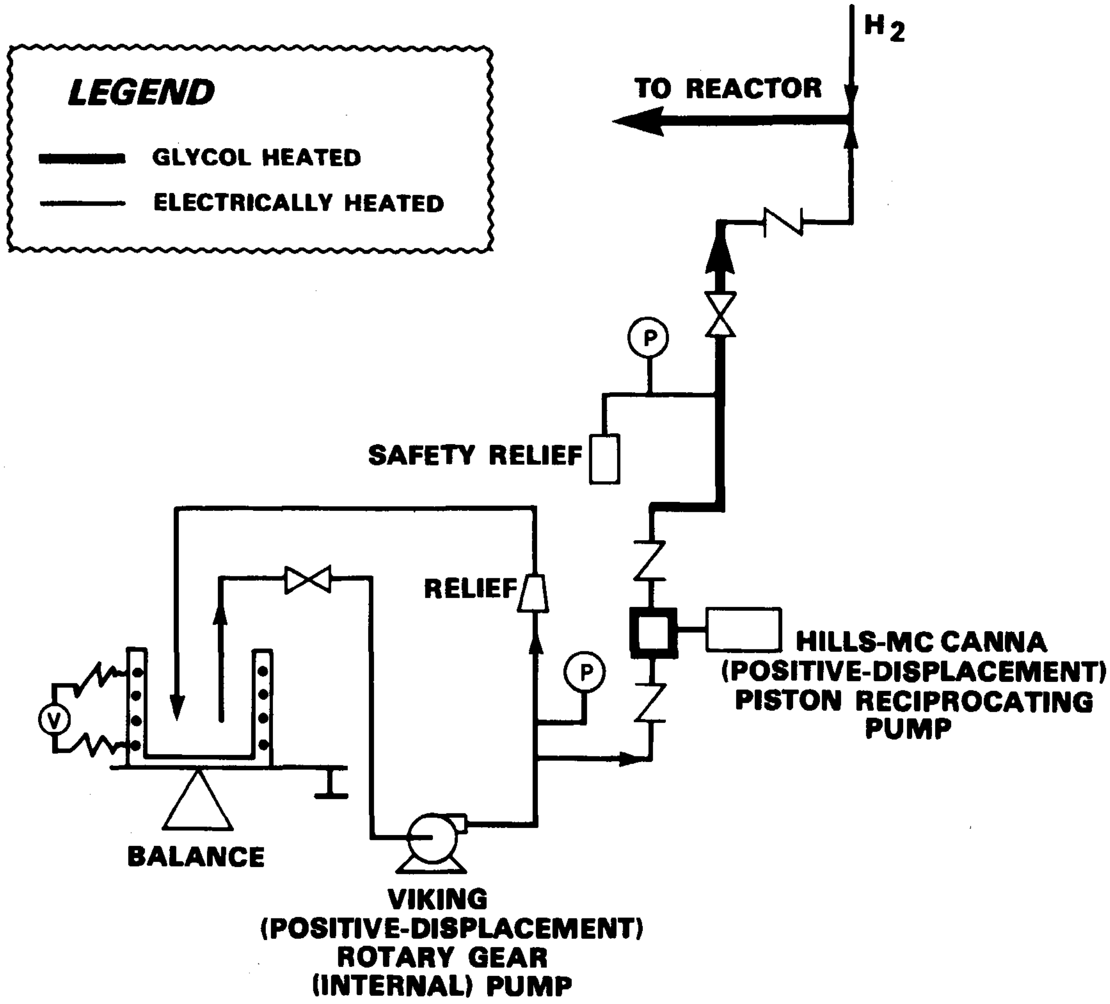


FIGURE 4

COMPARISON OF CONVERSION OF C_7 INSOLUBLES IN SRC AND SYNTHOIL DERIVED STOCKS

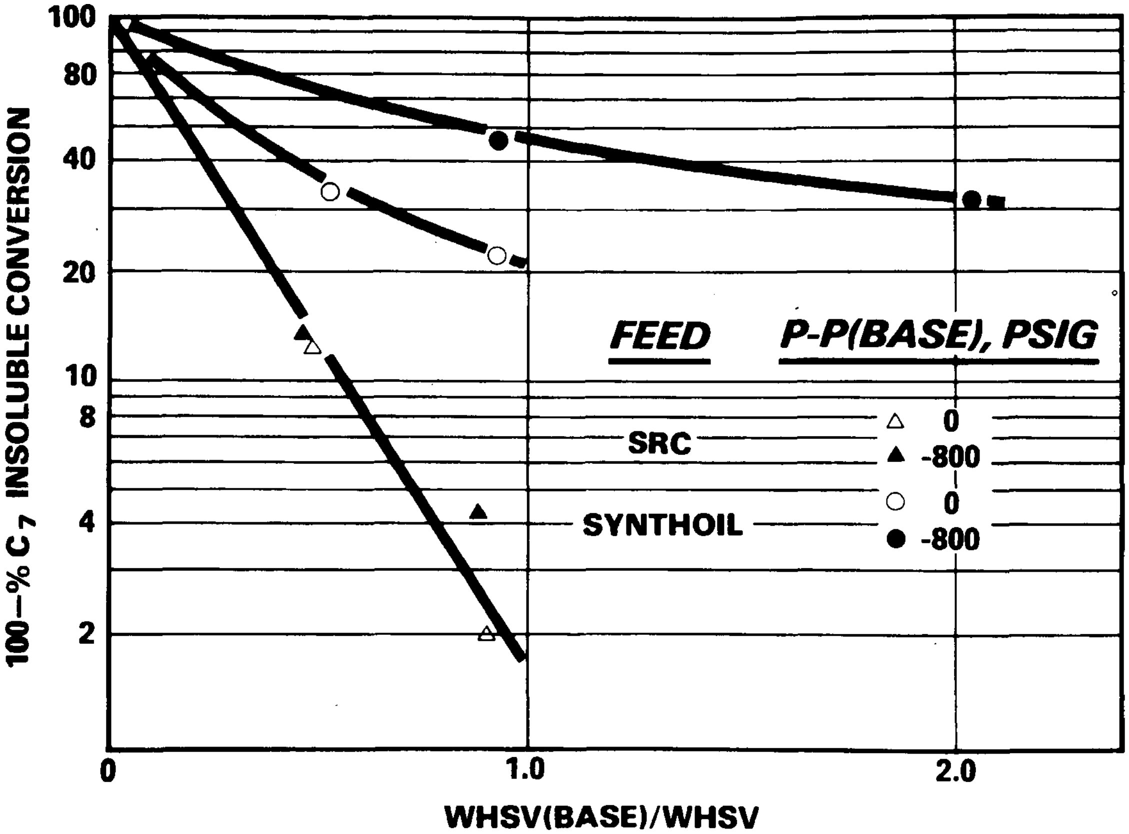


FIGURE 5

RESIDUAL C_7 INSOLUBLES VS. TIME

(PLANT 638H, RUN 3)

