

## EXTRACTION OF A NORTH DAKOTA LIGNITE WITH SUPERCRITICAL ALIPHATIC SOLVENTS

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### Introduction

Extraction of coal with various solvents has been a commonly used method for obtaining knowledge about the structure of coal and its chemical composition. Solvent extraction of coal has been classified into four different types by Oele and others (1), and Dryden (2,3). A recent review of solvent extraction was prepared by Pullen (4).

1. Nonspecific extraction - nonspecific solvents extract only a small percentage of the coal. These solvents tend to primarily dissolve the waxy and resinous compounds which reside in the coal's physical structure in the form of resin bodies and particles.
2. Specific extraction - specific solvents extract a larger portion of the coal (up to ~40%) with the extracted material closely resembling the insoluble coal residue. The effectiveness of these solvents has been attributed to the existence of an unshared pair of electrons on nitrogen or oxygen in the solvent molecule thereby making the solvent behave as a polar fluid (3,4).
3. Extractive disintegration or degradation - this type of extraction occurs at temperatures between 200° and 400°C where the percent extraction is dependent on the production of smaller soluble fractions by the thermal decomposition of the coal. Solvents under these conditions can dissolve up to ~40% of the coal at temperatures of 400°C.
4. Extractive chemical disintegration - these extractions dissolve the coal by thermally decomposing and chemically reacting with the coal to form smaller molecular fragments (1). Most of this work involves using hydrogen-donor solvents (i.e., solvents that can either donate hydrogen to the various reactive coal species or at least act as a hydrogen transfer agent) to manufacture liquid products from the coal.

Interest in the extraction of coal (and other substrates) with supercritical solvents has been increasing rapidly over the past fifteen years. This interest is primarily due to the enhanced solubility of substrates in the fluid phase that occurs at or above the critical point. Also, the solvent power of the solvent (which depends on the solvent density) can be conveniently controlled over a large range with small changes in the solvent pressure or temperature (5,6). Most of the coal extractions using supercritical fluids have been performed at temperatures above 350°C. Squires and others (7) reported that thermal decomposition processes were becoming significant above 325°C for the extraction of an Illinois No. 6 coal with supercritical methanol. This suggests that results from supercritical fluid extractions above this temperature are a combination of physical and chemical solvent-coal interactions.

The twofold objectives of this research are to investigate, in the context of the solvent extraction model presented above, the fundamental principles of solute-solvent interactions at or above the solvent critical point and to use supercritical solvent extraction (SCSE) as a method for determining various molecular fractions present in low-rank coals. In order to minimize the thermal decomposition component in the supercritical fluid extraction of low-rank coals, solvents were selected with critical temperatures below the temperature at which volatile matter is evolved by destructive distillation (i.e., <325°C).

### Experimental

#### Materials

The solvents used were n-pentane through n-octane and cyclohexane available commercially in HPLC grade. The coal used was Indian Head lignite (Indian Head mine, Zap, ND) vacuum dried for at least a week at 10 micron Hg and room temperature. The proximate and ultimate analyses for this lignite are shown in Table I.

Table I. Proximate and Ultimate Analyses for Indian Head Lignite (mf basis).

#### Proximate Analysis

Volatile Matter	39.8
Fixed Carbon (By difference)	46.7
Ash	13.5

#### Ultimate Analysis

Hydrogen	3.85
Carbon	60.79
Nitrogen	1.47
Sulfur	0.89
Oxygen (By difference)	19.51
Ash	13.5

### Supercritical Fluid Processing

Extractions of Indian Head lignite samples were performed using the aliphatic solvents mentioned above. These experiments were performed using a semicontinuous supercritical solvent extraction system. A flow sheet for this system is shown in Figure 1. In this system a fixed bed of coal (50 gm) was contained in a 25.4 cm by 1.75 cm ID section of high pressure tubing by one micron sintered metal frits. The preheating coils and fixed bed of coal were then immersed in a preheated fluidized sand bath where supercritical conditions were achieved in less than seven minutes. A Ruska positive displacement pump and high pressure accumulator were used to provide a pulseless flow of solvent through the system once supercritical conditions were reached. A solvent flow rate of 120 mL/hr was maintained for two hours. The pressure of the supercritical solvent was reduced to atmospheric pressure after passing a back pressure regulator. The extract and solvent were collected in a chilled sample

vessel. The noncondensable product gas was measured and collected for subsequent analysis.

### Analytical

After each experiment, the extracted lignite residue and solvent-extract mixture were rotary vacuum distilled at ~30 mm Hg and 80°C and weighed. This procedure insured that a solvent and moisture-free product was obtained for material balance purposes. The collected product gases were analyzed by gas chromatography. Residues were analyzed by thermogravimetric analysis (TGA). Proximate and ultimate analyses were performed on selected samples.

Analysis of the solid extracts obtained by the supercritical hydrocarbon extractions were accomplished by column separations, infrared spectroscopy, 60 MHz proton NMR and capillary GC. Separations of the acids from the extracts was accomplished by the following procedure. The extract was dissolved in a warmed chloroform-methanol mixture (1:1). The soluble portion was added to a column containing Sephadex A25 ion exchange resin. The eluent from the column was evaporated and the acid-free fraction was weighed. The column was eluted again with a solution of formic acid (7 m%) in chloroform-methanol (1:1, 33 m%). Evaporation of this eluent gave a fraction consisting of fatty and resin acids. The acid-free wax was dissolved in carbon tetrachloride and analyzed by an infrared calibrated for the ester carbonyl peak and the alcohol OH-stretching peak.

