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**HYDROPROCESSING OF SOLVENT REFINED COAL:
CATALYST SCREENING RESULTS**

By
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March 1982
Date Published

**Pittsburgh Energy Technology Center
Pittsburgh, Pennsylvania**

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UNITED STATES DEPARTMENT OF ENERGY

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HYDROPROCESSING OF SOLVENT REFINED COAL:
CATALYST SCREENING RESULTS

by

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ABSTRACT

This report presents the results of screening four catalysts for hydroprocessing a 50 wt% mixture of SRC-I in a prehydrogenated creosote oil using a continuous flow unit. All catalysts employed were nickel-molybdates with varying properties. Reaction conditions were 2000 psi, 8 SCFH of hydrogen, volume hourly space velocity of 0.6 to 1.0 cc of SRC-I/hr/cc of catalyst, and 48 hours at 750°F followed by 72 hours at 780°F.

The results indicate that the Shell 324 catalyst is best for hydrogenation of the feedstock but only marginally better than CB 81-44 for denitrogenation. The CB 81-44 catalyst may be slightly better than Shell 324 for the conversion of the +850°F fraction of the feedstock. Desulfurization was uniformly high for all catalysts. Catalysts with a bimodal pore size distribution (i.e., SMR7-6137(1)) appear to be better for denitrogenation than unimodal catalysts (i.e., SMR7-6137(4)) containing the same metals loading. Unimodal catalysts (i.e., Shell 324) with higher metals loadings are comparable to bimodal catalysts (i.e., CB 81-44) containing less metals. The results indicate that pore size distribution and metals loading are important parameters for high activity.

Catalysts with a unimodal pore volume distribution are capable of being restored to their original state, while bimodal ones experience a loss in surface area and pore volume and an increase in pellet density. This is attributed to the more efficient use of the interior surface area of the catalyst, which results in higher accumulation of coke and metals. Since coke can be removed via controlled oxidation, the irreversible loss is due to the higher concentrations of metals in the catalyst.

I. INTRODUCTION

Liquids derived by the direct liquefaction of coal have low hydrogen-to-carbon ratios and high sulfur and nitrogen concentrations, which render them unacceptable for direct use. Upgrading of these liquids is therefore mandatory before they can be used as feedstocks to existing refineries. The primary upgrading process usually involves the hydroprocessing of either the entire coal liquid product or individual fractions obtained by distillation. An extensive review of the hydrotreatment of coal liquids has recently been presented by Stiegel et al. (1981a).

The nitrogen concentration in coal liquids is much higher than that found in conventional petroleum crudes, whereas the sulfur concentration is generally less. Much of the research in catalysis for hydroprocessing petroleum has been directed to sulfur removal and consequently has resulted in the development of very efficient hydrodesulfurization catalysts. With the advent of coal liquids and heavy petroleum crudes with their high levels of nitrogen and ash, these hydrodesulfurization catalysts have not been found to be effective for the production of acceptable products. Besides, they also experience rapid deactivation, which seriously affects processing economics. As a result, catalysts that can effectively remove nitrogen as well as sulfur to acceptable levels with minimum hydrogen consumption and sufficient life need to be developed.

Unlike desulfurization, denitrogenation requires the saturation of the aromatic ring prior to scission of the carbon-nitrogen bond. Hydrogen consumptions are therefore usually high for feedstocks with high concentrations of

nitrogen. Conditions for denitrogenation must be established very carefully in order to assure that an optimum level of aromatic saturation occurs. Mobil Oil Corporation recently developed a model that describes the effect of various process parameters on the saturation of aromatics (Stein et al., 1977). This model is given below:

$$f_a = \left[\frac{k_r}{k_r + k_f PN} \right] + \left[f_o - \frac{k_r}{k_r + k_f PN} \right] \exp \left[\frac{-k_f PN + k_r}{LHSV} \right] \quad (1)$$

The model's predictions of aromatic saturation as a function of reaction temperature, pressure, and liquid hourly space velocity are shown in Figures 1, 2, and 3. As shown, higher pressures and lower space velocities result in a higher degree of saturation. An optimum temperature for maximum aromatic saturation also occurs. The figure indicates that for a given pressure and space velocity, the equilibrium between the aromatic and saturated states shifts to the aromatic state as temperature is increased beyond that required for optimum saturation. Also, as lower space velocities are employed, lower reaction temperatures must be employed to maximize aromatic saturation. Since nitrogen removal requires the saturation of the aromatic ring prior to the scission of the carbon-nitrogen bond, one must be extremely careful that the proper set of reaction conditions is selected; otherwise, poor denitrogenation will undoubtedly occur.

This report presents the results obtained for the upgrading of SRC-I using four nickel-molybdate catalysts. The purpose of the work was to compare catalysts for use in the LC-fining process. In particular, screening focused on conversion of the +850°F fraction of the feedstock, the extent of hydrogenation achieved, and the level of desulfurization and denitrogenation.

Figure 1.- Predicted effect of pressure on aromatic saturation for H-COAL distillate (Stein et al., 1977).

Figure 2.—Predicted effect of space velocity on aromatic saturation for SRC recycle solvent (Stein et al., 1977).

Figure 3.- Predicted effect of aromatic saturation for SRC recycle solvent (Stein et al., 1977).

All work was performed at the Pittsburgh Energy Technology Center of the U.S. Department of Energy; however, reaction conditions were established by C. E. Lummus and Cities Service during a joint meeting with PETC personnel.

II. REVIEW OF SRC-I HYDROPROCESSING

Considerable work has been reported in the literature on the hydroprocessing of SRC-I. In all investigations, this feedstock had to be diluted in a solvent to permit processing. The range of concentrations studied has varied from 33% to 90% SRC-I in various coal-derived and petroleum-derived solvents.

Mobil Oil Corporation under an EPRI Contract has reported on the hydroprocessing of SRC-I in a trickle-flow reactor (Stein et al. (1978)). They found that for a given space velocity, higher reaction temperatures resulted in less hydrogen consumption and a lower concentration of hydrogen in the product. These results are consistent with the aromatic saturation model presented in Equation 1. The SRC-I product derived from Illinois #6 (Burning Star and Monterrey) and Wyodak coals was evaluated to ascertain the differences in processing products derived from various coals. Product from Monterrey coal was found to be the most difficult to upgrade and required a space velocity of one half of that required for SRC-I derived from Burning Star coal in order to produce similar products. This was attributed to the higher level of both inorganic and organic sulfur in the Monterrey coal. The SRC-I from Wyodak was also more difficult to process than SRC-I product from Burning Star coal; this was attributed to the higher molecular weight components of the former.

A model has been proposed by Stein et al. (1978) for the conversion of SRC-I to oils. The model assumes a series reaction mechanism that involves the conversion of asphaltenes to resins to oils. The direct conversion of asphaltenes to oils was ruled out based on their experimental data. For first order reactions, the kinetic expressions are given by the following:

$$C_A = C_{A0} \exp (-k_{AR}/LHSV) \quad (2)$$

and

$$C_R = C_{R0} + \frac{k_{AR}C_{A0}}{k_{RO}-k_{AR}} \left(\exp\left(\frac{-k_{AR}}{LHSV}\right) - \exp\left(\frac{-k_{RO}}{LHSV}\right) \right) \quad (3)$$

The kinetic rate constants for the two reactions with an Arrhenius temperature dependence and an exponential aging function are given as

$$k_{ij} = k_{ij}^0 \exp (-at) \exp (-E/RT) \quad (4)$$

Statistically fitting their data to the model yielded the following parameters for Equation (4):

	$k_{ij}^0 (\text{hr}^{-1})$	$E_{ij} (\text{Btu/lh mole})$	$a (\text{day}^{-1})$
A $\rightarrow$ R	7.55×10^6	36,527	0.1633
R $\rightarrow$ O	9.69×10^5	31,493	

The above model predicts that after twenty days of processing, the catalyst possesses almost no activity for asphaltene conversion. Sullivan et al. (1979) have also indicated that catalyst deactivation is high.

The effect of catalyst pore diameter on the hydroprocessing of SRC-I has been investigated by Stein et al. (1978), Berg and McCandless (1978), and Kang and Gendler (1978). In these studies, larger pore catalysts were found to be desirable. Kang and Gendler (1978) observed that a Ni-Mo catalyst with a unimodal pore size distribution and one with a bimodal distribution had the same activity for denitrogenation on a volumetric basis; however, on a weight basis, the unimodal contains 30% more metals because of its higher density and therefore has a lower activity per unit weight of catalyst. Larger pores have also been found to yield products with hydrogen concentrations similar to those of products from smaller pore catalysts but with a lower heteroatom content. At high concentrations of SRC-I, the smaller pore catalysts produce a two-phase product, which indicates that the low-boiling fractions are preferentially upgraded. This can be attributed to the configurational diffusion effects experienced by the larger asphaltene molecules while trying to diffuse through pores having diameters not much larger than the molecular diameter of the asphaltenes. Implications from these results are that larger diameter pores in bimodal catalysts may have positive effects in the conversion of asphaltenes.

Givens et al. (1978) observed that in processing SRC-I filter feed, which contains about 25% SRC-I, using HDS-0402T cobalt-molybdate catalyst, an addition of 0.8 wt% hydrogen is required before any conversion of the +750°F fraction occurs. This fraction was also found to be converted faster than the +850°F fraction. Since only a very small fraction of SRC-I boils between 750°F and 850°F, this rapid conversion can be attributed to conversion of the solvent. Nickel-molybdate catalysts were found to possess a higher activity and selectivity for conversion of the +850°F fraction than

nickel-tungsten catalysts; however, there was no difference in hydrogen consumption.

Considerable experimental work has been reported by Potts et al. (1977, 1978, 1979, 1980) on the hydroprocessing of SRC-I in the LC-fining expanded bed process. Expanded or fluidized bed reactors should be much more adaptable to processing heavy hydrocarbon fluids because the turbulent action of the catalyst particle due to extensive backmixing in such reactors reduces the chance of reactor plugging. The turbulent action should also help to remove any crust around the catalyst particle due to coking and metals accumulation, thus maintaining a higher activity because of a reduction in external diffusion resistance. The conclusions from the work of Potts et al. (1977, 1978) are listed below:

1. Higher conversions of +850°F material are obtained with lower SRC/solvent ratios and space velocities.
2. Higher nitrogen, oxygen, and ash removals are obtained with lower SRC/solvent ratios and space velocities.
3. Desulfurization is uniformly high.
4. Hydrogen donor vehicle solvents enhance denitrogenation and deoxygenation.
5. Nickel-molybdenum catalysts are superior to cobalt-molybdenum and nickel-tungsten catalysts for nitrogen removal.