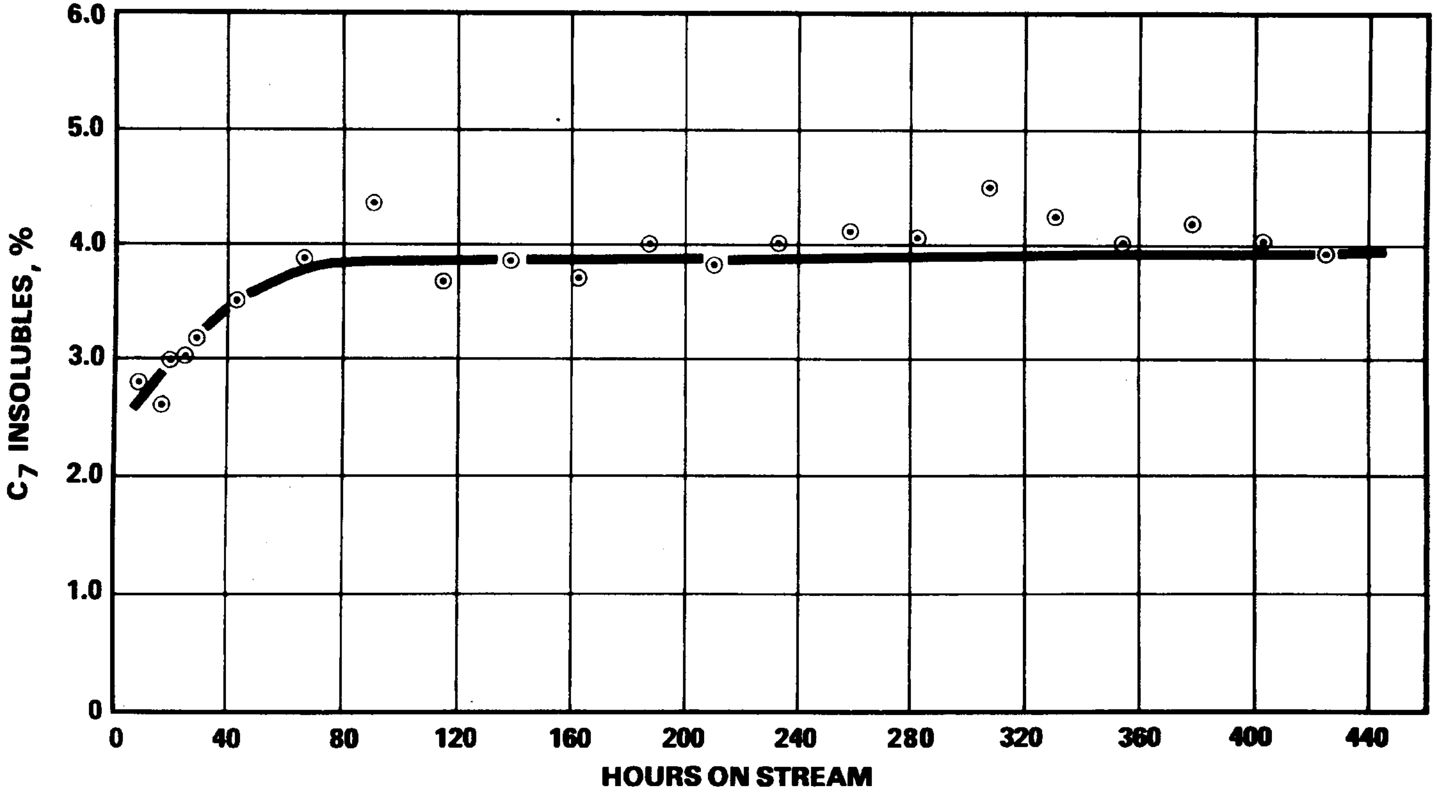


FIGURE 6

RESIDUAL C_7 INSOLUBLES VS. TIME

(Plant 638H, Run 4)