### Discussion and Results

#### Temperature and Pressure Effects

As mentioned above, one of the potential advantages of supercritical fluid extraction is the relatively large change in the solute solubility that can be achieved with small changes in solvent pressure or temperature. This premise was tested in the following way. A series of isobaric experiments using supercritical pentane to extract Indian Head lignite at various temperatures was carried out to investigate the effects of operating temperature on the percent conversions. The operating conditions of these runs and their resulting conversions are shown in Table II. As shown in

Table II. Operating Conditions and Results for Supercritical Pentane Extractions of Indian Head Lignite at Constant Pressure,  $P_r = 1.50$ .

Operating Temp., °C	$T_r^{**}$	Operating Pressure (Psia)	% Conversion (maf)*	% Yield (maf)*
206	1.020	735	1.50	1.1
235	1.083	735	1.50	0.34
270	1.158	735	1.50	1.4
300	1.222	735	1.50	0.63 (?)

\*% conversion  $\frac{\text{wt maf coal} - \text{wt maf residue}}{\text{wt maf coal}}$ ; % yield =  $\frac{\text{wt maf extract}}{\text{wt maf coal}}$

\*\* $T_r = \frac{\text{operating temperature of solvent (°K)}}{\text{critical temperature of solvent (°K)}}$ ;  $P_r = \frac{\text{operating pressure of solvent (psia)}}{\text{critical pressure of solvent (psia)}}$

Figure 2, the percent conversion initially decreased with an increase in operating temperature up to 235°C. This decrease was caused by the decrease in the solvent density that occurs with increasing temperature. The conversion then increased with further increases in the operating temperature up to 270° and 300°C, respectively. These increases were due to increased thermal effects in the coal which more than offset the decrease in solubility caused by the decreased solvent density.

Table III shows how temperatures affected the percent conversions and yields of three (two hexanes and one heptane) supercritical extractions. These results also indicate that percent conversions increase with increasing temperature. However, the differences observed between the isothermal hexane and heptane experiments indicate that higher conversions are obtained as the operating temperature approaches the solvent critical temperature (i.e.,  $T_r$  goes to one). These results are consistent with those reported by Blessing and Ross (8).

Table III. Operating Conditions and Results for Supercritical Hexane and Heptane Extractions of Indian Head Lignite at Constant Reduced Pressure,  $P_r = 2.0$ .

Solvent	Operating Temperature (°C)	$T_r$	Operating Pressures (Psia)	% Conversion (maf)	% Yield (maf)
n-Hexane	244	1.020	860	3.1	1.3
n-Hexane	278	1.087	860	5.3	1.6
n-Heptane	278	1.020	795	6.5	1.7

The effect of pressure on supercritical fluid extractions was investigated by performing a series of isothermal extractions using supercritical hexane at various pressures to extract Indian Head lignite. The operating conditions and results of these experiments are shown in Table IV. The percent conversions and yields for these experiments are plotted in Figure 3. The results displayed in Figure 3 suggest that a maximum in the solubility of Indian Head lignite in supercritical hexane occurs in the vicinity of  $P_r = 2.0$ . The existence of a maximum in solute solubility occurring as a function of pressure have been reported for a South African coal in supercritical toluene (9) and for biphenyl in supercritical  $CO_2$  (10). The reasons stated for these maxima were the differences between the pressure dependent solubility parameters of the coal and the solvent or by performing extractions at pressures above the upper critical region end point together with "free volume" effects (size asymmetry between the solute and solvent) as in the case of the biphenyl -  $CO_2$  system. Figure 4 illustrates the improved solvent power that resulted from small increases in the solvent pressure from  $P_r = 1.5$  to 2.0 for the extractions using supercritical heptane, octane and cyclohexane. This figure also suggests that changes in the operating pressure have a larger effect on the solvent power of the supercritical solvent at higher operating temperatures. It appears from the data presented above that the yields from the extraction of Indian Head lignite with supercritical aliphatic solvents were not affected to a large extent by either the operating temperature or pressure. This could be due to a limited amount of compounds present in the coal which are selectively extracted by aliphatic solvents under 325°C. The differences between the percent yield and conversion data were due to the production of gas (primarily  $CO_2$ ) and the formation of water from the coal.

Table IV. Operating Conditions and Results for Supercritical Hexane Extraction of Indian Head Lignite at Constant Temperature,  $T_r = 1.02$ .

Operating Temp. ( $^{\circ}\text{C}$ )	Operating Pressure (Psia)	$P_r$	% Conversion (maf)	% Yield (maf)
244	450	1.05	2.2	0.9
244	650	1.50	2.3	1.0
244	860	2.00	3.2	1.4
244	1080	2.50	2.6	1.3
244	1295	3.00	3.0	1.1

### Analytical Results and Discussion

The effect of supercritical extraction on the thermal characteristics of the resulting residues was investigated using thermogravimetric analyses. Table V shows the operating conditions and conversions obtained for each of the residues analyzed by TGA. Figure 5 displays the differential weight loss for the five supercritical fluid extracted residues as functions of the sample temperature. A sample of the vacuum dried "as run" Indian Head lignite was also plotted for comparison purposes. This figure suggests that the supercritical fluid solvents used in this paper were extracting more of the compounds that would devolatilize below  $\sim 400^{\circ}\text{C}$  with the increased operating temperature necessary with the longer solvent chain length.

Table V. Operating Conditions and Results for Supercritical Extraction of Indian Head Lignite at Constant Reduced Temperatures and Pressures,  $T_r = 1.02$ ,  $P_r = 2.0$ .