6. Catalyst deactivation is minimal.

III. EXPERIMENTAL

A. Process Description

All data reported herein were obtained from the continuous stirred tank reactor unit, which is shown schematically in Figure 4. The unit employs a one-liter continuous stirred tank reactor (CSTR). All process monitoring and control are performed from a remote operator control station. The unit is capable of operation to pressures and temperatures of 3500 psig and 500°C, with residence times from fifteen minutes up to several hours.

Hydrogen is supplied to a gas compressor station, where it is compressed to approximately 4500 psig and stored in an accumulator. Gas is drawn from the accumulator, regulated to a pressure slightly higher than the system operating pressure, and metered through a thermal mass flowmeter. A flow control valve controls the flow around an operator supplied set point. The gas is then fed to the reactor.

The feedstock is prepared in the mix tank and is transferred to the feed tank on an as-needed basis. Both vessels are equipped with an agitator and a recycle pump in order to maintain consistency in the feedstock. The feed can then be drawn off by either of two high pressure feed pumps and pressurized to system pressure. The pump discharge rate is adjusted manually and is monitored by the change in weight of the slurry feed tank over a specific period of time.

Figure 4.- Continuous unit for hydroprocessing SRC-I extract.

The feedstock and hydrogen are combined prior to entering the reactor. The residence time of the liquid phase reactants can be adjusted during the run by changing the liquid feed rate or prior to the run by adjusting the reactor holdup. The holdup (i.e., the effective reactor volume) can be varied by changing the height of the overflow tube that is inserted into the reactor from its base. This overflow tube controls the liquid level in the reactor. Baffles and an agitator with turbine impellers are used to maintain the gradientless nature of the CSTR.

Primary separation of reaction products occurs in the heavy oil separator. The liquid products are depressurized by isolating the primary separator and manually throttling the liquid products into the low pressure receiver. When depressurization is completed, the primary receiver is repressurized with product gas to system pressure and placed back in service. This technique eliminates any fluctuations or upsets in the system pressure caused by the removal of liquid products and minimizes disturbances in the product gas composition.

Water can be injected continuously into the gas stream from the heavy oil separator, and the resulting stream is further cooled in a water-cooled, double-pipe heat exchanger. The water and light oils are depressurized using the same technique as for the heavy oil products.

Gases that flash from the liquid products during depressurization are metered via the flash gas meter and then vented. A hot oil system provides high temperature heat transfer fluid to heat the mix tank and the heavy oil separation system. The feed tank, recycle pump, and high pressure feed pumps as well as all interconnecting lines are electrically heat traced.

The unit is monitored and controlled from a remote operator control station. All process variables to be controlled, such as system pressure, reaction temperature, and heat tracing temperature, with the exception of the slurry feed rate, are adjustable from the control station. System pressure can be maintained by an automatic electronic control system or manually via a back pressure regulating valve. All temperatures and pressures are displayed on digital indicators and permanently stored on strip charts. All motor and air operated valves are activated from the control station. In case of emergencies where temperature or pressures exceed preset upper limits or when hydrogen is detected in the vicinity, an automatic fail-safe system reverts the unit to a preprogrammed fail-safe mode.

B. Feedstock Data

All feedstocks used in the present investigation were obtained from C.E. Lummus, New Brunswick, N.J. The SRC-I feed was produced during 1977 at the Tacoma, Washington, SRC plant from Kentucky 9-14 coal obtained from the Colonial Mine. The run number from which this material was obtained is N-024; this should provide one with sufficient information to track down other process information, if desired. Three drums of SRC-I were used in the present investigation; their analyses are presented in Table 1. As shown, the hydrogen-to-carbon atomic ratio is relatively low compared to petroleum crudes, whereas the nitrogen content is very high. The SRC-I contains very little moisture and ash. Titanium, calcium, and iron were found to be the major metals constituting the ash. From the vacuum distillation results, approximately 94 vol% of the material boils above 850°F.

TABLE 1: Analyses of SRC-I Feedstocks

	SRC-I-2	SRC-I-3	SRC-I-4
Ultimate (wt%)			
Carbon	87.3	87.0	86.7
Hydrogen	6.0	6.0	6.0
Nitrogen	2.2	2.2	2.2
Sulfur	0.7	0.75	0.7
Oxygen (by diff)	3.7	3.95	4.3
Ash	0.1	0.1	0.1
Hydrogen/Carbon Atomic Ratio	0.82	0.83	0.83
Moisture (wt%)	0.5	0.5	0.6
Benzene Insolubles (wt%)	44.4	42.4	42.5
Specific Gravity	1.23	1.23	1.26
Heating Value (Btu/lb)	15,619	----	15,695
Ethyl Acetate Insolubles (wt%)	----	48.3	----
Cyclohexane Insolubles (wt%)	----	98.9	----
Vacuum Distillation			
IBP (°F)	----	620	----
5% (°F)	----	792	----
10% (°F)	----	900	----
18% (°F)	----	940	----
Recovery (wt%)	----	16.1	----
Residue (wt%)	----	81.1	----
Loss (wt%)	----	2.8	----

The analyses of the three solvent drums are shown in Table 2. This material, supplied by C. E. Lummus, is a creosote oil that has undergone hydrotreatment. As shown, the hydrogen-to-carbon atomic ratio is higher than that of the SRC-I feedstock. Very little asphaltenes and preasphaltenes are present in the solvent.

C. Catalysts

The catalysts used in the present investigation are all nickel-molybdenum catalysts; their properties are given in Table 3 and Figures B1 to B4. The four catalysts, i.e., Shell 324, SMR7-6137(1), SMR7-6137(4), and CB 81-44, were supplied by C. E. Lummus.

D. Procedures

Prior to operation of the unit, the SRC-I is ground in a ball mill and screened through a 20 mesh sieve. This enhances the dissolution of the SRC-I in the creosote oil and permits dissolution at a lower temperature. The ground SRC-I is thoroughly mixed to assure a uniform batch of feed. Each drum is ground in its entirety on an as-needed basis. Material not consumed in the first run is used for subsequent runs. A representative sample of the ground material is collected and sent for analysis prior to use. Only one set of analyses is obtained for materials from a drum, as it is assumed that no changes in the SRC-I will occur.

The prehydrogenated creosote oil is mixed thoroughly before any samples are withdrawn for analysis or use. Only one set of analyses is obtained for

TABLE 2: Analysis of Prehydrogenated Creosote Oil

	HCO-1	HCO-2	HCO-3
Ultimate Analysis (wt%)			
Carbon	92.5	92.0	91.60
Hydrogen	8.0	7.9	7.9
Nitrogen	0.4	0.4	0.45
Sulfur	0.04	0.04	0.1
Oxygen (by diff.)	----	----	----
Ash	0.003	0.003	0.02
Hydrogen/Carbon Atomic Ratio	1.04	1.03	1.04
Water Content (wt%)	0.03	0.03	0.05
Heating Value (Btu/lb)	17,611	17,671	----
Viscosity (cs @ 140°F)	12.2	11.7	16.0
Specific Gravity (60°F/60°F)	1.082	1.082	1.083
Fire Point (°F)	250	250	290
Flash Point (°F)	230	220	240
Solvent Analysis (wt%)			
Preasphaltenes	0.2	nil	nil
Asphaltenes	nil	nil	nil

TABLE 3: Catalyst Properties

TYPE	Shell 324 extrudate	SMR7-6137(1) extrudate	SMR7-6137(4) crushed granules	CB 81-44 extrudate
Bulk Density (g/cc)	0.855	0.487	0.757	0.509
Pellet Density (g/cc)	1.51	0.868	1.31	0.963
Pore Volume (cc/g)	0.396	0.758	0.463	0.794
P.V. > 1000 Å (%)	1.0	20.4	2.2	20.0
Surface Area (m ² /g)	188	192	266	216
Average Micro Pore Diameter (Å)	98	120	70	115
Average Macro Pore Diameter (Å)	----	4300	----	4500
NiO (wt%)	3.24	3.18	3.05	3.05
MoO ₃ (wt%)	20.10	12.30	12.45	18.00
Al ₂ O ₃ (wt%)	65.09	75.75	77.83	69.72
Na ₂ O (wt%)	0.13	0.81	0.81	0.94
SiO ₂ (wt%)	0.40	<0.20	<0.20	<0.20
P ₂ O ₅ (wt%)	6.87	<0.10	<0.10	<0.10
NiO + MoO ₃ concentration (g/cc of catalyst)	0.200	0.075	0.117	0.107

each drum of oil. This assumes that no changes in properties occur, such as aging or settling.

Prior to operation, the desired catalyst is measured to the specified volume in a 100 ml graduated cylinder. Filling of the cylinder is done very slowly while constantly tapping the outer surface to permit proper settling of the catalyst particles. The catalyst is then placed in an annular catalyst basket having a 35 mesh screen; a schematic diagram of the basket is shown in Figure 5. The annulus is approximately 5 mm wide. This results in a lower pressure drop through the catalyst bed and therefore results in better flow of reactants past the catalyst surface. The basket is filled very slowly, again tapping frequently to permit proper settling of the particles. Once the catalyst is loaded, glass beads are used to fill the remaining void space, and glass wool is placed around the top of the basket to secure the catalyst and glass beads in place.

The basket is then placed in the reactor, and the overflow tube is positioned such that the liquid level is at or very near to the catalyst- glass bead interface. When this has been completed, a measurement of the actual reactor volume is obtained using either kerosine or pentane with all internals in place. Upon completion of the reactor volume measurement, the material is drained and the reactor sealed.

Prior to operation, the unit is pressure tested with nitrogen at 4000 psig, followed by hydrogen at 3500 psig. After all leaks have been eliminated and no pressure loss is observed over a specified period of time, the system is brought to the presulfiding conditions outlined in Table 4.

Figure 5- Catalyst basket.