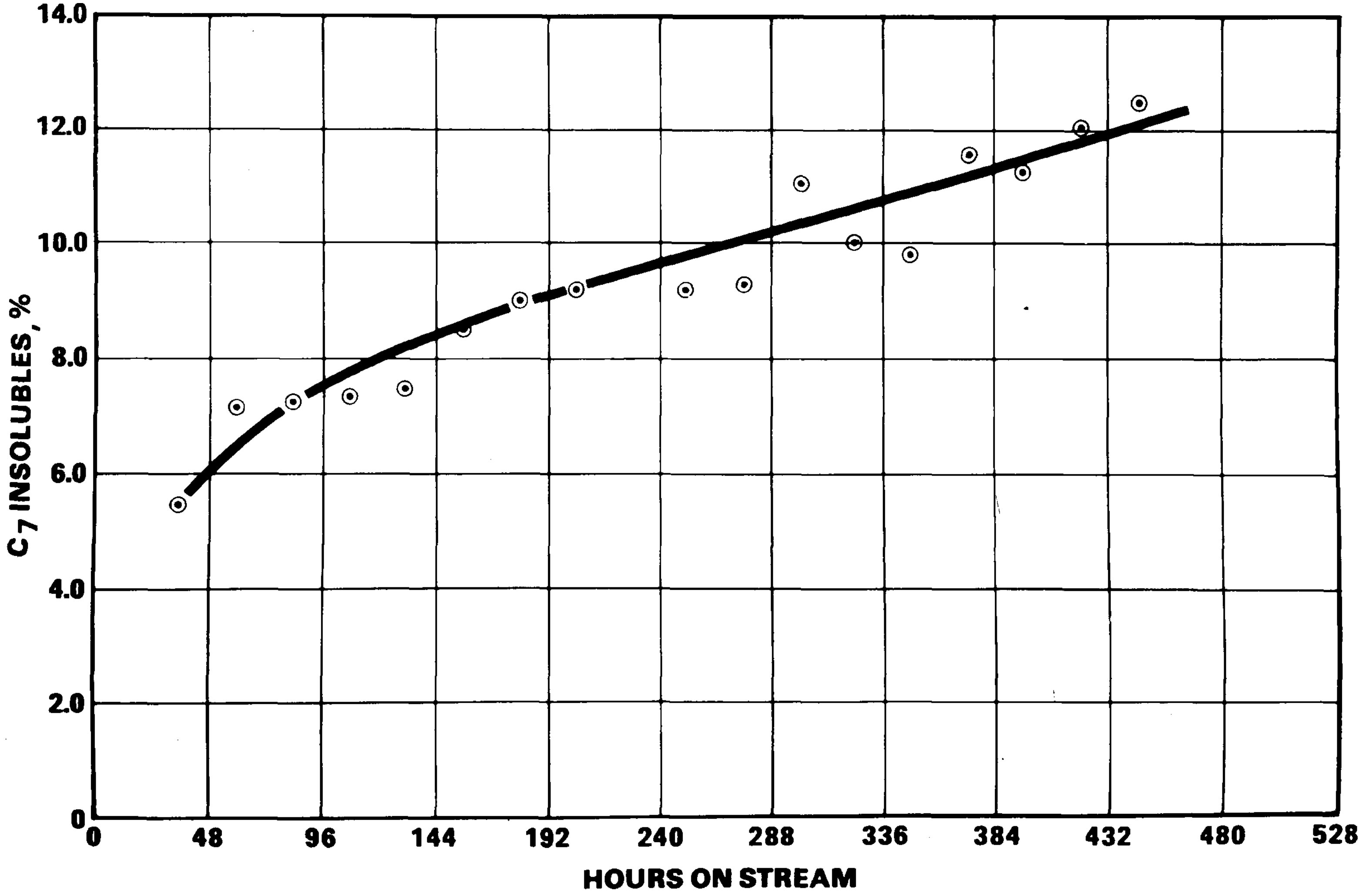


FIGURE 7

PRESSURE FILTRATION APPARATUS

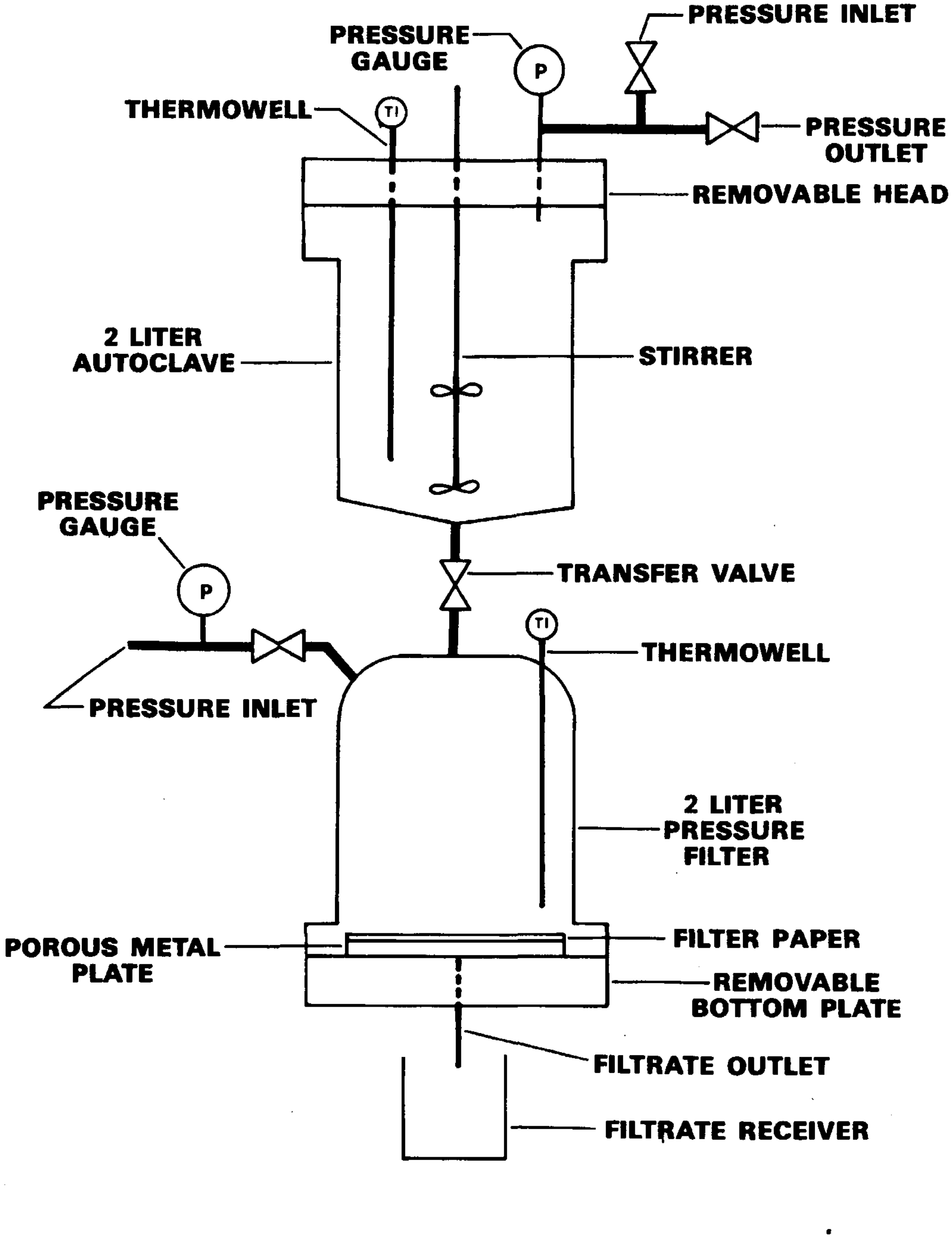


FIGURE 8

MODIFIED SARA SEPARATION SCHEME

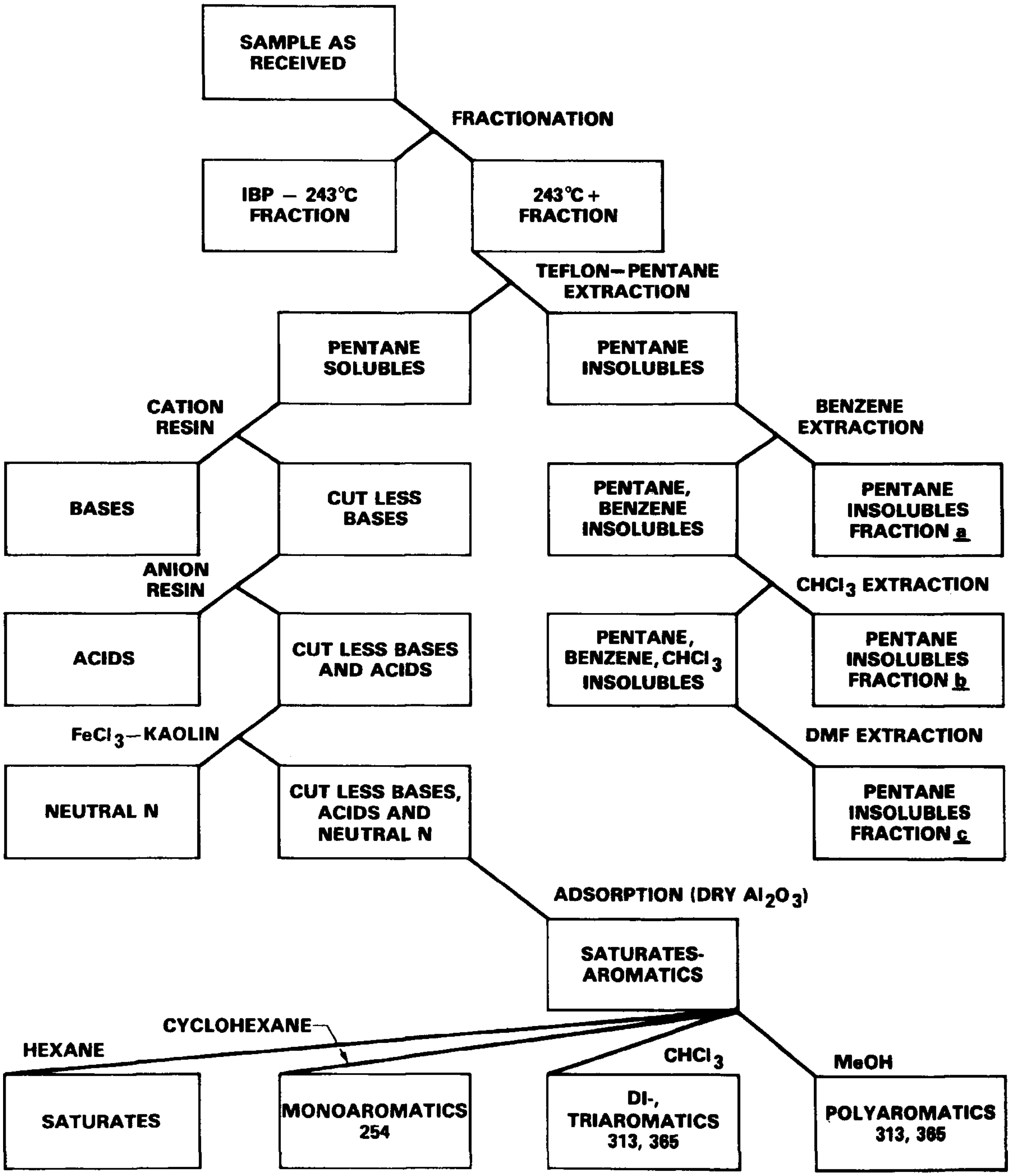
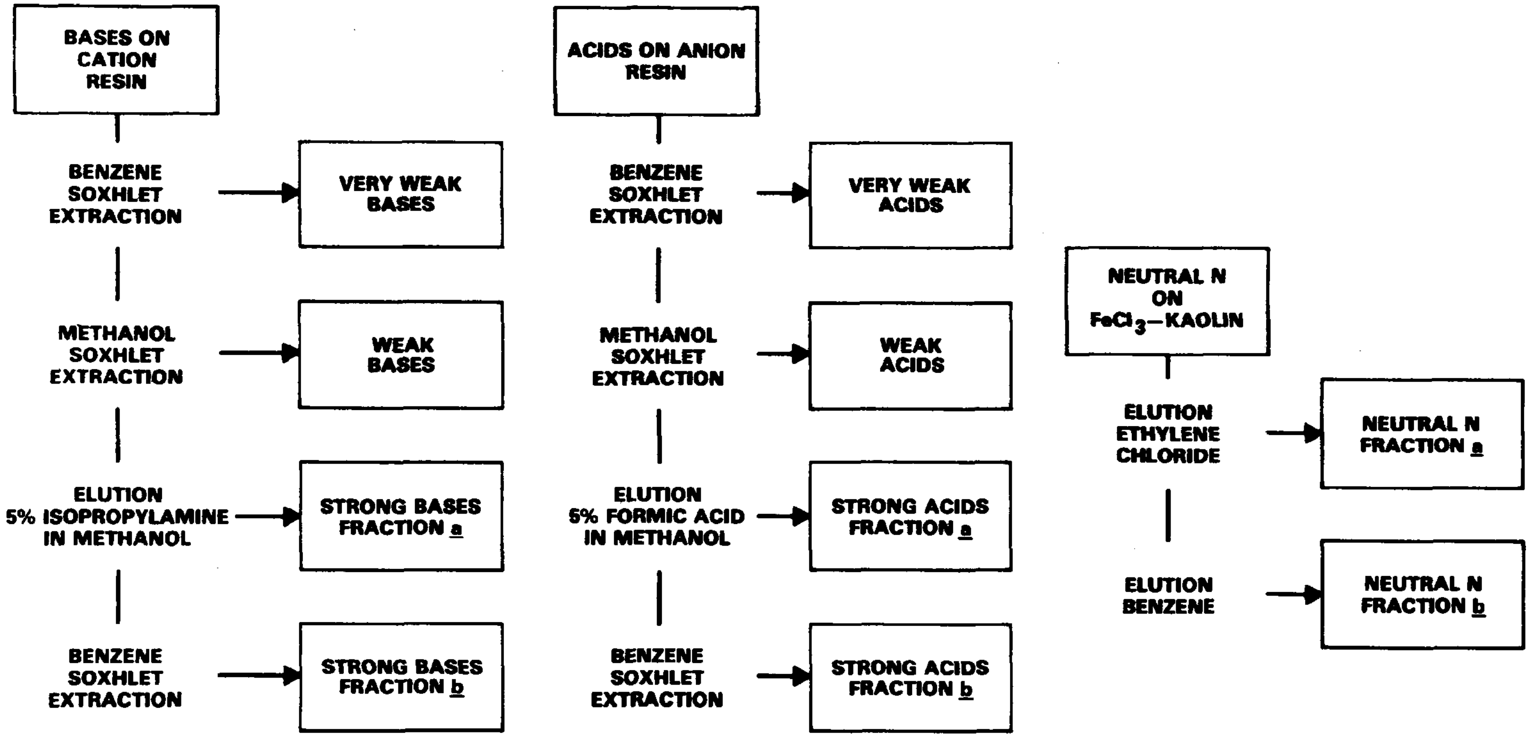


FIGURE 9

RECOVERY SCHEME OF BASES, ACIDS, AND NEUTRAL NITROGEN



A. APPENDIX

A. 1. Modified SARA (Saturates, Aromatics, Resins and Asphaltenes) Separation of Coal Oils

A.1.1. Apparatus

Resin and Pentane Insoluble Removal

Evaporating dish, porcelain No. 14.

Extraction thimble, 33 x 80 mm, double thick, Sargent-Welch S-31665, Size B.

Extraction thimble, 68 x 180 mm., Sargent-Welch S-31655, Size I.

Extraction thimble, 84 x 330 mm, Schleicher and Schuell.

Filter paper, glass fiber 18.5 cm, Reeve-Angel No. 934 AH.

Funnel, Buchner, Coors porcelain No. 5A

Funnel for 60 x 180 mm extraction thimble (see Figure A1).

Recycle Column (see Figure A2).

Soxhlet extraction assembly from Sargent-Welch S-31265 No. C., to hold 33 x 80 mm extraction thimbles.