Solvent	Operating Temp ( $^{\circ}\text{C}$ )	Operating Pressure (Psia)	% Conversion (maf)	% Yield (maf)
n-Pentane	206	980	3.1	0.6
n-Hexane	244	860	3.2	1.3
n-Heptane	278	795	6.5	1.7
n-Octane	307	720	9.8	2.2
Cyclohexane	291	1180	9.1	2.5

The analyses of the extracts revealed the presence of aliphatic esters, alcohols, acids and alkanes with little or no aromatics being extracted. Separations and quantitative infrared spectroscopy have been performed on the chloroform-methanol soluble fractions ( $\sim 50$  wt %) from the supercritical pentane and hexane extractions to date. The yields from this preliminary data averaged 0.19%, 0.06%, and 0.26% for the waxy esters, aliphatic alcohols and the fatty acids, respectively. Proton NMR showed that the aromatic content of the extracts tended to increase slightly with increasing operating temperature. Capillary GC analyses on whole samples and silica gel column separated samples using a 15 m SE-54 column provided data on the distribution of normal

and cyclic alkanes, waxy esters, and fatty alcohols and acids. The series of n-alkanes occurred between C<sub>21</sub> and C<sub>33</sub> with a maximum concentration of the C<sub>29</sub> alkane. A number of triterpanes and C<sub>15</sub> to C<sub>20</sub> cyclic alkanes were present. The fatty alcohols were found to be mainly C<sub>24</sub>. The fatty acids were converted to their methyl esters for analysis. A series of esters was observed with maximum concentration at C<sub>24</sub> and C<sub>26</sub>. From the composition and yield data, it appears that extraction of Indian Head lignite with supercritical aliphatic solvents with critical temperatures below 325°C still has the characteristics of nonspecific extraction.

#### Acknowledgment

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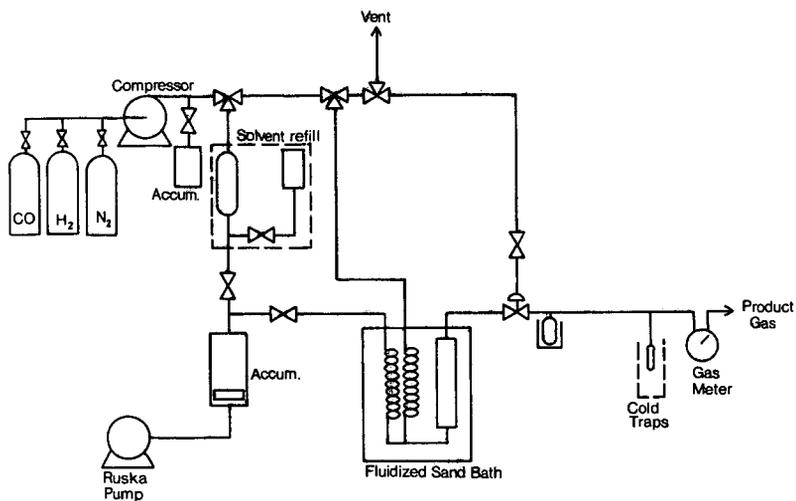


Figure 1. Equipment flowsheet for the semi-continuous supercritical solvent extraction system.

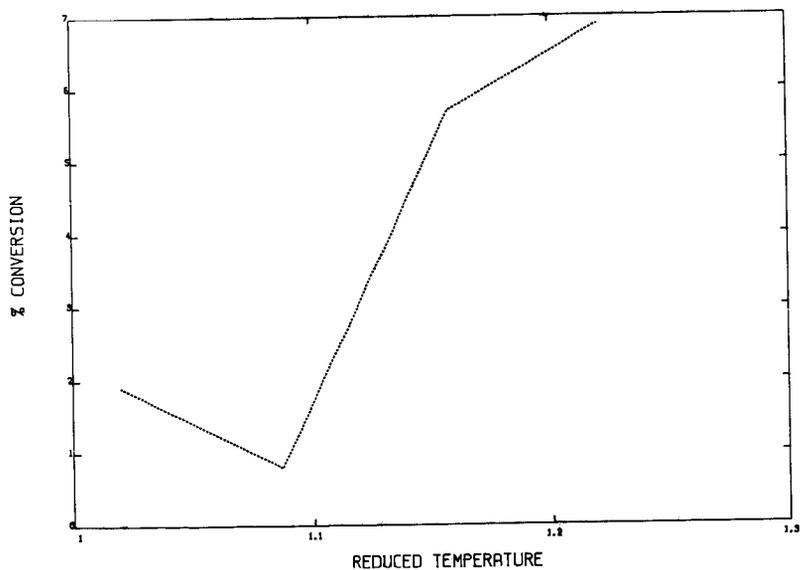


Figure 2. Temperature effects of supercritical pentane extraction on conversions.

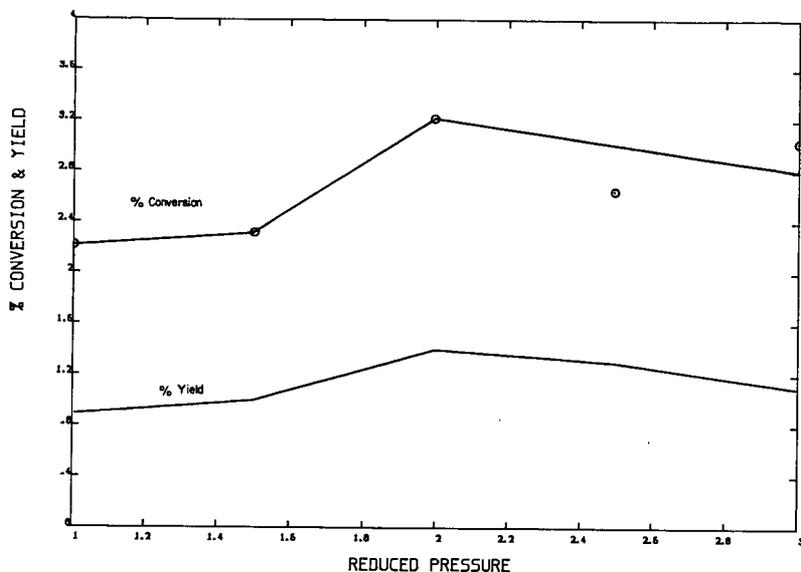


Figure 3. Pressure effects of supercritical hexane extractions on conversions and yields.