During the sulfiding period, a forty-kilogram batch of SRC-I and creosote oil is prepared in a one-to-one weight ratio. Twenty kilograms of the creosote oil are first charged to the mixing tank. This material is agitated and recirculated via the recirculating pump while being heated to 170°C via a hot oil heat transfer system. Once the desired temperature is attained, twenty-kilograms of ground SRC-I are slowly added to the solvent. When the addition is completed, the tank is sealed and pressurized with nitrogen to about 40 psig.

Shortly before the presulfiding is completed, the slurry feed section is heated by activating the appropriate controllers. When the thermocouples throughout the system indicate approximately 120°C, a predetermined amount of feedstock is transferred to the small feed vessel. The vessel is pressurized with nitrogen to about 40 psig, and recirculation is begun.

Upon completion of the sulfiding procedures, the reactor furnace controller is activated and the unit is pressurized. The hydrogen feed rate is then established. Slurry feed is started once the reactor internal temperature begins to approach the desired reaction temperature. The reaction conditions are presented in Table 4. The slurry feed rate is established by noting the change in weight of the feed tank over a specified period of time, as well as by noting the weight of the liquid products collected each hour.

The activity of the catalyst is followed throughout the run by collecting control samples at specified times. Six control samples are collected: three during the 750°F period of operation and three during the 780°F operation. The control periods last for four hours so that sufficient material is available

TABLE 4: Experimental Operating Conditions

Presulfiding	
Temperature ($^{\circ}\text{C}$)	350
Pressure, (psig)	50
Flowrate (slm)	1
Time (hrs)	5
H ₂ S/H ₂ Concentration (mole %)	10
Agitator Speed (rpm)	500-600
Reaction Conditions	
Temperature ($^{\circ}\text{F}$)	48 hrs @ 750 72 hrs @ 780
Pressure (psig)	2000
Hydrogen flowrate (SCFH)	8
SRC-I Concentration (wt%)	50
Slurry Feed Rate (g/hr)	120-175
Volume Hourly Space Velocity (cc of SRC-I/hr/cc of catalyst)	0.6-1.0
Catalyst Volume (cc)	70-80
Agitator Speed (rpm)	1500-2000

for analysis. Three material balance periods are also performed: one during the 750°F period of operation and two during the 780°F period of operation. These periods last for ten hours so that detailed analyses can be performed on the products. Four feedstock samples are collected: one at the beginning of the run and one during each material balance period. Three tail gas and three flash gas samples are collected during each material balance period.

Upon completion of a run, the unit is thoroughly flushed with solvent before the temperatures are reduced. After a sufficient period of time, all heaters are deenergized and the unit is slowly depressurized. When the unit is completely shut down, the reactor is opened and the catalyst is removed from the basket. Any remaining feedstock is discarded.

E. Analyses

All analyses presented in or used to generate the results presented in this report were performed by the Analytical Chemistry Division or the Process Sciences Division of the Pittsburgh Energy Technology Center, with the exception of the vacuum distillations from Run No. LC-R09, which were performed by Conoco Coal Development Company, Library, Pa.

All feedstock and heavy oil products from the material balance periods were subjected to the following analyses: 1) ultimate, 2) ash, 3) water content, 4) specific gravity, 5) vacuum distillation (ASTM D-1160), and 6) rapid microfiltration. The rapid microfiltration technique characterizes the material based on its solubility in various solvents. Tetrahydrofuran (THF), ethyl acetate, pentane, and cyclohexane were used for all samples. Conversion of

the various fractions is determined by the amount of insoluble material remaining after extraction with a particular solvent for both the feedstock and liquid products. Conversion can be calculated as follows:

$$X_i = \frac{100 (C_{Fi} - C_{Pi})}{C_{Fi}} \quad (5)$$

where X_i = conversion as measured with solvent i
 C_{Fi} = percent insolubles in the feed for solvent i
 C_{Pi} = percent insolubles in the product for solvent i

Additional details concerning the equipment and operating procedures are given in Appendix A.

The control samples collected are subjected to the following: 1) ultimate analysis, 2) vacuum distillation (ASTM D-1160), and 3) rapid microfiltration. All gas samples are analyzed using gas chromatography.

All spent catalysts are first extracted with THF to remove any excess oils from the catalyst surface. The extracted catalyst pellets are analyzed by mercury porosimetry to evaluate the pore size distribution, pore volume distribution, and surface area of the aged catalyst. The catalyst is also analyzed for carbon, hydrogen, and nitrogen as well as metals deposition.

The spent catalysts are also regenerated by controlled burn-off of the coke. Regeneration was conducted by subjecting the catalyst to increasing levels of oxygen in nitrogen (i.e., 0.5-21%) at a rate of 2.25 cc/min for nine hours at 450°C. These conditions are relatively mild and have been shown not to result in any changes in the physical properties of the catalyst.

F. Material Balance

All experimental and analytical data for each run are stored in the computer and can be retrieved using the material balance program that has been developed for this project. This program calculates the raw balances as well as forcing carbon and overall closure by adjusting either the feed slurry rate or liquid product rate. Adjustment of the feed slurry rate is believed to be more accurate because of the error involved in the weight measurement of the feed tank due to the line tracing and insulation. Product yield distributions and hydrogen consumptions as well as nitrogen, sulfur, THF, ethyl acetate, pentane, cyclohexane, and +850°F conversions as a function of time on stream are calculated. Conversions are calculated from the control samples and the average values of the feedstock samples. The material balances and product yields for all runs having material balance periods are presented in Tables C1 to C9 of Appendix C. Except in specific instances as noted, the data presented are those for carbon closure where the feed rate was adjusted. Overall and carbon closures on the raw data were usually better than 95%; however, after adjustment, these closures are greater than 98%. Hydrogen closure was not as good as expected during Run Nos. LC-R08 and LC-R09 because of a poorly calibrated gas meter. These meters also appear to lose their calibration after a few runs, resulting in somewhat poorer hydrogen closures. Adjustment of the tail gas rate would rectify this problem and would not seriously affect the closure calculations. Because of this, all reported hydrogen consumptions are based on the increase in hydrogen in the products and the hydrocarbon gases and not on molecular hydrogen in the gas streams.

Sulfur closure is uniformly low. This can be attributed primarily to the low concentration of sulfur in the feed slurry and products, and the results for the H_2S concentration obtained from the gas chromatograph. Concentrations of H_2S in the product gas of less than 0.1% are reported as align H_2S zero when realistically they are not. Therefore, the amount of sulfur in the product streams is always less than those in the feeds. Because of the low concentration of H_2S , no noticeable effects should be seen in the hydrogen closure or consumption resulting from the assumption of no H_2S in the tail gas.

Nitrogen closure is considerably better than that for sulfur. This can be attributed to the fact that both the feed and product streams contain fairly high concentrations of nitrogen, which reduce the error in their analysis. Nitrogen closure could be enhanced if components such as ammonia in the product gas were detected by the gas chromatograph. Although hydrogen is consumed during the formation of ammonia, the amount is too small to have any noticeable effect on hydrogen closure or consumption.

No data on oxygen closure are reported. Since no direct determinations of oxygen were made on either the feed or product streams, the concentration of oxygen was determined by difference. Therefore, all errors in the other analyses are accumulated in the oxygen values, resulting in poor closures in most cases.

IV. RESULTS AND DISCUSSION

Thirteen experimental runs using the four catalysts supplied by C. E. Lummus were conducted and are listed in Table 5. The first four runs were conducted at the initial reaction conditions established; LC-R04 was aborted because of a pump failure. Run Nos. LC-R05, LC-R06, and LC-R07 were conducted to establish a different space velocity to be used in future runs. The remaining runs were at the revised space velocity. Run LC-R10 was aborted because of pump problems, and Run LC-R13 was made to establish reproducibility. No thermal baseline runs (i.e., no catalyst present in the reactor) were conducted because of the lack of time and indications from C.E. Lummus that conversion of the +850°F fraction is low and denitrogenation is almost nonexistent in the absence of a catalyst. All data are presented in Appendices C and D.

A. Effect of Space Velocity

As shown in Tables C1 to C3 and Tables D1 to D3, the amount of nitrogen removed and the increase in the H/C ratio are very low using the initial set of reaction conditions. Because such results will not show any major differences between catalysts, it was deemed necessary to alter the reaction conditions. Since the initial space velocity specified was at the extreme upper end of those employed by C. E. Lummus, it was decided to lower the space velocity to a more reasonable value while maintaining all other conditions constant. Several experimental runs using Shell 324 were made to ascertain the effect of space velocity on nitrogen removal. Figure 6 presents all data obtained for nitrogen removal versus space velocity for Shell 324

TABLE 5: Experimental Runs

<u>Run No.</u>	<u>Catalyst</u>	<u>Time on Stream, hr</u>	<u>VHSV, hr⁽¹⁾</u>
LC-R01	Shell 324	71	1.01
LC-R02	SMR7-6137(1)	120	1.17,1.23,1.20
LC-R03	CB 81-44	120	1.08,1.02,1.02
LC-R04	SMR7-6137(4)	44	1.00(2)
LC-R05	Shell 324	23	1.00(2)
LC-R06	Shell 324	10	0.75(2)
LC-R07	Shell 324	48	0.71(2)
LC-R08	Shell 324	120	0.57,0.59,0.58
LC-R09	SMR7-6137(1)	120	0.68,0.62,0.59
LC-R10	CB 81-44	47	0.69
LC-R11	SMR7-6137(4)	120	0.66,0.63,0.59
LC-R12	CB 81-44	120	0.57,0.54,0.58
LC-R13	Shell 324	120	0.60,0.54,0.56

(1) Values are calculated during material balance periods.

(2) No material balance periods performed; values are those specified for the run.

Figure 6.- The effect of space velocity on nitrogen removal for Shell 324 at 750°F.

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at 750°F. As shown by this set of data, the space velocity has an effect on the removal of nitrogen. The data were correlated by Equation 6:

$$\%HDN = 16.56 (VHSV)^{-0.91} \quad (6)$$

Because of equipment limitations, a space velocity of 0.6 was selected for catalyst evaluation. This value should give values of nitrogen removal that are high enough for catalyst comparison while still not employing feed rates that are too low for the existing pumps to handle.