Soxhlet extraction assembly from Sargent-Welch S-31265 No. D to hold 60 x 180 mm extraction thimbles

Soxhlet extraction assembly similar to Sargent-Welch S-31340 modified to hold 84 x 330 mm Schleicher and Schuell extraction thimbles.

Saturates - Aromatics Separation (See Figure A3).

Column, stainless steel, 1/2" OD x 1 meter wrapped with heating tape for heating the column to 300°C.

Detectors, Altex 150 UV monitor with 254, 313 and 365 nm filters.

End fitting 1/2" x 1/16" with 5 micron sintered metal filter.

Heat controller for column heater.

Magnetic bar, 1-in.

Magnetic stirrer.

Precolumn, Laboratory Data Control, LC 1/2-13.

Pumps, Milton Roy mini pumps 396-89, 460 ml/hr.

Recorder, Dual Strip Chart.

Teflon tubing 1/16", 1/8" along with coupling from Laboratory Data Control.

Valve, 6 port injection from Waters C906 No. 26930 with 5 ml injection loops No. 79417.

DMF Extraction (See Figure A4). Extraction glass vessel is made from a 2-ℓ Erlenmeyer flask. Top of the Erlenmeyer is adapted to fit copper disc-cover of condenser (standard, modified ASTM D 473), which is a coiled block of tin tubing suspended from copper disc-cover, depressed to fit over tubular top of the extraction vessel. Thimble basket is made of stainless steel or nickel chromium alloy to hold extraction thimble suspended by nichrome wire (20-30 gauge) from condenser.

Source of heat is safety-approved electrical heating plate or cylindrical heating mantle controlled by Variac to heat metal beaker with small layer of sand.

A.1.2. Reagents

Resins and Pentane Insoluble Removal

Benzene, reagent grade.

Chloroform, reagent grade.

Chromosorb W, non-acid washed 60180.

N,N-Dimethylformamide (DMF) distilled to obtain 10-90% heart cut.

Ethylene chloride, 1,2-dichloroethane.

Ferric chloride hexahydrate.

Fluoropak 80, 60/80 mesh.

Formic acid, 88 percent.

Hydrochloric acid.

Ion exchange resins.
  Anion resin, Amberlite IRA904.
  Cation resin, Amberlyst 15.

Isopropyl amine.

Kaolin, N.F. Baker 2242.

Methyl alcohol, reagent grade.

n-Pentane, reagent grade.

Potassium hydroxide.

Saturate - Aromatic Separation

Alumina, Activated, F-20, 80-200 mesh.

Benzene, reagent grade.

Chloroform, reagent grade.

Cyclohexane, Burdick and Jackson, distilled in glass.

Hexaethyl benzene.

n-Hexane, UV grade Burdick and Jackson, distilled in glass.

Methyl alcohol, reagent grade.

1,3,5-trisopropyl benzene.

ESR Temperature Characterization Solvent. Distill a 314-369°C cut from SRC/UOP Filtrate, or similar cut from a coal oil, and store under N_2.

A.1.3. Preparation of Column Packings

Anion Exchange Resin, Amberlite IRA904. Wash approximately 1400 ml of Amberlite IRA904 resin four times with 10 volume percent aqueous HCl in methyl alcohol, and then rinse with deionized water until the washings are neutral to litmus paper. Activate the resin with 10 percent potassium hydroxide in methyl alcohol. Filter on the glass fiber filter paper. Wash with deionized water until the washings are neutral to litmus. Transfer the resin into a 84 x 330 extraction thimble and Soxhlet extract 24 hours with each of the following: Methyl alcohol, benzene and finally with n-Pentane. Dry the resin at 40°C in a vacuum oven for 24 hours.

Cation Exchange Resin, Amberlyst 15. Wash approximately 750 ml of Amberlyst 15 resin four times with a 10 wt-% potassium hydroxide in methyl alcohol. (Caution: Exothermic reaction; add the resin slowly to the caustic solution with constant stirring). Rinse the resin with methyl alcohol.

Transfer the resin into a 84 x 330 mm extraction thimble and Soxhlet extract the resin for eight hours with methyl alcohol. Activate the resin by adding it slowly to a 10 vol-% aqueous HCl in methyl alcohol, with constant stirring. Wash the resin with deionized water until the washings are neutral to litmus paper. Transfer the resin into a 84 x 330 mm extractor thimble and 24 hour Soxhlet extract with methyl alcohol, benzene, and finally with pentane. Dry the resin at 40°C in a vacuum oven for 24 hours.

Ferric Chloride on Kaolin-Chromosorb W. Mix 150 g of Chromosorb W 60/80 mesh non-acid washed with 300 g of kaolin. Dissolve 150 g of ferric chloride hexahydrate in 1130 ml of methyl alcohol. Add the Chromosorb W-Kaolin to the methyl alcohol solution. Keep the adsorbent in contact with the solution for one hour. Filter the packing on the glass fiber filter paper. Wash the coated adsorbent several times with pentane. Transfer the packing into a 84 x 330 mm extraction thimble. Soxhlet extract the packing with pentane overnight. Remove the packing from the thimble, and allow it to air dry.

Alumina, Zero Percent Water. Charge about 480-490 ml of weighed F-20 alumina to the Pyrex furnace tube of vertical hinged furnace. Position the furnace tube in a vertical position. Wipe out alumina clinging to the surface of the tube down to the top of the furnace. Seal the space between the tube and the top and bottom of the furnace with glass wool. Purge the alumina with a downward flow of nitrogen at a flow rate of approximately 50 liters per hour. Gradually bring the temperature of the furnace up to 400°C and maintain it at this temperature overnight. Shut off nitrogen. Connect the bottom of the furnace tube to a vacuum pump through a safety, cyclone-type dry ice trap, and turn the vacuum pump on. Continue vacuum for 24 hours. Shut off heat. Seal off vacuum pump and disconnect. Cautiously bleed dry nitrogen into the top of the tube. When the pressure reaches one atmosphere, open the bottom of the tube and continue purging the alumina with dry nitrogen while it cools. Reverse the dry nitrogen flow from the top to the bottom of the tube. Clean the top of the tube. Transfer the dried alumina into two dried and tared 8-ounce bottles. Reweigh the filled bottles.

Pack the separation column with freshly dried alumina. Purge the column with nitrogen and heat the column at 300°C overnight. Turn off the heat the following morning, and continue the nitrogen purge until the column has reached room temperature. Fill the precolumn with the dried alumina.

A.1.4. Separation Procedure

Separate the coal oil using the general outlines provided in Figures 8 and 9.

Top the sample at 243°C using a vacuum distillation. Prepare a homogeneous blend of the 243°C plus bottoms.

Pentane Extraction. Dissolve 5 g, weighed to 0.1 mg, of the bottoms sample in chloroform. Place the dissolved sample in the evaporating dish, and add 15 grams of Fluoropak 80. Evaporate the chloroform using a nitrogen purge, until dry. Evaporation time may be reduced by warming the evaporating dish on a steam bath. Transfer the dried coated Fluoropak 80 to the 33 x 80 mm double thick extraction thimble. Dissolve any chloroform-soluble residue remaining in the evaporating dish with chloroform. Add 7 g of Fluoropak 80 and again strip the chloroform from the adsorbent. Transfer this dried coated Fluoropak to the same thimble and plug the top of the thimble with glass wool. Strip any residual solvent by drying the filled thimble in a vacuum oven at 50°C for two hours.

Dissolve any chloroform-insoluble material remaining in the evaporating dish with dimethylformamide, DMF, and save it to combine with the extract from the DMF extraction of the thimble later. Filter before combining to remove any Fluoropak 80.

Place the filled thimble in the Size C Soxhlet extractor. Add approximately 350 ml of pentane to the 500-ml extraction flask that contains several boiling chips.

Fill the recycle column, Figure A2, with the activated cation resin, Amberlyst 15. Rinse the packing with approximately 500 ml of pentane and discard. Add fresh pentane to the column until the resin is just covered.

Start the pentane Soxhlet extraction of the sample. When the extract has good color, transfer the extract to the top of the recycle column packed with the pentane-wetted Amberlyst 15 cation exchange resin. Pass the pentane extract through the resin bed making sure that the resin is always wetted by the pentane. Continue the Soxhlet extraction of the sample in the thimble with fresh pentane, periodically transferring the pentane extract to the top of the cation exchange resin column.

Continue the Soxhlet extraction of the sample for 24 hours. Any material that drops out of solution should not be transferred to the cation exchange resin bed, but should be dissolved in benzene, and later be included with the benzene-soluble, pentane-insoluble fraction.

Transfer the final pentane extract from the thimble containing the sample onto the top of the cation exchange resin column and recycle pentane through the column until the effluent is colorless.

Procedures for basic components retained on this column and for the column effluent are described in later sections.

Recovery of the Benzene-Soluble, Pentane-Insoluble Fraction. Add approximately 350 ml of benzene to the 500 ml Soxhlet extraction flask. Soxhlet extract the pentane-insoluble portion of the original sample remaining on the Fluoropak 80 for at least 24 hours or until the extract is colorless.