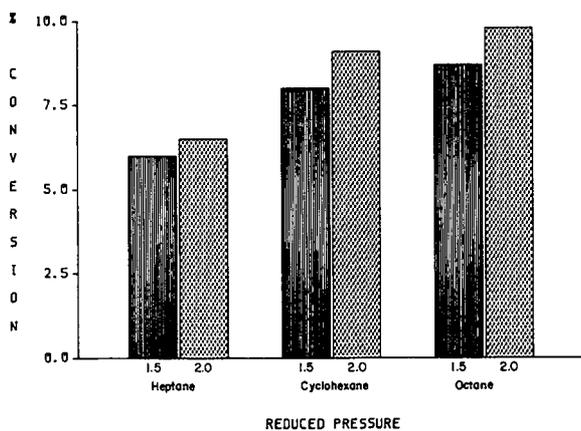


Figure 4. Pressure effects of heptane, cyclohexane and octane supercritical extractions on conversion.

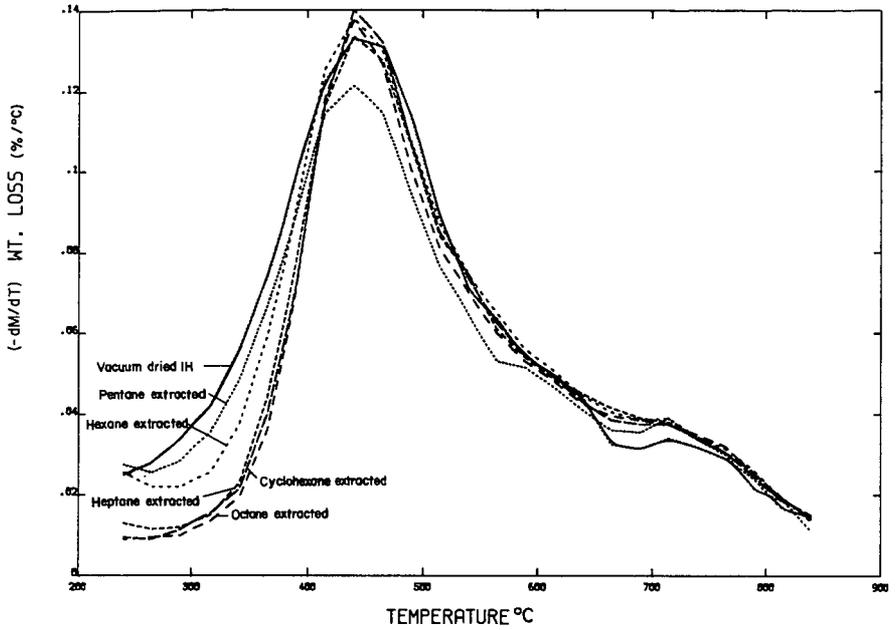


Figure 5. TGA rate of weight loss for supercritical solvent extracted residues.

## FRACTIONAL DESTRUCTION OF COAL-DERIVED RESIDUUM

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### ABSTRACT

An apparatus has been developed to fractionate coal-derived residuum by exploiting the solvent power of fluids near their critical points. Termed Fractional Destruction, the method fractionates residuum according to the solubility of its constituent components in a supercritical fluid. The novel aspect of the approach is the incorporation of a system to promote reflux of less-soluble components onto a packed bed. Fractionation of residuum will facilitate the determination of previously unattainable information concerning the composition and process-related behavior of this complex material. This paper describes operation of the unit to fractionate a residuum sample produced at the Wilsonville Advanced Coal Liquefaction Test Facility.

### INTRODUCTION

Describing the behavior of undefined mixtures, whether from natural or synthetic sources, often begins with the separation of these complex systems into effective pseudocomponents by distillation (1). Each pseudocomponent is then characterized as if it were a pure compound, and its characterization data are used in appropriate correlations. The presence of nonvolatile residuum poses a serious limitation to such methodology. For coal-derived liquids, heavy crude oils, tar sands, and shale oil, more than 50 percent of the fluid may not be distillable (1). Since this nonvolatile residue cannot be separated using conventional techniques, new methods of separation and characterization must be developed to provide the necessary information for design and operation of plants utilizing the fossil fuels mentioned above (2).

Apart from the need to fractionate residuum-containing fossil fuels for the measurement and prediction of thermophysical properties, other important problems could be resolved better through the study of residuum pseudocomponents. Two examples in the area of coal liquefaction are the role of residuum (a) in hydrogen utilization and hydrogen transfer and (b) in the manifestation of harmful biological effects.

Work at the Pittsburgh Energy Technology Center has been directed at the development of novel technology for the separation of fossil fuel residuum into effective pseudocomponents. In this respect, application of supercritical fluids in a manner similar to that reported by Zosel (3) is being developed. This approach is similar to conventional distillation in that an apparatus is used not only to extract the residuum but also to cause part of the residuum in the fluid phase to return as reflux onto a packed bed. This liquid reflux is caused by increasing the temperature of the supercritical fluid phase at constant pressure, thereby decreasing the density of the supercritical fluid and its carrying capacity for the residuum. Operation of a system in this region of retrograde condensation has recently been reported in the literature (4). Other recent investigations support the hypothesis that supercritical solubility is a density-driven phenomenon in the absence of strong associating forces in the solvent (5). The method is called either Supercritical Distillation or, as Zosel suggested, Fractional Destruction. This report describes the use of this technology to

fractionate a coal-derived residuum from the Wilsonville Advanced Coal Liquefaction Test Facility.