B. Interlaboratory Comparison of Analytical Results

In order to check the reproducibility of the analytical procedures used at C. E. Lummus and PETC, an additional feedstock sample and a product sample from the second material balance period of LC-R08 were collected and sent to C. E. Lummus. Table 6 presents the results obtained at both laboratories. As can be seen, the ultimate analyses are quite reproducible on both the feedstock and product samples. The H/C ratios, the percent change in the H/C ratio, and the percent denitrogenation are comparable. However, there appears to be a significant discrepancy between the values obtained for the conversion of +850°F material. Moreover, this property of the catalyst is of major importance. Further work will have to be performed in order to improve the precision (and accuracy) of our vacuum distillation data. Perhaps a clue to resolve this question can be obtained from the data in Table D5; the distillation data there (obtained by Conoco) have much less scatter than the distillation data in the other tables. Presumably, this data is also more accurate than the other data.

TABLE 6: Interlaboratory Comparison of Feed and
Product Samples from Run No. LC-R08

	<u>Lummus</u>	<u>PETC</u>
Ultimate Analysis of Feed, wt%		
Carbon	88.83	89.6
Hydrogen	6.64	6.9
Nitrogen	1.19	1.25
Sulfur	0.36	0.40
H/C atomic ratio	0.898	0.925
Ultimate Analyses of Product, ⁽¹⁾ wt%		
Carbon	89.11	89.0
Hydrogen	7.86	7.9
Nitrogen	0.75	0.8
Sulfur	0.19	0.15
H/C atomic ratio	1.059	1.066
% Change in H/C atomic ratio	17.9	14.9
% Denitrogenation	37.0	36.0
% Conversion of +850°F	32.5	4.3

(1) Feed and product samples were obtained from the second material balance period.

C. Experimental Reproducibility

Run No. LC-R13 was performed following the completion of the four catalytic runs at the lower space velocity for the purpose of checking the reproducibility of the unit, run procedures, analyses, etc. Tables C5, C9, and D4, and Figures 7, 8, and 9 present this comparison. Except for the one point at the beginning of the run, LC-R08, the differences in the H/C ratio between the two runs are about 3%. Denitrogenation is also quite reproducible, and the effect of the increase in reactor temperature can also be seen. Desulfurization is uniformly high for these and all other runs. Because of the low concentrations of sulfur in both the feed and products, small errors in its measurement can cause significant fluctuations in the results. As stated in Section IV-B, the distillation results that measure the conversion of +850°F material are somewhat lower in precision and have scatter in the data. As shown in Figure 8, some data points are quite reproducible while others are not. In light of the discussion in Section IV-B, this scatter can probably be attributed to analytical error. A comparison of the results in Tables C4 and C9 (both for Shell 324) shows that the product distribution and hydrogen consumption are quite similar; however, one must keep in mind the problems with the vacuum distillations.

D. Catalyst Comparison

As discussed earlier, hydrogenation of the aromatic rings is essential for the removal of nitrogen from heterocyclic compounds. The extent of hydrogenation can be measured by the increase in the H/C atomic ratio of the products versus that of the feedstock. Figures 10, 11, and 12 present this

Figure 7. - Comparison of the increase in the H/C ratio of the products over the feed for Shell 324.

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Figure 8.- Reproducibility of desulfurization and denitrogenation results for Shell 324.

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Figure 9.-Reproducibility of +850°F conversion results for Shell 324.

L-82077

Figure 10.- Comparison of the increase in the H/C ratio of the products over the feed for Shell 324 and CB 81-44.

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Figure II. - Comparison of the increase in the H/C ratio of the products over the feed for Shell 324 and SMR7-6I37(1).

L-82070

Figure 12.- Comparison of the increase in the H/C ratio of the products over the feed for Shell 324 and SMR7-6137 (4).

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comparison of the three catalysts (i.e. CB 81-44, SMR7-6137(1), and SMR7-6137(4)) with the data obtained using Shell 324 as a standard. With the exception of two points for CB 81-44 at the beginning of the run, the Shell 324 is superior for hydrogenation activity. A comparison of SMR7-6137(1) and SMR7-6137(4) is shown in Figure 13. From these data, it appears that there is no difference in hydrogenation activity. A slight process upset caused by a feed pump failure occurred at about 65 hours into the run for SMR7-6137(1) (Run No. LC-R09). This caused a loss of feed for approximately 15 minutes and allowed the reactants to remain in contact with the catalyst longer. This upset would carry over into the control sample indicated at 77 hours and accounts at least partially for its high value. This upset is also indicated on subsequent figures regarding this catalyst.

Figures 14, 15, and 16 present the comparisons of heteroatom removal for the various catalysts. In all cases, desulfurization activity is high. For denitrogenation activity, CB 81-44 appears to be almost as good as Shell 324; its lower hydrogenation activity may limit this. This is followed by SMR7-6137(4) and SMR7-6137(1). Since SMR7-6137(1) and SMR7-6137(4) have the same metals concentration, the difference in denitrogenation activity, as shown in Figure 17, could be attributed to differences in catalyst surface areas and densities, and the presence of macropores. As discussed earlier, the presence of macropores enhances denitrogenation, and therefore SMR7-6137(1) should be better than SMR7-6137(4). However, the higher density of SMR7-6137(4) results in a 56% increase in the amount of nickel and molybdenum present in the reactor. The higher concentration of metals per unit volume of catalyst probably offsets the effect of the macropores. Catalyst CB 81-44 contains about the same amount of metals per unit volume

Figure 13. - Comparison of the increase in the H/C ratio of the products over the feed for SMR7-6137(1) and SMR7-6137(4).

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Figure 14.- Comparison of the extent of desulfurization and denitrogenation for Shell 324 and CB 81-44.

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Figure 15. - Comparison of the extent of desulfurization and denitrogenation for Shell 324 and SMR7-6137(1).

L-82073

Figure 16.- Comparison of the extent of desulfurization and denitrogenation for Shell 324 and SMR 7-6137(4).

L-82074

Figure 17. - Comparison of the extent of desulfurization and denitrogenation for SMR 7-6137 (I) and SMR 7-6137 (4).

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as SMR7-6137(4), but has a higher denitrogenation activity, which can be attributed to the presence of macropores. Shell 324 has about twice the amount of metals per unit volume as does the CB 81-44, but only a slightly higher denitrogenation activity. The comparable activity of CB 81-44 is probably due to the presence of macropores and to the substantial percentage of the pore volume from pores greater than 1000 Å. These results confirm the findings of Kang and Gendler (1978).

Figures 18, 19, 20, and 21 present the comparisons for the conversion of +850°F material in the feed. From Figure 18, it appears that CB 81-44 may have a higher activity for converting the +850°F fraction than does Shell 324. If true, this could be attributed to the presence of macropores, which reduces the intraparticle diffusional resistances encountered by the larger molecules and allows more effective use of the internal surface. These results are also in agreement with others (Stein et al., 1978; Berg and McCandless, 1978; Kang and Gendler, 1978). Conversion of the +850°F fraction using either SMR7-6137(1) or SMR7-6137(4) appears to be comparable to that obtained using Shell 324, as shown in Figures 19 and 20. The comparison in Figure 21 shows that SMR7-6137(4) may be slightly better than SMR7-6137(1) for the conversion of +850°F material. The data presented in Figures 18, 19, 20, and 21 must be viewed with caution in light of the scatter in the data.

Because of the lack of precision of the distillation data, no comparison between catalysts will be made from the product distribution data.

Figure 18.- Comparison of the +850°F conversion for Shell 324 and CB 81-44.

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Figure 19.- Comparison of the +850°F conversion for Shell 324 and SMR 7-6137 (1).

L-82079

Figure 2Q-Comparison of the +850°F conversion for Shell 324 and SMR 7-6137 (4).

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Figure 21. - Comparison of +850°F conversion for SMR 7-6137 (1) and SMR 7-6137 (4).

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E. Catalyst Deactivation

From data such as that in Figures 14, 15, and 16, it is apparent that the catalyst is undergoing some deactivation. As a result, all spent catalysts were analyzed, regenerated, and then reanalyzed. Regeneration was conducted by subjecting the catalyst to increasing levels of oxygen in the nitrogen (i.e., 0.5-21%) at a rate of 2.25 cc/min for nine hours at 450°C. These conditions have been shown to be relatively mild and should not cause any sintering of the support or metal crystallites (Stiegel et al., 1981b).

Tables 7 and 8 present the properties of catalysts that were aged to different extents, as shown in Table 5. Figures 22 and 23 present the effects of aging on pore volume and surface area. In Figure 22, it is interesting to note that the bimodal catalysts (i.e., CB 81-44 and SMR7-6137(1)) tend to follow the same curve, while the unimodal catalysts (i.e., Shell 324 and SMR7-6137(4)) follow a separate curve. The pore volumes for the unimodal catalysts appear to reach a steady-state level sooner than do the bimodal ones. Figure 23 shows that the surface area of the Shell 324 catalyst drops much more rapidly and to a greater extent than do the surface areas of the bimodal CB 81-44 or SMR7-6137(1) catalysts. Figure 24 presents the percentage change in surface area and pore volume as a function of time on stream. The same trends as discussed above are seen here for both the unimodal and bimodal catalysts. No trend is evident for the SMR7-6137(4) catalyst because of the few, and scattered, data available.

Figure 25 presents a correlation between the change in the catalyst surface area and pore volume. The correlation is given by equation 7. It

TABLE 7: Properties of Aged Shell 324 Catalyst

<u>Time on Stream hr</u>	<u>Bulk Density g/cc</u>	<u>Pellet Density g/cc</u>	<u>Pore Volume cc/g</u>	<u>Pore Volume >1000Å, %</u>	<u>Surface Area m²/g</u>	<u>Average Micro Pore Dia., Å</u>
0	0.855	1.51	0.396	1.0	188	98
10	0.900	1.67	0.238	0.0	158	61
48	0.967	1.72	0.179	0.0	118	57
71	0.947	1.89	0.158	0.0	108	55
120	0.967	1.83	0.166	0.0	107	62
120	0.916	1.87	0.163	0.0	109	55

TABLE 8: Properties of Aged Catalysts

Time on Stream hr	Bulk Density g/cc	Pellet Density g/cc	Pore Volume cc/g	Pore Volume >1000Å, %	Surface Area m ² /g	Average Micro	Average Macro
						Pore Dia., Å	Pore Dia., Å
SMR7-6137(1)							
0	0.487	0.868	0.758	20.4	192	120	4300
120	0.731	1.293	0.413	26.4	151	67	3800
120	0.696	1.289	0.435	26.4	157	75	3700
SMR7-6137(4)							
0	0.757	1.310	0.463	2.2	266	70	----
44	0.946	1.640	0.204	2.0	186	42	----
120	0.948	1.615	0.236	1.7	207	43	----
CB 81-44							
0	0.509	0.963	0.794	20.0	216	115	4500
47	0.533	1.210	0.456	24.8	174	68	3700
120	0.704	1.323	0.394	27.2	151	64	4200
120	0.571	1.276	0.422	26.1	168	78	3800

Figure 23. - Effect of aging on catalyst surface area.