Transfer the benzene extract and the benzene solution of pentane-insoluble material (above) into a 500 ml volumetric flask, cool and dilute to the mark at ambient temperature. Withdraw a suitable aliquot for ESR temperature characterization.

Transfer the remainder of the extract, in portions to a tared 200-ml round-bottom flask and strip the solvent on a steam bath using a nitrogen purge. Rinse the volumetric flask with benzene and add this to the sample. Complete the solvent stripping on a rotary flash evaporator at 20 torr and 95°C with a nitrogen purge. Weigh.

Calculate the weight present in the total 500 ml and the weight percent benzene-soluble pentane-insoluble fraction of the original 5 grams.

Benzene-Soluble, Pentane-Insoluble Sample for ESR Temperature Characterization. Add 2 grams of the ESR temperature characterization solvent to a tared 100 ml round bottom flask. Quantitatively transfer the aliquot (10 ml) withdrawn for ESR temperature characterization. Solubilize sample. Strip benzene solvent on a rotary flash evaporator at 20 torr and 95%°C with a nitrogen purge. Weigh.

Calculate the weight percent benzene-solubles pentane-insoluble in the sample from the weight of benzene-solubles pentane-insolubles contained in the aliquot and the weight of the ESR temperature characterization sample.

Recovery of the Chloroform-Soluble, Benzene and Pentane-Insoluble Fraction. Add approximately 350 ml of chloroform to the 500 ml extraction flask. Soxhlet extract the thimble containing the benzene-pentane insoluble portion of the sample for at least 24 hours, or until the extract is colorless.

Transfer the extract into a 500 ml volumetric flask. Cool and dilute to the mark at ambient temperature. Withdraw a suitable aliquot for the ESR temperature characterization.

Transfer the remaining chloroform-soluble sample into a tared 100 ml round bottom flask and strip the solvent on a steam bath using a nitrogen purge. Complete the stripping on a rotary flash evaporator at 20 torr and 95°C using a nitrogen purge. Weigh.

Dissolve any chloroform-insoluble residue that remains in the extraction flask or volumetric flask, in DMF and save it to combine with the DMF extraction solution later.

Calculate the weight present in the total 500 ml of solution and the weight percent chloroform-soluble, pentane and benzene-insoluble fraction of the original 5 grams.

Chloroform-Soluble, Benzene-, and Pentane-Insoluble Sample for ESR Temperature Characterization. Follow the preceding procedure for benzene-soluble pentane-insoluble sample for ESR temperature characterization, using 10 ml aliquot of chloroform extract.

Recovery of DMF-Soluble, Chloroform-, Benzene-, and Pentane-Insoluble Fraction. Vacuum dry the extraction thimble, after the chloroform Soxhlet extraction, for two hours at 50°C, flushing the oven chamber intermittently with nitrogen.

Soxhlet extract the thimble with benzene for approximately two hours, discard the benzene. Vacuum dry the thimble at 50°C for two hours, intermittently flushing the oven chamber with nitrogen.

Extract the thimble with 200 ml of DMF for six hours using a 2-liter modified vapor phase Soxhlet extractor. (See Figure A4). Remove the DMF extract and extract the thimble again with fresh DMF for 18 hours. Combine the DMF extracts, including the DMF solutions of chloroform-insoluble residues retained previously, and dilute to 500 ml at ambient temperature. Withdraw a suitable aliquot for ESR temperature characterization.

Transfer the remainder of the DMF extract to a tared 200-ml round bottom flask. Strip the solvent at 20 torr and 95°C using a nitrogen purge. Wash the DMF residue three times with 50 ml of hot water. Filter the residue using Whatman 42 (12.5 cm) filter paper. Wash the DMF-soluble, water insoluble residue into the tared flask with water. Flash off the water using a rotary flash evaporator at 20 torr and 95°C using a nitrogen purge. Weigh.

Calculate the weight of DMF-soluble, water-insoluble residue present in the total 500 ml and the weight percent of the DMF-soluble fraction.

DMF-Soluble, Chloroform-, Benzene-, and Pentane-Insoluble Sample for ESR Temperature Characterization. Follow the preceding procedure for benzene-soluble, pentane-insoluble sample for ESR temperature characterization, using 10 ml aliquot of DMF extract.

Basic Components Removal From Pentane Solubles. After the pentane has completely extracted the soluble portion of the original sample, pass the final pentane extract over the Amberlyst 15 resin column and recycle the pentane until the effluent is colorless.

Transfer the resin from the recycle column into a 50 x 180 mm extraction thimble. Place the thimble into a No. D Soxhlet extractor. Soxhlet extract with pentane until the extract is colorless. Combine the pentane extract from the cation exchange resin recycle with the pentane Soxhlet extract. Retain the extract for acid removal.

Recovery of Benzene-Soluble Bases, Very Weak Bases. Soxhlet extract the Amberlyst 15 resin with benzene for 8 hours, or until the extract is colorless. Strip the benzene to dryness on a steam bath using a nitrogen purge. Redissolve the residue in benzene and filter through Whatman 42 (12.5 cm) filter paper into a tared 100-ml round bottom flask. Wash the filter paper and residue containers with benzene to quantitatively transfer the sample into the tared flask. Discard any undissolved residue. Strip the solvent on a steam bath using a nitrogen purge. Finish stripping the solvent on a rotary flash evaporator at 20 torr and 95°C using a nitrogen purge. Weigh.

Determine the weight percent benzene-soluble bases, very weak bases.

Recovery of Methyl Alcohol-Soluble Bases, Weak Bases. Soxhlet extract the Amberlyst 15 resin with methyl alcohol for 8 hours or until the effluent is colorless. Strip the solvent to dryness on a steam bath using a nitrogen purge. Redissolve the residue in benzene and filter through Whatman 42 (12.5 cm) filter paper into a tared 100-ml round bottom flask. Wash the filter paper and residue container with benzene to quantitatively transfer the sample to the tared flask. Discard any undissolved residue. Strip off the solvent on a steam bath using a nitrogen purge. Finish stripping on a rotary flash evaporator at 20 torr and 95°C with nitrogen stripping.

Weigh the dried residue, and determine the weight percent methyl alcohol soluble bases, weak bases.

Recovery of Strong Bases, Fraction a Soluble in 5 Percent Isopropylamine-Methyl Alcohol. Transfer the Amberlyst 15 resin thimble into the 60x180 mm extraction thimble funnel. (See Figure A1). Pass 5 percent isopropylamine in methyl alcohol through the resin until the effluent is basic to litmus paper and the effluent is colorless. Strip the solvent on a steam bath using a nitrogen purge. Redissolve the residue in benzene and filter through Whatman 42 (12.5 cm) filter paper into a tared 100-ml round bottom flask. Wash the filter paper and residue container with benzene to quantitatively transfer the sample into the tared flask. Discard any undissolved residue. Strip the solvent on a steam bath using a nitrogen purge. Finish stripping the solvent on a rotary flash evaporator at 20 torr and 95°C with nitrogen stripping.

Determine the weight percent strong bases, Fraction a soluble in isopropylamine in methyl alcohol.

Recovery of Strong Bases, Fraction b from Second Benzene Extraction of Amberlyst 15 Resin. Replace the thimble in the Soxhlet extractor. Soxhlet extract the thimble with benzene for 8 hours, or until the effluent is colorless. Strip the benzene on a steam bath with a nitrogen purge to dryness. Redissolve the residue in benzene, and filter through Whatman 42 (12.5 cm) filter paper into a tared 100-ml round bottom flask. Wash the filter paper and the residue container with benzene to quantitatively transfer the sample to the tared flask. Discard anyundissolved residue. Strip off the solvent on a steam bath using a nitrogen purge. Finish stripping on a rotary flash evaporator at 20 torr and 95°C with nitrogen stripping.

Determine the weight residue present in the benzene, and calculate the second weight percentage of benzene soluble bases, strong bases, Fraction b.

Acid Components Removal From Pentane-Solubles Minus the Bases. Pack the recycle column, Figure A2, with activated Amberlite IRA904 anion exchange resin. Rinse the packing with approximately 500 ml of n-pentane. Discard the pentane rinse. Add fresh pentane to the column until the packing is just covered. Pass the base-free pentane extract, the cation exchange column effluent, through this column. Recycle pentane through the column until the effluent is colorless. Retain the pentane extract.

Transfer the Amberlite IRA904 resin into a 60 x 180 mm extraction thimble and place the thimble into a No. D Soxhlet extractor. Soxhlet extract the thimble with pentane until the effluent is colorless. Combine the recycle pentane effluent with the pentane Soxhlet extract and retain for removal of neutral nitrogens.

Recovery of Benzene Soluble Acids, Very Weak Acids. Soxhlet extract the Amberlite IRA904 resin with benzene. Continue the extraction for 8 hours, or until the effluent is colorless. Strip the benzene to dryness on a steam bath using a nitrogen purge. Determine the weight percent benzene-soluble acids, very weak acids.