## EXPERIMENTAL

The experimental unit, called the Fractional Destruction Unit (FDU), has been designed to contact a 3-4 kg charge of residuum with a continuous flow of supercritical fluid at conditions up to 673 K and 27.6 MPa. The heart of the FDU is the Fractional Destruction Vessel (FDV) shown in Figure 1. The FDV consists of a modified 3.8-L 316 stainless steel pressure vessel onto which is attached a 78-cm column fabricated of 316 stainless steel (6.03-cm o.d., 1.11-cm wall). The column contains a packed bed and a condenser section. In the experiments reported here, the 30-cm bed section was packed with 0.41-cm stainless steel Pro-Pak protruded metal distillation packing from Scientific Development Co., State College, Pa. This is the same packing used in a conventional Podbelniak distillation column. The condenser consists of a removable 38-cm finger made of 316 stainless steel (2.67-cm o.d., 0.78-cm wall) that is heated by an internal cartridge heater to promote reflux. A triple zone furnace is used to control the temperature in the extraction zone. Temperature control on the column is accomplished with independently controlled band heaters on the packed bed and condenser sections.

The desired charge of residuum is placed in the extraction section of the FDV, and the entire unit is purged with nitrogen. The FDU is then brought up to the operating temperature before beginning solvent flow. The destruction fluid is then pumped as a liquid through a preheater to raise its temperature above the critical point before it is introduced into the FDV through the sparging device at the bottom. The pressure is controlled by a high-temperature Badger-Meter control valve located near the outlet of the FDV. After traveling up the column, the fluid stream, which now contains destructed residuum, exits at the top of the FDV and is partially depressurized through the heated control valve into a separator constructed of a 2.25 L (approximately 10.2-cm o.d., 42.5-cm long) 304 stainless steel cylinder. The separator is operated slightly above the critical temperature of the solvent ( $T_R \approx 1.02$ ) at a pressure of 0.8 MPa. Separation of the residuum from the supercritical fluid is accomplished by the reduction in pressure. The residuum is drained and collected from the bottom of the separator at periodic intervals, while the solvent is flashed to atmospheric pressure, condensed, and recovered as a liquid. The operation of the FDU will be reported in detail in a later publication.

Toluene ( $T_C = 591.7$  K,  $P_C = 4.115$  MPa) and cyclohexane ( $T_C = 553.4$  K,  $P_C = 4.074$  MPa) were used as the supercritical fluids in the work reported here. They were obtained in drum quantities at greater than 99 percent purity and used as received. Owing to inefficiency in the separator, some of the destructed residuum is collected with the solvent. This material is recovered in a rotary evaporator. The distilled solvent is then reused in the FDU. In the figures in this report that depict residuum overhead data, correction has been made for the residuum recovered in the spent solvent.

The residuum used in the work reported here was collected from the T102 vacuum distillation tower during Run 242 at the Wilsonville Advanced Coal Liquefaction Test Facility. This run was made using Illinois No. 6 coal from the Burning Star mine in what is termed a Short-Contact-Time Integrated Two-Stage Liquefaction (SCT-ITSL) mode (6). During the time this particular sample was collected, the T102 unit was operated at 594 K and 3.4 KPa. The residuum was crushed to minus 0.64 cm and mixed by riffing before use.

## DISCUSSION

Operation of the FDU with coal-derived residuum was preceded by tests on pure compounds and distillable coal liquids using n-pentane as the supercritical fluid (7). The results of tests with the coal-derived distillate showed that the FDU was basically performing as expected. Liquid reflux was generated by means of the hot finger when the device was operated at a temperature slightly above the critical temperature of the transport fluid. When reflux was established, fractionation based upon volatility was observed. Poorer separation was achieved in the absence of reflux.

The first work on the T102 bottoms involved operation in the non-reflux mode to obtain base-line data on the transport of this residuum in various hydrocarbon solvents. Using n-pentane, cyclohexane, and toluene at a  $T_R$  of 1.02 and at a  $P_R$  of 2, the residuum brought overhead was 23, 54, and 67 percent of that charged, respectively. Based on this information, further studies were performed using cyclohexane as the supercritical fluid, since a large portion of the residuum could be destructed at a temperature similar to or less than that in the T102 separator.

A two-step destruction procedure was developed to maximize the amount of T102 residuum brought overhead. In the first step, toluene is used in a manner similar to conventional supercritical extraction to produce a nearly ash-free material for subsequent fractionation. This first step is called the non-reflux mode because the column of the FDU is maintained at the same temperature as the extraction section. In the second step, called the reflux mode, the column and finger are heated to a higher temperature than the extraction section, which causes the density of the fluid to decrease as it travels up the column and thus promotes reflux of the less-soluble components. These two steps are described below.

In the non-reflux mode, the FDU was used to process five 800-gram charges of the T102 bottoms. Repetitive operation of the unit was performed to produce sufficient quantities of the final fractions for subsequent characterization and experimentation. Figure 2 summarizes the operation of the FDU during these five destructions. Shown is the amount of residuum brought overhead as a function of the time on stream at a  $P_R$  of 2. As previously mentioned, the residuum overhead data include residuum recovered from both the separator and the spent solvent. The FDU was maintained at a  $T_R$  of 1.02, with overall variance in temperature for the five tests being  $\pm 5$  K. Temperature variance during any one test was  $\pm 2$  K. The differences observed, especially in the final amounts destructed, appear to be due to this small temperature variance between runs. The higher yields were consistently obtained at temperatures nearer the critical point. This phenomenon appears to be particularly sensitive to the temperature of the extraction zone when the fluid is first introduced. The fact that the initial dissolution of the residuum in the fluid influences the overall yield suggests that components in the residuum may be acting as cosolvents.