L-82082

Figure 22.- Effect of aging on catalyst pore volume.

L-82083

Figure 24.- Percentage change in pore volume and surface area as a function of time on stream.

L-82114

Figure 25.-Correlation between the change in catalyst surface area and pore volume.

L-82113

is interesting to note that all of the catalysts, regardless of whether they are unimodal or bimodal, follow the same curve; the significance of this is not known at the present time.

$$\left(\frac{-\Delta S}{S_0}\right) = 0.00161 \left(\frac{-\Delta V}{V_0}\right)^{2.49} \quad (7)$$

The decline in pore volume and surface area is most likely due to the accumulation of coke. The rapid loss of surface area and pore volume within the first 60 hours of operation can be attributed to the additive coke contained in the feed. This coke accumulates rapidly at the pore mouths and results in increased diffusion resistance. Table 9 shows that within 50 hours, the carbon content of the Shell 324 catalyst appears to have leveled off. Macropores help to prevent an increase in diffusion resistance and allow more effective use of the interior surface area. This is illustrated by the higher concentrations of carbon and titanium on the bimodal catalysts, which could change the mode of deactivation from pore-mouth poisoning to a uniform poisoning mechanism. Such a change is beneficial, as previously shown by Wheeler (1951), and could help to explain the observed behavior of the bimodal catalysts discussed previously.

Table 9 also presents the concentrations of titanium, iron, and calcium in the spent catalysts. As shown, the bimodal catalysts (i.e. SMR7-6137(1) and CB 81-44) accumulate more metals than the unimodal catalysts. Titanium, in all cases, is present in the highest concentration, while the concentration of calcium is the lowest.

TABLE 9: Composition of Spent Catalysts

<u>Time on Stream</u>	<u>Carbon</u>	<u>Hydrogen</u>	<u>Nitrogen</u>	<u>Sulfur</u> ⁽¹⁾	<u>Titanium</u>	<u>Iron</u>	<u>Calcium</u>
<u>Shell 324</u>							
10	8.3			5.8	0.3	0.1	0.1
48	11.3			6.8	0.6	0.2	0.2
71	11.0		0.5	6.1	0.4	0.2	0.1
120	11.4			6.8	0.7	0.2	0.1
<u>SMR7-6137(1)</u>							
120	13.4	1.2	0.5	3.8	1.5	0.5	0.4
<u>SMR7-6137(4)</u>							
44	12.5		0.6	3.6	0.4	0.2	0.1
<u>CB 81-44</u>							
120	12.8		0.4	5.0	1.7	0.5	0.3

(1) Most of the sulfur is due to catalyst presulfiding.

The properties of the regenerated catalysts are presented in Tables 10 and 11. From the data on the pellet density, pore volume, and surface area, it appears that the unimodal catalysts can be effectively restored to their original states, while the bimodal ones suffer a loss in pore volume and surface area and an increase in pellet density. These results can be attributed to differences for coke and metals deposition, as shown in Table 9.

TABLE 10: Properties of Regenerated Shell 324 Catalyst Samples

<u>Time on Stream hr</u>	<u>Bulk Density g/cc</u>	<u>Pellet Density g/cc</u>	<u>Pore Volume cc/g</u>	<u>Pore Volume >1000Å, %</u>	<u>Surface Area m²/g</u>	<u>Average Micro Pore Dia., Å</u>
0	0.855	1.510	0.396	1.0	188	98
10	0.765	1.486	0.404	0.0	174	106
23	0.818	1.383	0.411	0.0	184	102
71	0.769	1.533	0.362	0.0	155	108
120	0.809	1.520	0.379	0.2	174	100
120	0.778	1.557	0.375	0.0	172	102

TABLE 11: Properties of Regenerated Catalysts

<u>Time on Stream hr</u>	<u>Bulk Density g/cc</u>	<u>Pellet Density g/cc</u>	<u>Pore Volume cc/g</u>	<u>Pore Volume >1000Å, %</u>	<u>Surface Area m²/g</u>	<u>Average Micro Pore Dia., Å</u>	<u>Average Macro Pore Dia., Å</u>
<u>SMR7-6137(1)</u>							
0	0.487	0.868	0.758	20.4	192	120	4300
120	0.597	-----	0.673	21.4	174	112	4000
120	0.566	1.062	0.694	20.6	173	118	4400
<u>SMR7-6137(4)</u>							
0	0.757	1.310	0.463	2.2	266	70	-----
44	0.778	1.328	0.473	0.4	264	74	-----
120	0.782	1.341	0.472	0.6	263	74	-----
<u>CB 81-44</u>							
0	0.509	0.963	0.794	20.0	216	115	4500
47	0.509	0.973	0.771	19.2	190	120	4600
120	0.566	1.104	0.659	17.9	185	117	4200
120	0.541	1.038	0.723	19.2	182	113	4500

V. CONCLUSIONS

From the data obtained, the following conclusions are made:

1. Equipment and experimental/analytical procedures have been developed to reproducibly test and compare catalysts for coal liquids upgrading.
2. Shell 324 is best for hydrogenation of the feedstock; the remaining catalysts are quite similar in their hydrogenation activity.
3. Shell 324 is best for hydrodenitrogenation but is followed closely by CB 81-44.
4. CB 81-44 may be slightly better than Shell 324 for conversion of the +850°F fraction. Caution, however, must be exercised in viewing the distillation results, due to the question of the precision of the analysis.
5. Active metals loading per unit volume of catalyst and pore size distribution appear to be major factors contributing to the activity of these catalysts. The better performance of Shell 324 is probably due to its high metal loading, about twice the amounts as are on SMR7-6137(4) and CB 81-44 and three times that on SMR7-6137(1). The almost equal denitrogenation activity and perhaps slightly better +850°F conversion of CB 81-44 may be due to the beneficial effects of a bimodal pore size distribution even with the lower metal loading.

6. Both unimodal and bimodal catalysts suffer a large reduction in surface area, pore volume, and average pore diameter during use. The major portion of this reduction occurs during the first 50 hours on stream. The bimodal catalysts show a smaller overall reduction in the surface area but a larger reduction in pore volume.
7. The unimodal catalysts (i.e., Shell 324 and SMR7-6137(4)) are capable of being restored to their original state upon regeneration, while the bimodal catalysts (i.e., CB 81-44 and SMR7-6137(1)) undergo a small loss of surface area and pore volume and have slightly higher densities after regeneration. This is attributed to the slightly higher levels of metals (Ti, Fe, Ca) deposition experienced by the bimodal catalysts during their use.

VI. RECOMMENDATIONS

Based on the results obtained and the experience gained through the operation of the unit, the following recommendations are made.

1. Because of the short duration of a run and the fact that the continuous stirred tank reactor requires about thirty hours to line out, over 50% of the run is conducted in an unsteady-state fashion. To eliminate much of this, operation should be conducted at a single reactor temperature throughout a given run. Data obtained for different catalysts at a reaction temperature of 750°F may not be substantially different, making catalyst comparisons difficult. Reaction temperatures of 800°F or above may result in excessive coking and have adverse effects on catalyst activity, as noted for Shell 324. These temperatures are at the upper end of those usually employed in running fixed-bed hydroprocessing reactors. A reaction temperature of 780°F is recommended, since the denitrogenation and conversion levels are high enough for catalyst comparison and it is an intermediate temperature in hydroprocessing.
2. A more detailed investigation of the effects of pore size and metals loading should be conducted. Because of the apparent effect of pore size distribution, a series of catalysts with different distributions should be developed and evaluated in order to obtain an optimum pore size. Catalysts with higher metals loadings, such as Shell 324, should be synthesized and tested using the optimum pore structure obtained previously.

3. Operation at higher concentrations of SRC-I (e.g., 70:30, SRC-I:solvent) should be attempted in order to enhance the deactivation rates during a short term run and to provide more useful operating data.
4. Thermal baseline experiments should be conducted.
5. Since these catalysts will be used in the second stage of integrated two-stage liquefaction, the proper test feedstock would be short contact time product, and runs should be made using this material.
6. The precision of the distillation and nitrogen analytical data should be improved, if at all possible, since conversion of +850⁰F material and nitrogen removal are crucial characteristics for any catalyst test.

VII. ACKNOWLEDGMENT

The authors would like to acknowledge the assistance of the Analytical Chemistry Division for their efforts in analyzing the products on a timely basis. Also, the dedicated efforts of the technicians of the Process Sciences Division are greatly appreciated. All catalysts and feedstocks were supplied by C.E. Lummus. The encouragement and support of PETC management are acknowledged.

VIII. NOMENCLATURE

a	decay constant
A	asphaltenes
C _A	concentration of asphaltenes
C _R	concentration of resins
C _{A0}	initial concentration of asphaltenes
C _{R0}	initial concentration of resins
C _{Fi}	percent insolubles in the feed for solvent i
C _{Pi}	percent insolubles in the products for solvent i
E	activation energy
f _a	fraction of carbon atoms that are aromatic
f ₀	fraction of initial carbon atoms that are aromatic
k _f	forward reaction rate constant
k _r	reverse reaction rate constant
k _{AR}	first order rate constant for asphaltenes to resins
k _{RO}	first order rate constant for resins to oils
LHSV	liquid hourly space velocity
N	exponent
P	pressure
R	universal gas constant
t	time
ΔS	change in catalyst surface area
S ₀	initial catalyst surface area
T	temperature
ΔV	change in catalyst pore volume
V ₀	initial catalyst pore volume

VHSV volume hourly space velocity

X_i conversion for solvent i

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X. APPENDICES

APPENDIX A

MICROFILTRATION EQUIPMENT AND PROCEDURES

Microfiltration Test for Determining Coal Conversions

Description

This method is designed to determine the insoluble solids portion of a coal liquefaction product. The content of insolubles will vary qualitatively and quantitatively depending on the solvent used.