Recovery of Methyl Alcohol-Soluble Acids, Weak Acids. Soxhlet extract the Amberlite IRA904 resin with methyl alcohol for 8 hours, or until the effluent is colorless. Strip the solvent to dryness on a steam bath using a nitrogen purge. Redissolve the residue in benzene and filter through Whatman 42 (12.5 cm) filter paper into a tared 100 ml round bottom flask. Wash the filter paper and residue container with benzene to quantitatively transfer the sample to the tared flask. Discard any undissolved residue. Strip the benzene on a steam bath using a nitrogen purge. Finish stripping on a rotary flash evaporator at 20 torr and 95°C with nitrogen stripping.

Weigh the dried residue, and determine the weight percent methyl alcohol-soluble acids, weak acids.

Recovery of Strong Acids, Fraction a, Soluble in 5 Percent Formic Acid - Methyl Alcohol. Transfer the IRA904 resin into the 60 x 180 mm extraction thimble funnel. (See Figure A1). Pass 5 percent formic acid in methyl alcohol through the thimble until the effluent is acid to litmus paper and the effluent is colorless. Strip the solvent on a steam bath using a nitrogen purge. Redissolve the residue in benzene, and filter through Whatman 42 (12.5 cm) filter paper into a tared 100 ml round bottom flask. Wash the filter paper and residue container with benzene to quantitatively transfer the sample to a tared flask. Discard any undissolved residue. Strip the solvent on a steam bath using a nitrogen purge. Finish stripping the solvent on a rotary flash evaporator at 20 torr and 95°C with a nitrogen purge.

Determine the weight percent strong acids, Fraction a, soluble in formic acid in methyl alcohol.

Recovery of Strong Acids, Fraction b, from the Second Benzene Extraction of Amberlite IRA904. Replace the extraction thimble into the Soxhlet extractor. Soxhlet extract the thimble with benzene for 8 hours, or until the effluent is colorless. Strip the benzene on a steam bath with a nitrogen purge to dryness. Redissolve the residue in benzene. Filter through

Whatman 42 (12.5 cm) filter paper into a tared 100 ml round bottom flask. Wash the filter paper and the residue container with benzene to quantitatively transfer the sample to the tared flask. Discard any undissolved residue. Strip the solvent on a steam bath using a nitrogen purge. Finish stripping on a rotary flash evaporator at 20 torr and 95°C with nitrogen stripping.

Determine the weight percent benzene-soluble acids, strong acids, Fraction b.

Removal of Neutral Nitrogen Components. Pack the recycle column with the ferric chloride on chromosorb-kaolin adsorbent. Rinse the packing with approximately 500 ml of pentane. Discard the pentane rinse. Add fresh pentane until the packing is just covered. Pass the base- and acid-free pentane extract through the packing until the effluent is colorless. Transfer the ferric chloride packing into a 60 x 180 mm extraction thimble. Place the thimble into the Soxhlet extractor and Soxhlet extract with pentane until the effluent is colorless. Combine the recycle and Soxhlet pentane extracts and retain for the separation of the saturates and aromatics.

Recovery of Ethylene Chloride-Soluble Neutral Nitrogen Components, Fraction a. Add approximately 350 ml of ethylene chloride to the 500 ml extraction flask. Soxhlet extract the ferric chloride packing with ethylene chloride for at least 8 hours, or until the effluent is colorless. Fill the recycle column with the activated Amberlite IRA904 resin. Rinse the column with approximately 500 ml of pentane. Discard the rinse. Add fresh pentane to the column until the packing is just covered. Pass the ethylene chloride extract through the resin and recycle the ethylene chloride until the effluent is colorless. After dissociation of the iron complex, strip the ethylene chloride on a steam bath using a nitrogen purge. Redissolve the residue with ethylene chloride and filter through Whatman 42 (12.5 cm) into a tared 100 ml round bottom flask. Wash the filter paper and the residue container. Transfer the washings to a tared 100 ml round bottom flask. Discard any undissolved residue. Strip the solvent on a steam bath using a nitrogen purge. Complete the stripping with a rotary flash evaporator at 20 torr and 95°C using a nitrogen purge.

Determine the weight percent ethylene chloride-soluble neutral nitrogens, Fraction a.

Recovery of Benzene Soluble Neutral Nitrogen Components, Fraction b. Soxhlet extract the ferric chloride packing with benzene until the effluent is colorless. Pass the benzene extract through the Amberlite IRA904 resin column, and recycle benzene through the column until the effluent is colorless. Strip the solvent on a steam bath using a nitrogen purge.

Redissolve the residue in benzene. Filter through Whatman 42 (12.5 cm) filter paper into a tared 100 ml round bottom flask. Wash the filter paper and the residue container with benzene to quantitatively transfer all of the sample to the tared flask. Discard any undissolved residue. Strip off the solvent on a steam bath using a nitrogen purge. Complete the stripping on a rotary flash evaporator at 20 torr and 95°C using a nitrogen purge.

Determine the weight percent benzene-soluble neutral nitrogens, Fraction b.

Separation of Saturated and Aromatic Components. Reduce the volume of the pentane extract from the ferric chloride column such that a 5 ml aliquot will contain less than 0.5 g of aromatics. Separate the saturates and aromatics by using the apparatus shown in Figure A3. Pump hexane at 460 ml per hour through the 100 ml round bottom mixing flask, the precolumn, the injection valve, and finally through the separation column. Place a 254 nm filter in the first UV detector and a 313 nm filter in the second one. Set the recorder at a chart speed of 15 inches per hour.

Check the activity of the separation column by chromatographing a 5 ml aliquot of a blend consisting of 30 mg of each of the following: Hexaethylbenzene, triisopropylbenzene and benzene dissolved in 40 ml of hexane.

A column with satisfactory activity should be capable of partially separating the hexaethyl- from triisopropylbenzene and provide baseline separation of benzene from the previously eluted components, using hexane as the eluent. Elute the test blend until the 254 nm response has returned to the baseline. If a satisfactory separation of the test blend is not provided, discard the alumina, and prepare a fresh batch of zero percent water alumina.

Inject a 5 ml aliquot of the base-, acid- and neutral nitrogen-free pentane concentrate, containing an approximate total of 0.5 g of saturates aromatics, onto the separation column. Elute the saturates with n-hexane until the 254 nm detector starts to respond at a sensitivity setting of 0.2 absorbance units full scale. When the 254 nm response is just indicated, shut off the hexane, switch receivers. Remove the precolumn and the injection valve from the flow system and start pumping cyclohexane, allowing n-hexane to be displaced from mixing flask.

Identify the hexane fraction as the saturates.

Continue to pump cyclohexane until the 254 nm response has peaked and returned to the baseline, after which replace the 254 nm filter with 365 nm filter.

Switch receivers and identify the cyclohexane fraction as monoaromatics.

Stop pumping cyclohexane, and begin with chloroform. Continue pumping chloroform until the 313 nm and 365 nm response both have peaked and returned to the baseline.

Switch receivers and identify the chloroform fraction as di- and triaromatics.

Shut off the chloroform and elute the polyaromatics and polar compounds with methyl alcohol until the 313 nm and 365 nm responses peak and return to baseline.

After the polyaromatics have been collected, prepare fresh alumina and separate the remaining pentane concentrate, successively repeating this procedure with 5 ml injections, collecting the various fractions in their respective receivers.

Recovery of Hexane-Eluted Saturated Components. The hexane solution is quantitatively transferred into a 2-liter flask and the solvent is stripped on a steam bath using a nitrogen purge. Redissolve the residue in C.P. hexane and filter through Whatman 42 (12.5 cm) filter paper, into a tared 100 ml round bottom flask. Wash the residue container and the filter paper with hexane to quantitatively recover all sample. Discard any undissolved residue. Strip the solvent off on a steam bath using a nitrogen purge. Finish stripping the solvent on a rotary flash evaporator at 20 torr and 95°C with a nitrogen purge.

Determine the weight percent of hexane-eluted saturates.

Recovery of Cyclohexane-Eluted Monoaromatic Components. Quantitatively transfer the cyclohexane effluent to a 2-liter flask and strip the solvent on a steam bath using a nitrogen purge. Redissolve the residue in cyclohexane and filter through Whatman 42 (12.5 cm) filter paper into a tared 100-ml round bottom flask. Wash the residue container and the filter paper with cyclohexane to quantitatively recover all of the sample. Discard any undissolved residue. Strip off the solvent on a steam bath using a nitrogen purge. Finish stripping the solvent on a rotary flash evaporator at 20 torr and 95°C with a nitrogen purge.

Calculate the weight percent cyclohexane-eluted monoaromatics.

Recovery of Chloroform-Eluted di- and tri-Aromatic Components. Transfer the chloroform effluent into a 2-liter round bottom flask and strip the solvent on a steam bath using a nitrogen purge. Redissolve the residue in C.P. chloroform, and filter through Whatman 42 (12.5 cm) filter paper into a tared 100 ml round bottom flask. Wash the filter paper and residue container with chloroform. Discard any undissolved residue. Strip off the solvent on a steam bath using a nitrogen purge. Complete stripping the solvent on a rotary flash evaporator at 20 torr and 95°C using a nitrogen purge.

Determine the weight percent chloroform-eluted di-triaromatics.