Table 1 contains the elemental analysis of the T102 bottoms, the material brought overhead with toluene, the residue remaining after the toluene destruction, and the starting coal used at Wilsonville during Run 242. The toluene overhead represented 66.8 percent of the material charged to the FDU, and the residue accounted for 27.9 percent. Other material collected from the FDU includes 4.2 percent in the spent solvent and 2.7 percent recovered during cleaning of the FDU and separator with tetrahydrofuran. The total material balance is 101.6 percent. This number also includes any residual toluene or tetrahydrofuran in the various samples. The overhead collected from the five destructions was ground and combined before use in the reflux mode experiments.

As previously mentioned, cyclohexane was chosen for the fractionation solvent for the second step, since it could transport sufficient quantities of residuum at reasonable temperatures. In the reflux mode, the column of the FDU is operated at

a higher temperature than the extraction zone. As the carry-over of residuum decreases, the temperature of the column is reduced to cause the density in this region to increase and consequently more residuum is transported overhead. This is repeated until the column is at the same temperature as the extraction zone. In this work, four fractions were brought overhead by operating the column initially at 593 K and then decreasing the temperature to 578, 573, and 563 K as the residuum carry-over approached 1.0 gram per gram-mole of cyclohexane. This concentration value is calculated from the amount of residuum collected from the bottom of the separator after a 30-minute collection period and from the amount of cyclohexane pumped during that period. The column temperatures were selected both from density estimation and from actual experimentation. A more detailed discussion of the development of the operational parameters for the reflux mode will be presented in a future paper.

Figure 3 illustrates the difference between operation of the FDU in the non-reflux and the reflux modes with cyclohexane. This figure depicts the results in terms of the overhead concentration of residuum. The reflux mode data represent one of three replicate fractionations that were performed on the T102 toluene distraction overhead. Each point represents a 30-minute sample collection period. Owing to the limited quantity of toluene overhead produced, no non-reflux mode experiments were conducted using this material. From the earlier development work, however, several non-reflux mode experiments were performed on the T102 residuum sample from Run 242. The non-reflux mode data in Figure 3 were derived from one of these experiments and adjusted for comparability to the data from the reflux mode. The adjustment compensates for separator inefficiency and for residuum insoluble in supercritical toluene. All but the last three data points in the non-reflux mode data represent 15-minute sample periods. The only other difference between the two tests was the solvent delivery rate, which was 0.24 mole per minute for the non-reflux mode, and 0.43 mole per minute in the reflux mode.

As shown in Figure 3 the temperature of the column was initially 30 degrees higher than the pot, which produced the reduced carry-over rate by causing reflux to occur. An expanded view of the carry-over concentration is shown in Figure 4. This view shows more clearly how residuum carry-over is manipulated by changes in the column temperature. Figure 5 contains the same information for the three replicate cyclohexane fractionations performed on the toluene overhead. Conditions in all three experiments were similar; however, the small deviations due to inherent limitations of the process controllers produced some overlap between successive fractions. The amount of overlap is estimated at 2.6 percent between Fractions 1 and 2, 2.5 percent between Fractions 2 and 3, and 3.0 percent between Fractions 3 and 4. Also, 32 grams that should have been in the 573 K fraction were inadvertently collected in the 578 K fraction. The respective fractions and residues from the three fractional distractions were ground and combined before characterization.

Table 2 contains the analysis of the four overhead fractions and the residue. The overall material balance was 96.1 percent, with 57.2 percent of the charge being brought overhead (includes residuum recovered from spent solvent) and 31.7 percent remaining in the residue. An additional 7.2 percent was recovered upon cleaning the unit with tetrahydrofuran. The trends evident from the elemental analysis indicate that the components that have lower molecular weights, higher hydrogen-to-carbon ratios, and lower heteroatom contents are concentrated in the earlier fractions. Also note that the separator inefficiency is highest for the earlier fractions, indicating that the more volatile components are more readily carried through the separator with the solvent. The material carried through the separator with the solvent was not mixed with the respective fractions collected from the separator. Independent characterization of these samples will provide valuable insight into the operation of the separator.

The molecular weight data in Table 2 were determined by vapor pressure osmometry (VPO) and gel permeation chromatography (GPC). The molecular weight increases

regularly from Fraction 1 to the residue. In comparison, the VPO molecular weights for six fractions collected in the non-reflux mode cyclohexane destraction shown in Figure 3 range from 441 to 471, with no consistent trend. The polydispersity values ( $M_w/M_n$ ) shown for the four fractions in Table 2 are less than those for the non-reflux mode fractions, which ranged from 1.47 for the first fraction to 1.88 for the sixth fraction. This number is a measure of the breadth of the molecular weight distribution and shows that operation in the reflux mode produces fractions with narrower molecular weight distributions than those prepared without reflux.

In Figure 6 the GPC traces for the four fractions and for the residue from each of the three cyclohexane fractional destractions are overlaid. The trend to higher molecular weight distributions as the fractionation proceeded is evident, as well as the reproducibility of the fractionation process. Additional characterization of similar samples produced in the FDU is the subject of another paper (9).

### CONCLUSIONS

The main conclusion to be drawn from the experimental data presented here is that fractionation of residuum through the use of a supercritical fluid system incorporating internal reflux produced by retrograde condensation results in sharper fractions than those obtained by ordinary supercritical extraction. The capability of the FDU to process coal-derived residuum in the internal reflux mode has been demonstrated. The density-driven separation does appear to fractionate the residuum on the basis of volatility, with lower molecular weight species preceding larger ones.