Summary

A representative sample of the coal liquid is dissolved (and/or dispersed) in the designated solvent. The solution is poured into a Millipore filter apparatus that is prefitted with a 10-mm Teflon filter. The vial that contained the sample is washed with solvent, and the solvent is added to the Millipore filter apparatus, which is then sealed. Four hundred ml of the same solvent is added to the large reservoir above the filtration unit; and the filtration apparatus is pressurized to 40 psig (dry nitrogen). After liquid stops flowing out of the filtration apparatus, the filter cake is removed, dried, and weighed. The dried residue should be a friable powder containing no tarry material.

Precision

Standard deviation = ± 0.50 (tetrahydrofuran)

± 0.50 (ethyl acetate)

± 0.50 (pentane)

Calculations

$$\% \text{ Conv.} = \frac{AW - I}{AW (1-C)} \times 100 \quad (A-1)$$

A - weight fraction of MF coal in feed charge to reactor

W - sample weight used in microfiltration determination

I - weight of insolubles (based on solvent used)

C - weight fraction of ash in MF coal.

Equipment Needed

1. Solvent
 - Tetrahydrofuran (Fisher Histological Grade)
 - Ethyl Acetate (Fisher Certified Pesticide Grade)
 - N-Pentane (Fisher Certified Pesticide Grade)
2. Waring Blender (Model 31 BL 42)
3. Eberbach #9590 Semi-Micro Container Assembly
4. Eberbach Teflon gasket kit for blender assembly #8762
5. Millipore 47-mm stainless steel filtration cell, 190 ml (#XX40-047-00)
6. Millipore 47-mm teflon Mitex filters, 10-mm pores (LCWP o47-00)
7. Millipore Teflon cap O-ring (XX40-047-19)
8. Millipore Teflon sealing O-ring (XX40-047-16)
9. Whitey 1000-ml stainless steel sampling cylinder (304-HDF4-1000)
10. Bottles, 22-ml.
11. Aluminum weighing pan
12. 1000-ml flask
13. Small ultrasonic bath (American Beauty #069-S-30)

Procedure:

1. Add coal liquefaction product to the blender containing solvent, and gradually increase the blender speed to maximum over a 1-minute period.
2. Pipette samples of 5-6g out of the blender into 22-ml preweighed vials. Then weigh again the preweighed sample bottles to determine the exact weight of the aliquot. Prepare six samples.
3. Partially assemble Millipore apparatus by placing a preweighed 10-mm filter and preweighed Teflon sealing O-ring into the cell. Place a piece of Teflon tubing between the outlet of the filtering apparatus and the 1000-ml glass flask.

4. Dilute the samples (in the sample vials) with either tetrahydrofuran, ethyl acetate, or pentane. Stir each sample with a glass rod, and put the vial into the ultrasonic bath for approximately 3 minutes.
5. Pour the contents of the sample vial (obtained from Step 4) into the filtration cell and wash out the sample bottle with the particular solvent being used. Then fill the cell with solvent.
6. Assemble the Millipore apparatus as shown in the attached diagram.
7. Close Valve V_1 . Add 400 ml of solvent to the large reservoir. Then connect filtration apparatus to a dry low pressure nitrogen source (40 psig).
8. Close valve 3, and open valves 1 and 2. Leave 40 lb pressure on the cell until the solvent has passed through. There will be a pressure surge when all of the solvent has passed through the filter and nitrogen begins passing through the filter cake. Allow the nitrogen to pass through the cake for 3 minutes.
9. Close valve 2 and open valve 3 to vent the apparatus. Discard liquid collected in filter flask.
10. Disassemble the filter cell, and put the Teflon sealing O-ring, filter paper, and residue into the preweighed weighing pan. Inspect the filter cell and scrape any residue on the walls into the weighing pan.
11. Dry the residues (one from each of the three solvents) in a vacuum oven at 100°C for one hour.
12. Remove pan from oven, cool, and weigh. Reject any determination that does not give a friable filter cake or shows evidence of a tarry residue.
13. Repeat Steps 4 thru 12 for each of the solvents: tetrahydrofuran, ethyl acetate, and pentane.

Example:

Samples of liquefaction product from a run having a feedstock consisting of 25 wt% Illinois #6 (Burning Star mine) coal in creosote oil are collected. The coal contains 10.1% ash on a moisture-free basis. The following data were obtained from the filtration determinations:

<u>Solvent</u>	<u>Tetrahydrofuran</u>	<u>Ethyl Acetate</u>	<u>Pentane</u>
weight of sample	5.643 g	5.878 g	5.784 g
weight of filter			
cake (insols)	0.238 g	0.469 g	1.004 g

$$\text{THF conv.}^{(1)} = \frac{(5.643)(0.2500) - 0.238}{(5.643)(0.2500)(1-0.101)} \times 100 = 92.5\%$$

$$\text{EA conv.} = \frac{(5.878)(0.25) - 0.469}{(5.878)(0.25)(1-0.101)} \times 100 = 75.7\%$$

$$\text{C}_5 \text{ conv.} = \frac{(5.784)(0.2500) - 1.004}{(5.784)(0.2500)(1-0.101)} \times 100 = 34.0\%$$

(1) Coal conversion as measured by solubility in tetrahydrofuran.

Figure A1,- Microfiltration unit.

9-25-79 L-16991

APPENDIX B

CATALYST PORE SIZE DISTRIBUTIONS

Figure B1.- Pore size distribution of Shell 324.

L-82066

Figure B2.-Pore size distribution of SMR 7-6137 (1).

L-82064

Figure B3.- Pore size distribution of SMR7-6I37 (4).

L-82063

Figure B4.-Pore size distribution of CB 81-44.

L-82065

APPENDIX C

MATERIAL BALANCE AND PRODUCT YIELD RESULTS

TABLE C1: Material Balance and Product Yields for Run No. LC-R01;
Catalyst; Shell 324

Operating Conditions

Elapsed Time, hr	18.0
Reactor Temperature, °F	750.4
Reactor Pressure, psig	2017.0
VHSV, hr ⁻¹	1.01
Residence Time, min	127.

<u>Elemental Analysis</u>	<u>Feed g/hr</u>	<u>Product g/hr</u>	<u>Closure %</u>
Carbon	156.00	154.94	100.00
Hydrogen	11.97	13.36	95.8
Nitrogen	2.26	1.91	84.6
Sulfur	0.87	0.35	45.8
Total	173.53	173.50	101.2

Product Yields

Gas, wt% feed	
C1-C4	0.62
C5-C7	0.16
CO, CO ₂	0.00
H ₂ S	0.03
Total	0.81

Liquids, vol% feed

IBP-390°F
390°-500°F
500°-650°F
650°-850°F
850°-EPT.
Residue
Total

Hydrogen Consumption, g/100g feed	1.25
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TABLE C2: Material Balance and Product Yields for Run No. LC-R02;
Catalyst: SMR7-6137(1)

Operating Conditions

Elapsed Time	34.0	78.0	105.0
Reactor Temperature, °F	752.7	780.0	780.0
Reactor Pressure, psig	2002.	2005.	2016.
VHSV, hr ⁻¹	1.17	1.23	1.23
Residence Time, min	109.	104.	104.

Elemental Analysis	Feed g/hr	Product g/hr	Closure %	Feed g/hr	Product g/hr	Closure %	Feed g/hr	Product g/hr	Closure g/hr
Carbon	179.40	178.85	100.0	189.30	187.44	100.0	185.82	183.68	100.0
Hydrogen	13.85	14.84	92.5	14.58	15.22	91.3	14.04	15.17	92.3
Nitrogen	2.61	2.61	99.9	2.75	2.50	91.1	2.68	2.46	91.7
Sulfur	1.00	0.60	63.5	1.06	0.42	64.7	1.03	0.41	55.8
Total	203.67	200.50	100.5	211.28	208.50	100.0	206.47	205.00	100.6

Product Yields

Gas, wt% feed			
C1-C4	0.34	1.08	1.47
C5-C7	0.01	0.04	0.06
CO, CO ₂	0.00	0.00	0.00
H ₂ S	0.02	0.13	0.10
Total	0.37	1.25	1.40

Liquids, vol% feed

IBP-390°F	0.00	0.00	0.40
390°-500°F	3.93	3.24	4.41
500°-650°F	19.65	16.15	20.42
650°-850°F	33.23	33.61	29.57
850°-EPT.	10.60	7.38	5.83
Residue	34.75	45.55	37.16
Total	102.23	105.93	97.79

Hydrogen Consumption,
g/100g feed

0.84	0.80	1.08
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TABLE C3: Material Balance and Product Yields for Run No. LC-R03;
Catalyst: CB 81-44

Operating Conditions

Elapsed Time	26.5	73.5	105.0
Reactor Temperature, °F	749.9	779.9	779.8
Reactor Pressure, psig	1996.	2018.	2002.
VHSV, hr ⁻¹	1.08	1.02	1.02
Residence Time, min	119.	116.	117.