Recovery of Methyl Alcohol Eluted Polyaromatic and Polar Components. Transfer the methyl alcohol extract to a 2-liter round bottom flask. Strip off the solvent on a steam bath using a nitrogen purge. Redissolve the residue in C.P. benzene and filter through Whatman 42 (12.5 cm) filter paper into a tared 100 ml round bottom flask. Wash the filter paper and residue container with benzene. Discard any undissolved residue. Strip off the solvent on a steam bath using a nitrogen purge. Complete stripping the solvent on a rotary flash evaporator at 20 torr and 95°C with a nitrogen purge.

Determine the weight percent methyl alchohol eluted polyaromatics and polar compounds.

This completes the separation. Recovery data for the various fractions may be collected for reporting. Fractions are available for further characterization.

A.2. Membrane Filtration

A.2.1. Apparatus

Filter holder, stainless 47 mm pressure holder of 100 ml capacity, Millipore xx 40 047 00.

Filters, Fluoropore filter, 0.2 μm pore size, Millipore FGLP 04700.
Heating tape to heat filter holder.
Flask, 125 ml glass stoppered Erlenmeyer.
Petri dish.

A.2.2. Reagents

Dimethylformamide (DMF) distilled 10-90% heart cut.
Xylenes, reagent grade.
Solvent, 2 parts by weight DMF to 1 part of weight xylenes.
Benzene, reagent grade.

A.2.3. Procedure

Weigh 25 g of the coal oil to 0.1 mg in 125 ml glass stoppered Erlenmeyer flask.

Add 75 g weighed to 0.1 mg of solvent. Thoroughly mix to completely solubilize.

Sample may be warmed gently, not exceeding 80°C, to help solubilize. Weigh Fluoropore filter to 0.1 mg in Petri dish before filtration. Transfer sample to filtration apparatus and filter with pressure at 80°C. When filtration is complete, wash flask with benzene and filter. Keep washings separate. Flask should be washed free of any particulates. Continue washing until filtrate is colorless. Continue nitrogen purge to dry filter cake. Remove filter cake with filter from apparatus. Place in Petri dish and dry in oven at 105°C for 1 hour. Place dried sample in desiccator for 1 hour. Weigh sample to 0.1 mg. Calculate percent particulates in coal oil from weight of filter cake and weight of coal oil. Filter cake and filtrate are analyzed for metals (Fe, Ti, Al, Ca, Mg, Na and Si) by atomic absorption spectroscopy.

A.3. Wet Digestion of Filter Cake and Metal Analysis by Atomic Absorption Spectrometry (AAS)

A.3.1. Wet Digestion of Filter Cake

Place the dried weighed filter cake into a clean 250 ml Vycor beaker and char the filter cake with 10 ml of concentrated sulfuric acid. Digest the char by adding nitric acid dropwise until residue and solution are almost white in color. Fume off sulfuric acid to 1-2 ml (almost dry). Place beaker and contents into well ventilated muffle at 1200°F for 2 hours or until Fluoropore filter membrane is dissipated. Remove beaker from muffle and cover with watch glass, place in desiccator for 1 hour and record weight to nearest tenth of milligram.

A.3.2. Dissolution of Muffled Ash

Rinse down sides of beaker with 8-10 ml of water using fine spray wash bottle. Cautiously add 8 ml of concentrated sulfuric acid, repeat water rinse. Cover beaker with ribbed watch glass and heat to near boil, reduce volume to 10-12 ml. Repeat 8-10 ml H_2O rinse, include watch glass. Add 5 ml concentrated hydrochloric acid and repeat heating, reduce to 10-12 ml. Remove beaker from hot plate, cool and quantitatively transfer to 25 ml volumetric flask. If SiO_2 is present (visually) even in trace amount, transfer quantitatively to Whatman 42 filter paper and pass filtrate into 25 ml flask. Determine percent SiO_2 via standard chemical gravimetric method. If SiO_2 is visually absent, record <0.001% SiO_2.

A.3.3. Percent Sulfated Ash

Place the rinsed and acid treated beaker into the muffle for 1 hour at 1200°F. Cool in desiccator for 1 hour. Record tare weight of beaker. Subtract this weight from recorded weight of desiccator beaker containing ash before acid dissolution. This is the weight of sulfated ash. Calculate as percent sulfated ash based on weight of coal oil.

A.3.4. Determination of Acid soluble Metals by AAS

Use routine AAS method of standard addition as calibration for Al, Ca, Fe, Mg, Na, and Si. In determining Ti, spike aliquots with 1000 γ per ml of Al. Calculate ppm metal based on weight of coal oil. A blank determination using a Fluoropore filter is carried through the entire procedure.

A.4. Standard Analytical Methods

Method Title	UOP* Method No.	ASTM** Method No.
API Gravity of Liquid Petroleum Products		D-287
Specific Gravity of Road Oils, Tars, etc.		D-70
Distillation - Engler, Vacuum		D-1160
Distillation - Fractional Type A	U-79	
Heptane Insoluble Matter - Membrane Filter	U-614	
Benzene Insoluble Matter - Membrane Filter	Mod. U-614	
Ash from Petroleum Oils (Gravimetric)		D-482
Trace Metals in Gas Turbine Fuels (Atomic Absorption Method)		D-2788
Molecular Weight of Hydrocarbons by Thermoelectric Measurement of Vapor Pressure		D-2503
Conradson Carbon Residue of Petroleum Products		D-189
Softening Point of Asphalts and Tars		D-36
Pour Point of Petroleum Oils		D-97
Viscosity, Saybolt Universal or Furol		D-88
Elution, ASTM for Aromatics		D-2549
Gas Composition by GC	U-539	
Boiling Range Distribution by GC		D-2887
Water in Petroleum Products by Solvent Distillation		D-95
Chloride in Oils by Sodium Biphenyl, - Pot. Titration	U-588	
Hydrogen and Carbon (Micro)	U-638	
Oxygen, Total, in Organic Materials	U-649	
Sulfur in Petroleum Products		D-1552
Nitrogen by Acid Extraction + Kjeldahl (Liqs.)	U-384	
Nitrogen by Organic Compounds (Micro Dumas)	U-653	

* "UOP Laboratory Test Methods for Petroleum and Its Products", UOP Process Division, Des Plaines, Illinois.