Other methods of fractionation with supercritical fluids are conceivable. One such possibility could involve manipulation of the pressure during the destraction or upon subsequent separation of the fluid and residuum. The relative merits of such possibilities remain to be explored. Successful development of such technology will result in the ability to fractionate and characterize material currently intractable by conventional methods.

### DISCLAIMER

Reference in this report to any specific product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

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TABLE 1. Analysis of Feed Coal to Run 242, T102 Bottoms After Grinding and Mixing, and Materials Produced by Supercritical Extraction of T102 Bottoms With Toluene in the Non-Reflex Mode.

	ILLINOIS <sup>a</sup> NO. 6 COAL	RUN 242 <sup>b</sup> T102 BOTTOMS	TOLUENE OVERHEAD	TOLUENE RESIDUE
C	68.4	79.1	87.4	60.3
H	4.4	5.9	6.7	3.5
O	11.9 <sup>c</sup>	4.0 <sup>c</sup>	4.0 <sup>d</sup>	7.1 <sup>d</sup>
N	1.4	1.3	1.3	1.4
S	3.2	1.0	0.7	0.9
Cl	0.1	---	---	---
ASH	10.6	8.7	<0.1	29.4
H/C	0.77	0.89	0.91	0.69
M <sub>N</sub> (VPO, 353 K, PYRIDINE)	---	---	574	e

<sup>a</sup>Analysis from Wilsonville report, see reference 6. <sup>b</sup>Approximately 8 percent unconverted coal content. <sup>c</sup>Determination by difference. <sup>d</sup>Direct determination. <sup>e</sup>Insufficient solubility in pyridine.

TABLE 2. Characterization of Materials Produced From the Cyclohexane Fractional Destruction of the Toluene Overhead Sample in Table 1.

	FRACTION DESIGNATION <sup>a</sup>				RESIDUE
	593 K	578 K	573 K	563 K	
C	87.8	87.3	87.4	87.0	87.0
H	7.6	7.5	7.2	6.5	5.9
O <sup>b</sup>	3.5	3.7	3.3	3.7	4.9
N	0.9	0.9	1.2	1.4	1.8
S	0.5	0.6	0.6	0.7	0.9
ASH	---	---	---	---	<0.1
H/C	1.03	1.02	0.98	0.89	0.81
RESIDUAL CYCLOHEXANE, % <sup>c</sup>	0.5	0.5	0.8	0.6	0.5
RECOVERY, % <sup>d</sup>	23.9	13.0	13.8	6.4	31.7
SEPARATOR INEFFICIENCY, % <sup>e</sup>	27.5	17.8	8.4	11.1	---
MELTING RANGE, K	333-338	363-373	393-403	448-463	~573
M <sub>N</sub> , VPO <sup>f</sup>	393	479	578	645	1226
M <sub>N</sub> , GPC <sup>g</sup>	407	449	527	564	715
M <sub>w</sub> , GPC	504	601	851	1010	1996
M <sub>w</sub> /M <sub>N</sub>	1.24	1.34	1.62	1.79	2.79

<sup>a</sup>The temperature refers to the reflux and packed bed zone. The residue is the material remaining in the extraction zone. <sup>b</sup>Direct determination. <sup>c</sup>Determination by Headspace Chromatography, see reference 8. <sup>d</sup>Total recovery of material based upon weight of toluene overhead charged to the unit. Except for the residue this includes both residuum recovered from the fraction receiver and from the spent solvent. <sup>e</sup>Percent of total material overhead recovered in the spent solvent. <sup>f</sup>Determination in pyridine at 353 K. <sup>g</sup>Determination on PLgel 100A column with THF eluent.

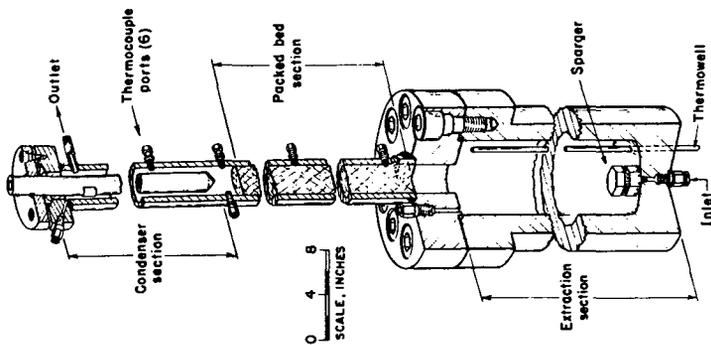


Figure 1. Sectional view of fractional distraction unit.

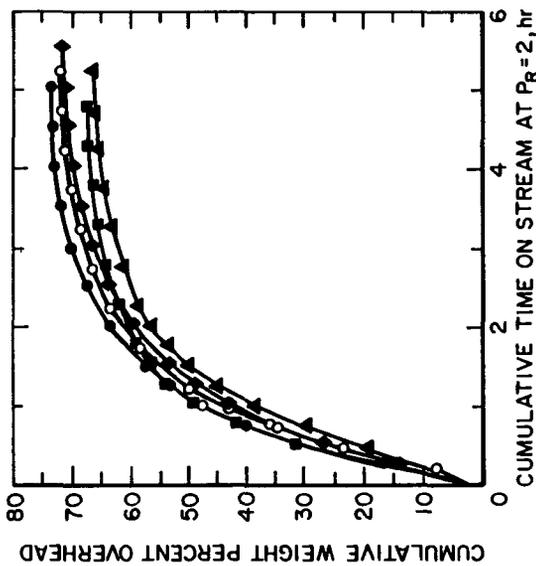


Figure 2. Comparison of five replicate distractions (non-reflux mode) of Wilsonville Run 242 T102 residuum using toluene.