<u>Elemental Analysis</u>	<u>Feed</u> <u>g/hr</u>	<u>Product</u> <u>g/hr</u>	<u>Closure</u> <u>%</u>	<u>Feed</u> <u>g/hr</u>	<u>Product</u> <u>g/hr</u>	<u>Closure</u> <u>%</u>	<u>Feed</u> <u>g/hr</u>	<u>Product</u> <u>g/hr</u>	<u>Closure</u> <u>g/hr</u>
Carbon	166.69	166.07	100.0	156.98	154.47	100.0	158.23	156.77	100.0
Hydrogen	12.96	13.69	91.4	12.06	12.96	92.5	12.16	12.88	90.8
∞ Nitrogen	2.41	2.01	83.4	2.27	1.96	86.3	2.29	1.91	83.6
Sulfur	0.74	0.37	53.4	0.79	0.26	55.0	0.79	0.26	63.4
Total	185.21	182.50	99.3	174.82	170.50	99.8	176.20	174.00	100.3

Product Yields

Gas, wt% feed		
C1-C4	0.39	1.69
C5-C7	0.03	0.06
CO, CO2	0.00	0.23
H2S	0.02	0.11
Total	0.44	2.09

Liquids, vol% feed

IBP-390°F	0.00	0.26
390°-500°F	3.51	2.83
500°-650°F	18.35	13.39
650°-850°F	35.36	31.62
850°-EPT.	3.21	5.00
Residue	40.29	33.95
Total	100.72	87.05

Hydrogen Consumption,
g/100g feed

0.76	1.20	0.97
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TABLE C4: Material Balance and Product Yields for Run No. LC-R08;
Catalyst: Shell 324

Operating Time									
Elapsed Time		32.0		70.0				104.0	
Reactor Temperature, °F		749.8		779.3				779.6	
Reactor Pressure, psig		2003.		2008.				2034.	
VHSV, hr ⁻¹		0.57		0.59				0.58	
Residence Time, min		203.		211.				220.	
Elemental Analysis									
	Feed	Product	Closure	Feed	Product	Closure	Feed	Product	Closure
	<u>g/hr</u>	<u>g/hr</u>	<u>%</u>	<u>g/hr</u>	<u>g/hr</u>	<u>%</u>	<u>g/hr</u>	<u>g/hr</u>	<u>g/hr</u>
Carbon	101.45	101.24	100.0	103.36	102.53	100.0	102.41	101.36	100.0
Hydrogen	7.79	9.19	80.3	7.96	9.10	80.7	7.55	9.08	79.1
8 Nitrogen	1.41	1.02	72.4	1.44	0.92	63.9	1.43	0.96	67.5
Sulfur	0.45	0.17	39.8	0.46	0.17	39.2	0.46	0.17	42.4
total	112.85	113.50	98.6	115.36	115.20	98.9	114.42	113.50	97.7
Product Yields									
Gas, wt% feed									
C1-C4		0.19		0.88				1.01	
C5-C7		0.09		0.04				0.16	
CO, CO ₂		0.00		0.00				0.00	
H ₂ S		0.01		0.01				0.02	
Total		0.29		0.92				1.18	
Liquids, vol% feed									
18P-390°F		0.00		0.00				0.00	
390°-500°F		3.13		3.48				3.73	
500°-650°F		21.01		25.11				24.17	
650°-850°F		37.17		38.95				40.70	
850°-EPT.		14.91		13.71				14.71	
Residue		28.19		26.36				27.77	
Total		109.41		107.61				111.08	
Hydrogen Consumption, g/100g feed		1.73		1.63				1.99	

TABLE C5: Material Balance and Product Yields for Run No. LC-R09;
Catalyst: SMR7-6137(1)

Operating Conditions									
Elapsed Time		32.0		72.0		100.0			
Reactor Temperature, °F		749.9		780.1		780.3			
Reactor Pressure, psig		2030.		2033.		2015.			
VHSV, hr ⁻¹		0.68		0.62		.59			
Residence Time, min		182.		196.		196.			
<u>Elemental Analysis</u>	<u>Feed</u>	<u>Product</u>	<u>Closure</u>	<u>Feed</u>	<u>Product</u>	<u>Closure</u>	<u>Feed</u>	<u>Product</u>	<u>Closure</u>
	<u>g/hr</u>	<u>g/hr</u>	<u>%</u>	<u>g/hr</u>	<u>g/hr</u>	<u>%</u>	<u>g/hr</u>	<u>g/hr</u>	<u>g/hr</u>
Carbon	121.11	120.56	100.0	108.55	107.70	100.0	103.52	101.70	100.0
Hydrogen	9.16	10.26	81.3	8.40	9.64	83.0	8.29	8.93	81.3
87 Nitrogen	1.68	1.49	88.2	1.52	1.13	74.3	1.44	1.13	78.5
Sulfur	0.54	0.27	50.8	0.49	0.12	24.5	0.46	0.17	38.7
Total	134.71	135.00	99.0	121.69	119.00	97.5	115.16	113.0	98.7
Product Yields									
Gas, wt% feed									
C1-C4		0.44			0.84			1.81	
C5-C7		0.07			0.04			0.17	
CO, CO ₂		0.00			0.00			0.00	
H ₂ S		0.00			0.00			0.01	
Total		0.52			0.89			1.99	
Liquids, vol% feed									
IBP-390°F		1.43			0.57			0.19	
390°-500°F		3.02			3.90			4.22	
500°-650°F		19.29			19.04			19.52	
650°-850°F		38.13			39.30			36.61	
850°-EPT.		2.09			3.57			3.28	
Residue		42.64			35.75			32.88	
Total		106.60			102.13			96.70	
Hydrogen Consumption,									
g/100g feed		1.13			1.65			1.40	

TABLE C6: Material Balance and Product Yields for Run No. LC-R10;
Catalyst; CB 81-44

Operating Conditions

Elapsed Time	33.0
Reactor Temperature, °F	749.7
Reactor Pressure, psig	2020.
VHSV, hr ⁻¹	0.69
Residence Time, min	173.

<u>Elemental Analysis</u>	<u>Feed g/hr</u>	<u>Product g/hr</u>	<u>Closure %</u>
Carbon	121.60	121.21	100.0
Hydrogen	9.40	10.51	92.9
Nitrogen	1.70	1.50	88.2
Sulfur	0.54	0.27	50.8
Total	136.17	136.50	101.4

Product Yields

Gas, wt% feed

C ₁ -C ₄	0.26
C ₅ -C ₇	0.10
CO, CO ₂	0.00
H ₂ S	0.00
Total	0.36

Liquids, vol% feed

IBP-390°F	0.00
390°-500°F	0.26
500°-650°F	4.89
650°-850°F	37.17
850°-EPT.	34.96
Residue	25.76
Total	103.04

Hydrogen Consumption,
g/100g feed

1.31

TABLE C7: Material Balance and Product Yields for Run No. LC-R11;
Catalyst: SMR7-6137(4)

Operation Conditions

Elapsed Time	31.0	70.0	100.0
Reactor Temperature, °F	750.0	779.9	780.3
Reactor Pressure, psig	2016.	2047.	2018.
VHSV, hr ⁻¹	0.66	0.63	0.60
Residence Time, min	179.	188.	199.

<u>Elemental Analysis</u>	<u>Feed</u> <u>g/hr</u>	<u>Product</u> <u>g/hr</u>	<u>Closure</u> <u>%</u>	<u>Feed</u> <u>g/hr</u>	<u>Product</u> <u>g/hr</u>	<u>Closure</u> <u>%</u>	<u>Feed</u> <u>g/hr</u>	<u>Product</u> <u>g/hr</u>	<u>Closure</u> ⁽¹⁾ <u>g/hr</u>
Carbon	116.12	115.71	100.0	111.84	110.78	100.0	105.35	104.04	100.0
Hydrogen	9.10	10.11	99.1	8.75	9.76	97.1	8.16	9.41	103.5
Nitrogen	1.63	1.28	78.8	1.62	1.16	71.3	1.54	1.10	69.1
Sulfur	0.52	0.19	36.9	0.56	0.18	32.5	0.47	0.17	36.8
Total	130.03	128.00	101.58	124.96	122.00	100.9	118.3	116.12	103.9

Product Yields

Gas, wt% feed			
C1-C4	0.34	0.95	1.69
C5-C7	0.07	0.14	0.15
CO, CO ₂	0.00	0.00	0.00
H ₂ S	0.00	0.00	0.00
Total	0.41	1.09	1.84

Liquids, vol% feed

IBP-390°F	0.86	0.00	1.83
390°-500°F	5.14	3.87	6.38
500°-650°F	24.86	21.43	27.65
650°-850°F	35.23	48.31	37.96
850°-EPT.	7.99	0.00	0.00
Residue	28.81	30.80	31.64
Total	102.89	104.41	105.46

Hydrogen Consumption,
g/100g feed

1.38	1.54	1.98
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(1) Based on adjustment of product rate

TABLE C8: Material Balance and Product Yields for Run No. LC-R12;
Catalyst: CB 81-44

Operation Conditions

Elapsed Temperature	33.0	72.0	100.0
Reactor Temperature, °F	750.1	780.2	779.7
Reactor Pressure, psig	2021.	2024.	2039.
VHSV, hr ⁻¹	0.57	0.54	.58
Residence Time, min	213.	212.	212.

	Feed g/hr	Product g/hr	Closure %	Feed g/hr	Product g/hr	Closure %	Feed g/hr	Product g/hr	Closure g/hr
<u>Elemental Analysis</u>									
Carbon	103.39	103.06	100.0	96.77	95.90	100.0	103.46	102.59	100.0
Hydrogen	8.15	9.01	88.5	7.58	8.55	88.5	8.00	9.05	87.7
Nitrogen	1.38	1.08	78.7	1.35	0.95	70.2	1.51	1.09	72.1
Sulfur	0.46	0.11	24.8	0.43	0.11	25.0	0.46	0.17	37.0
Total	114.75	114.00	100.32	108.24	105.50	99.4	115.98	114.50	99.9
 Product Yields									
Gas, wt% feed									
C1-C1		0.27			0.74			0.83	
C5-C7		0.10			0.17			0.12	
CO, CO ₂		0.00			0.29			0.00	
H ₂ S		0.00			0.00			0.00	
Total		0.37			1.21			0.95	
 Liquids, vol% feed									
IBP-390°F		0.05			0.00			0.41	
390°-500°F		5.78			3.22			4.49	
500°-650°F		22.28			20.75			24.79	
650°-850°F		38.68			43.95			34.70	
850°-EPT.		4.49			1.66			7.71	
Residue		29.11			29.82			33.93	
Total		100.39			99.40			105.62	
Hydrogen Consumption, g/100g feed		1.35			1.65			1.63	

TABLE C9: Material Balance and Product Yields for Run No. LC-R13;
Catalyst: Shell 324

Operating Conditions

Elapsed Time	31.0	70.0	100.0
Reactor Temperature, °F	750.0	780.1	779.8
Reactor Pressure, psig	2036.	2027.	2013.
VHSV, hr ⁻¹	0.60	0.54	0.56
Residence Time, min	199.	215.	-----