** "1976 Annual Book of ASTM Standards", American Society for Testing and Materials, Philadelphia, Pa., 1976.

FIGURE A1

FUNNEL FOR 60 x 180 mm EXTRACTION THIMBLE

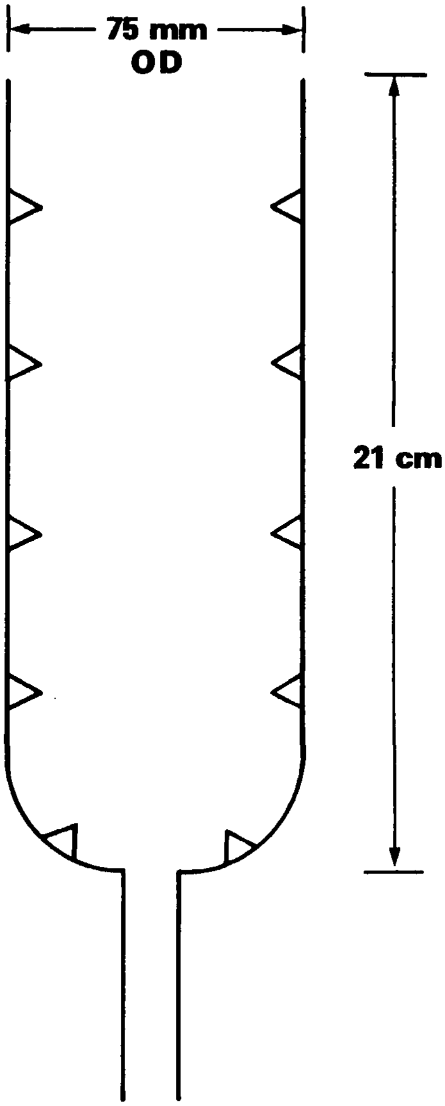


FIGURE A2

RECYCLE COLUMN

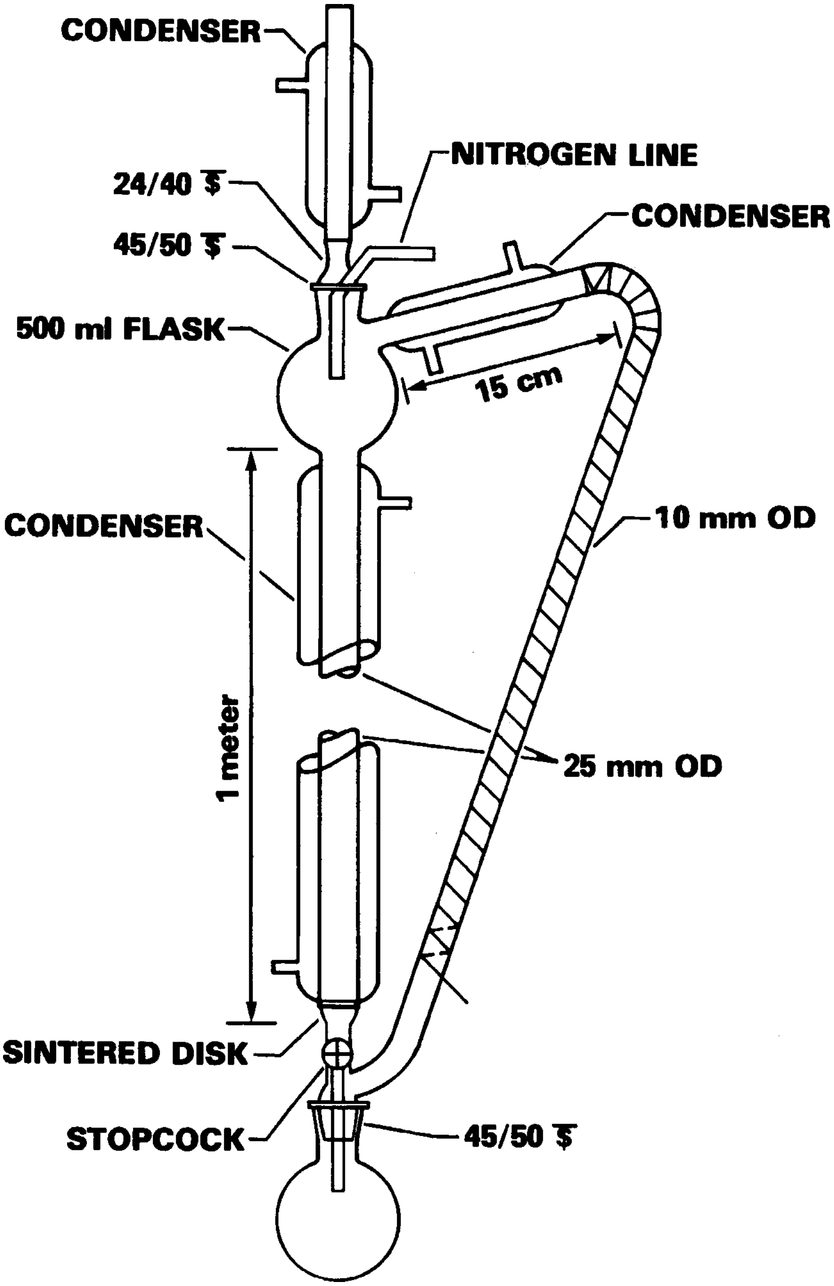
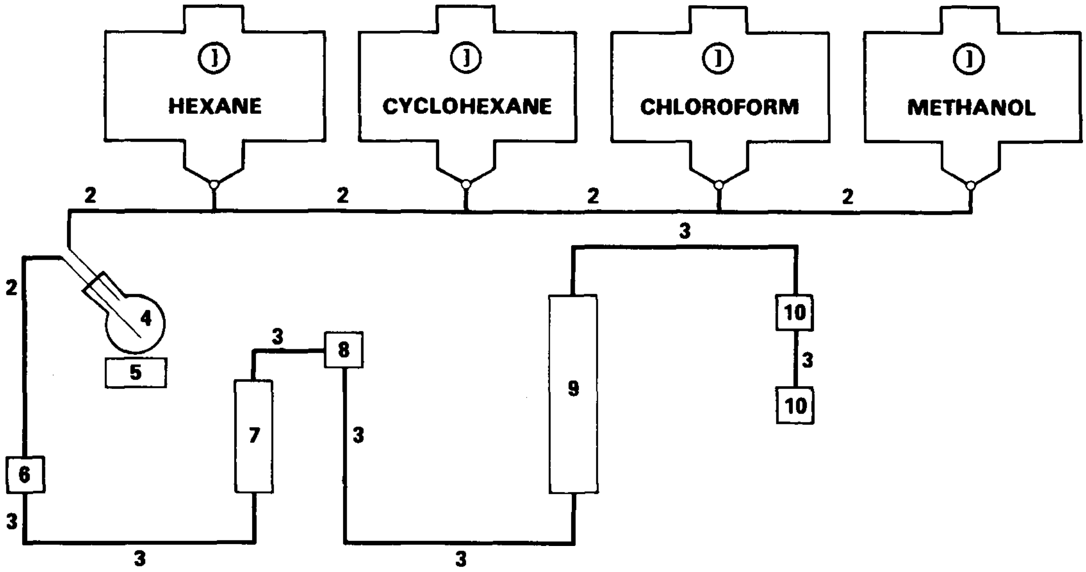


FIGURE A3

APPARATUS FOR SEPARATION OF SATURATES AND AROMATICS

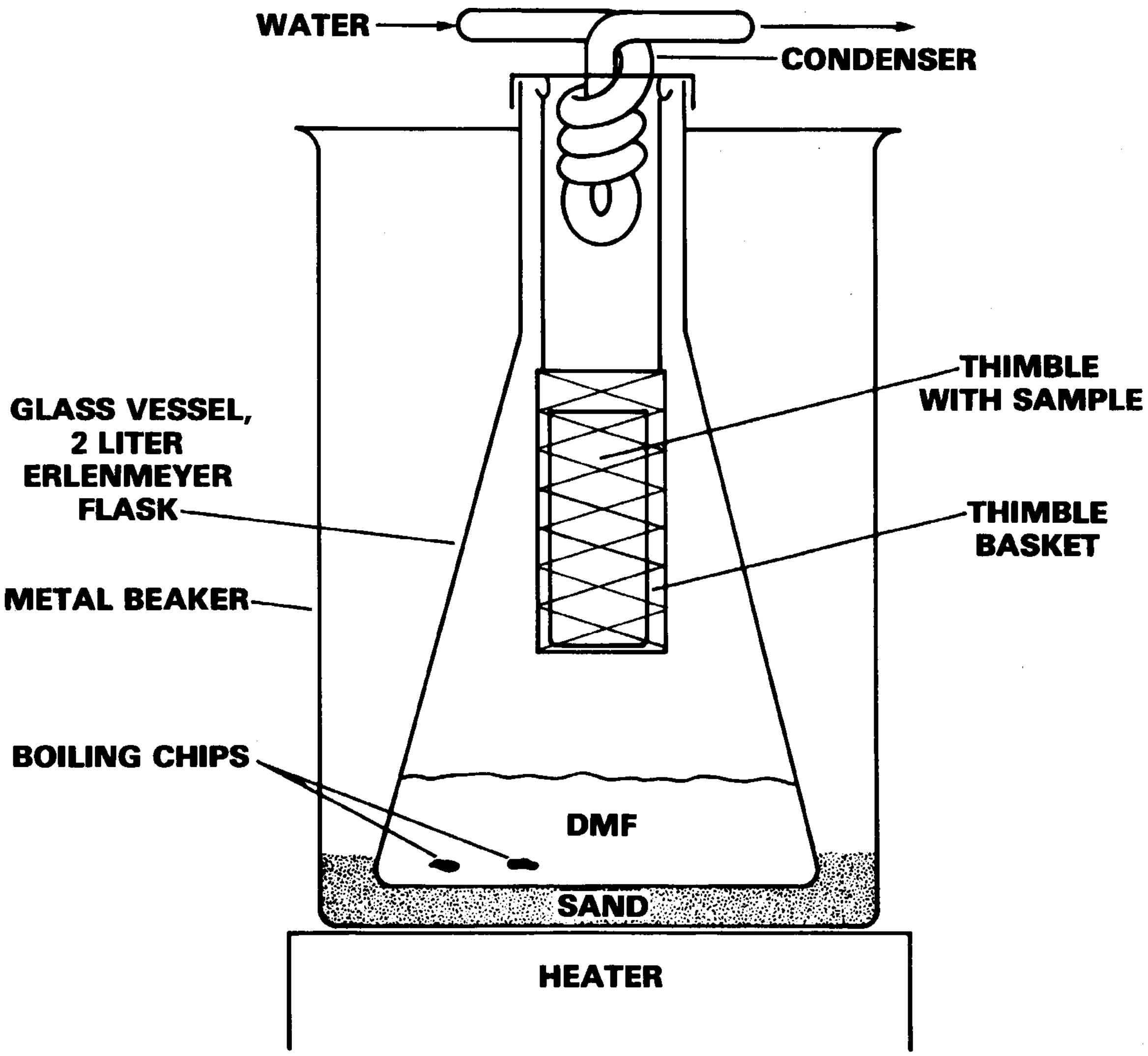


LEGEND

1 SOLVENT RESERVOIR, 1 liter
2 TEFLON TUBING, 1/8 in. OD
3 TEFLON TUBING, 1/16 in. OD
4 ROUND BOTTOM FLASK, 100 ml
5 MAGNETIC STIRRER
6 MILTON ROY MINI PUMP SET
7 PRECOLUMN, 1/2 in. OD x 33 cm
8 INJECTION VALVE PLUS SAMPLE LOOP
9 SEPARATION COLUMN, STAINLESS STEEL, 1/2 in. OD x 1meter
10 UV DETECTORS IN SERIES

FIGURE A4

DIMETHYLFORMAMIDE (DMF) EXTRACTION APPARATUS



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