Elemental Analysis	Feed g/hr	Product g/hr	Closure %	Feed g/hr	Product g/hr	Closure %	Feed g/hr	Product g/hr	Closure g/hr
Carbon	108.48	108.05	100.0	96.70	95.55	100.0	100.16	99.12	100.0
Hydrogen	8.41	9.68	89.9	7.48	8.67	86.7	7.76	9.10	88.6
Nitrogen	1.58	1.21	76.4	1.41	0.86	60.7	1.46	1.05	72.1
Sulfur	0.55	0.24	44.1	0.49	0.16	33.3	0.51	0.22	43.8
Total	121.88	121.00	100.1	108.41	107.00	99.6	112.53	111.00	99.6

Product Yields

Gas, wt% feed		
C ₁ -C ₄	0.40	1.21
C ₅ -C ₇	0.04	0.13
CO, CO ₂	0.00	0.00
H ₂ S	0.00	0.00
Total	0.44	1.34

Liquids, vol% feed

IBP-390°F	2.22	2.10	3.13
390°-500°F	4.59	4.93	4.07
500°-650°F	27.63	26.57	48.84
650°-850°F	37.88	34.38	41.22
850°-EPT.	0.00	5.60	1.37
Residue	32.49	27.21	38.36
Total	104.81	100.79	96.99

Hydrogen Consumption,
g/100g feed

1.61	1.89	1.92
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APPENDIX D

CONVERSION DATA

TABLE D1: Conversion Data from Run No. LC-R01; Catalyst: Shell 324

Elapsed Time, hr	Conversion ⁽¹⁾ +850°F, vol%	Conversion, wt%					H/C in Products	% Change in H/C
		<u>Ethyl Acetate</u>	<u>Cyclohexane</u>	<u>Pentane</u>	<u>HDS</u>	<u>HDN</u>		
11.5		79.45	46.03	38.16	60.00	23.08	1.03	11.78
24.5		56.31	44.32	28.97	60.00	15.38	1.04	12.73
31.0		57.78	41.39	37.93	60.00	15.38	1.04	12.53
41.5		56.68	36.26	35.86	60.00	15.38	1.01	9.96
50.5		69.22	53.36	49.20	20.00	7.69	1.08	17.83
63.5		65.94	51.40	48.28	60.00	15.38	1.05	13.74

(1) No data available

TABLE D2: Conversion Data from Run No. LC-R02; Catalyst: SMR7-6137(1)

Elapsed Time, hr	Conversion ⁽¹⁾ +850°F, vol%	Conversion, wt%					H/C in Products	% Change in H/C
		<u>Ethyl Acetate</u>	<u>Cyclohexane</u>	<u>Pentane</u>	<u>HDS</u>	<u>HDN</u>		
16.5		56.73	29.98	28.79	60.00	7.69	1.00	8.15
24.5		50.88	32.85	29.02	60.00	7.69	0.99	7.68
31.5		52.94	35.73	29.94	60.00	7.69	0.99	6.71
39.0		53.68	36.45	34.97	40.00	0.00	1.00	7.91
47.5		48.09	38.13	28.79	60.00	7.69	1.00	8.51
63.5		60.84	43.65	37.72	60.00	7.69	1.00	8.27
76.5		57.47	46.04	36.81	60.00	7.69	1.00	8.63
83.0		56.10	42.45	34.75	60.00	7.69	0.98	5.62
89.5		56.10	40.05	35.66	60.00	7.69	0.98	6.59
102.5		64.32	43.17	34.06	60.00	7.69	0.98	6.36
110.0		56.79	42.69	37.72	60.00	7.69	0.99	7.43
120.0		56.89	43.17	36.12	60.00	7.69	0.98	5.89

(1) No data available

TABLE D3: Conversion Data from Run No. LC-R03; Catalyst: CB 81-44

Elapsed Time, hr	Conversion ⁽¹⁾ +850°F, vol%	Conversion, wt%					H/C in Products	% Change in H/C
		<u>Ethyl Acetate</u>	<u>Cyclohexane</u>	<u>Pentane</u>	<u>HDS</u>	<u>HDN</u>		
16.5		55.17	39.70	35.59	52.94	13.73	1.02	9.66
24.5		50.58	36.93	36.05	52.94	13.73	1.01	8.84
31.5		51.69	36.18	33.52	52.94	13.73	0.99	6.46
39.5		47.15	34.17	31.23	52.94	13.73	0.99	6.93
51.5		60.64	50.00	45.49	52.94	13.73	1.00	7.17
65.5		55.35	46.98	41.55	52.94	13.73	1.01	8.48
78.5		56.57	44.72	41.32	64.71	9.80	1.01	8.36
85.5		64.65	54.27	47.28	52.94	21.57	1.05	11.70
94.0		57.21	45.48	41.32	52.94	13.73	1.00	8.00
103.5		57.03	47.99	41.55	41.18	13.73	1.00	8.00
110.0		57.73	44.72	38.57	64.71	13.73	1.01	8.36
120.0		54.83	44.47	37.42	41.18	13.73	0.98	5.62

(1) No. data available

TABLE D4: Conversion Data from Run No. LC-R08 and LC-R13; Catalyst: Shell 324

Elapsed Time, hr	Conversion +850°F, vol%	Conversion, wt%					H/C in Products	% Change in H/C
		Ethyl Acetate	Cyclohexane	Pentane	HDS	HDN		
17.0	17.63	65.97	61.94	57.88	42.86	30.61	1.14	24.40
29.0	16.57	71.87	49.08	43.76	65.71	26.53	1.07	16.89
37.0	13.37	56.68	51.71	45.71	65.71	26.53	1.09	18.88
47.0	20.96	63.25	62.99	57.77	77.14	38.78	1.06	15.85
62.0	0.58	68.16	43.03	41.81	65.71	22.45	1.05	14.91
75.0	21.84	64.44	62.99	55.45	65.71	34.69	1.07	16.20
90.0	1.11	58.54	53.27	53.26	77.14	34.69	1.06	15.85
109.0	19.74	62.06	74.02	58.37	65.71	30.61	1.08	17.28
118.0	5.98	57.48	69.84	60.07	8.57	30.61	1.08	17.82
12.0	20.47	67.63	62.64	58.27	65.71	30.77	1.10	18.24
26.0	19.80	67.41	60.74	56.20	65.71	26.92	1.07	14.85
36.0	27.49	79.04	62.64	51.82	54.29	23.08	1.08	15.75
46.0	3.51	64.28	60.74	49.05	54.29	19.23	1.08	15.88
62.0	26.98	72.29	69.07	66.11	65.71	34.62	1.11	18.89
75.0	23.85	68.34	69.78	61.96	65.71	38.46	1.09	16.93
90.0	6.20	70.70	65.73	61.27	54.29	26.92	1.10	18.77
105.0	32.16	70.86	65.97	58.04	54.29	26.92	1.10	18.64
118.0	10.14	70.43	67.40	60.81	54.29	26.92	1.09	16.80

TABLE D5: Conversion Data from Run No. LC-R09; Catalyst: SMR7-6137(1)

Elapsed Time, hr	Conversion +850°F, vol%	Conversion, wt%					H/C in Products	% Change in H/C
		<u>Ethyl Acetate</u>	<u>Cyclohexane</u>	<u>Pentane</u>	<u>HDS</u>	<u>HDN</u>		
12.0	15.56	66.99	54.45	32.39	62.50	20.00	1.02	10.85
26.0	14.76	64.90	50.96	36.41	62.50	16.00	1.04	12.92
37.0	14.32	64.96	44.74	43.50	50.00	12.00	1.02	10.76
48.0	14.96	65.69	53.20	37.83	62.50	16.00	1.03	11.47
64.0	14.67	73.41	61.67	58.63	75.00	20.00	1.04	12.67
77.0	21.38	66.54	63.91	63.83	75.00	24.00	1.07	16.48
90.0	24.22	63.90	61.92	47.75	75.00	20.00	1.04	13.17
105.0	23.65	73.65	67.39	47.75	62.50	20.00	1.05	14.24
118.0	20.77	65.69	65.90	65.72	62.50	16.00	1.03	12.09

TABLE D6: Conversion Data from Run No. LC-R11; Catalyst: SMR7-6137(4)

Elapsed Time, hr	Conversion +850°F, vol%	Conversion, wt%					H/C in Products	% Change in H/C
		<u>Ethyl Acetate</u>	<u>Cyclohexane</u>	<u>Pentane</u>	<u>HDS</u>	<u>HDN</u>		
12.0	19.04	63.14	53.32	49.84	62.50	24.00	1.07	12.59
26.0	15.30	93.85	54.68	46.82	62.50	24.00	1.07	13.22
36.0	21.75	58.91	54.68	42.03	62.50	20.00	1.05	10.82
46.0	19.77	59.58	49.25	43.04	62.50	16.00	1.07	12.84
62.0	15.43	69.29	64.99	56.65	62.50	24.00	1.07	13.10
75.0	35.45	69.47	60.11	55.14	62.50	24.00	1.06	11.73
90.0	12.47	67.36	60.65	54.88	62.50	24.00	1.06	12.22
105.0	34.36	73.88	60.38	51.61	62.50	24.00	1.09	14.64
118.0	26.11	67.72	62.28	53.37	62.50	24.00	1.09	15.15

TABLE D7: Conversion Data from Run No. LC-R12; Catalyst: CB 81-44

Elapsed Time, hr	Conversion +850°F, vol%	Conversion, wt%					H/C in Products	% Change in H/C
		<u>Ethyl Acetate</u>	<u>Cyclohexane</u>	<u>Pentane</u>	<u>HDS</u>	<u>HDN</u>		
12.0	27.75	78.70	73.90	70.63	75.00	36.00	1.10	17.23
26.0	28.78	70.38	61.88	51.39	62.50	24.00	1.09	15.95
38.0	21.31	70.98	61.61	52.91	75.00	24.00	1.05	11.83
46.0	5.96	69.65	58.70	48.10	62.50	20.00	1.06	13.08
62.0	36.52	72.07	68.76	57.97	75.00	20.00	1.06	13.24
77.0	25.55	73.09	67.44	58.48	75.00	28.00	1.07	14.03
90.0	4.00	68.81	66.12	55.70	62.50	24.00	1.06	12.45
105.0	7.67	74.06	67.97	51.39	62.50	24.00	1.06	12.83
118.0	12.14	70.38	63.20	56.46	50.00	20.00	1.06	12.99