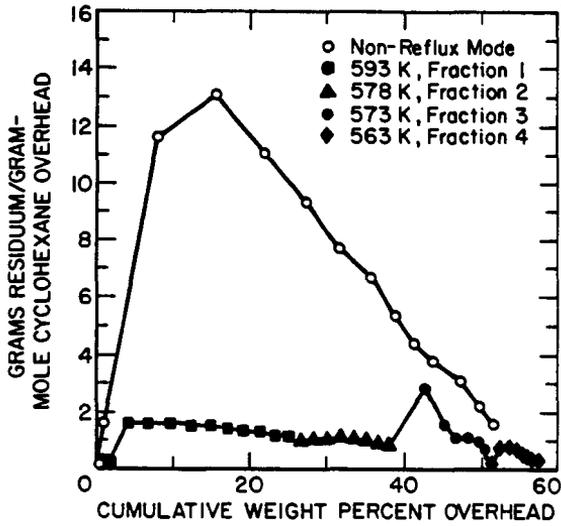


Figure 3. Comparison of non-reflux and reflux modes of operation using cyclohexane. Temperatures indicated are those of the column in the reflux mode. Pot temperature was 563 K in both modes.

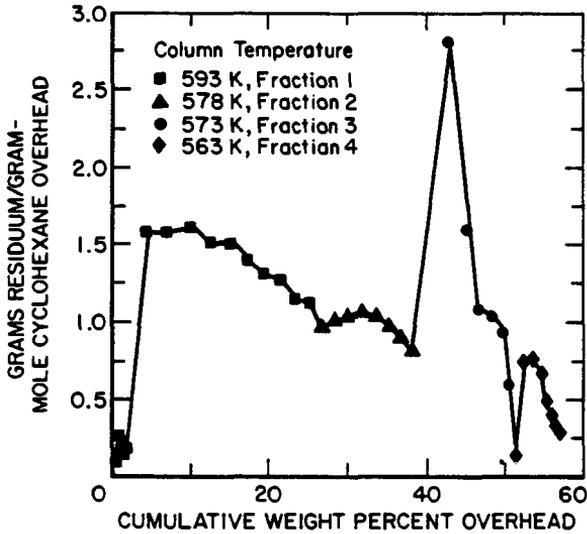


Figure 4. Fractional destruction of toluene overhead using cyclohexane.

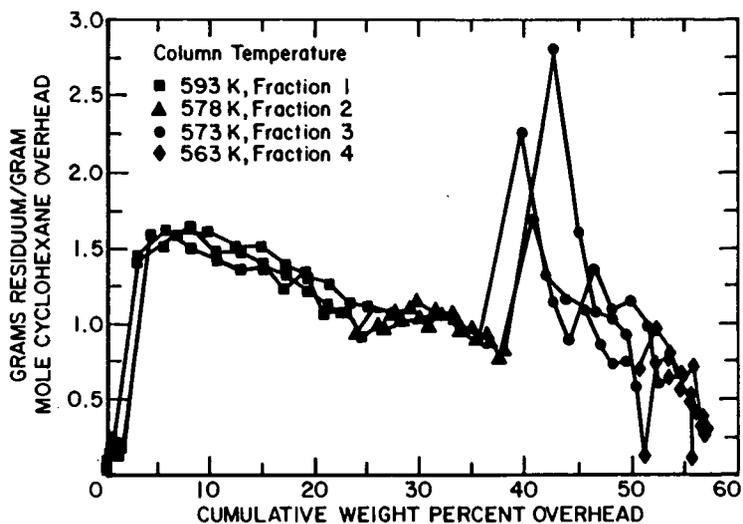


Figure 5. Comparison of three replicate fractional distractions (reflux mode) of toluene overhead using cyclohexane.

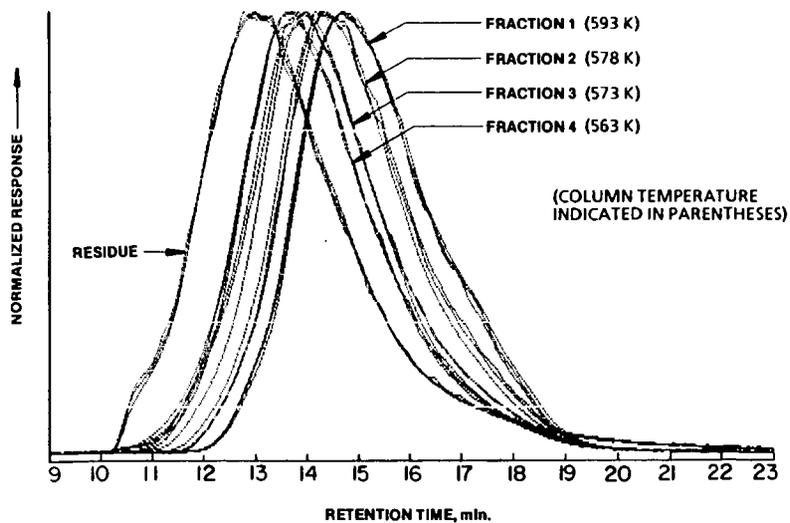


Figure 6. Comparison of the GPC results for the three replicate fractional distractions of toluene overhead using cyclohexane.

## SEPARATION OF HEAVY OILS USING SUPERCRITICAL FLUIDS

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### INTRODUCTION

This paper focuses on separations of heavy oils and materials from synthetic fuels which are of sufficiently high molecular weight that they cannot be separated by distillation. There is, however, the possibility of fractionating these heavy oils by solvent extraction. This is done commercially by use of low molecular weight paraffins to extract a high-quality deasphalted oil (DAO) from the low-quality asphaltene fraction.

Since 1960 consideration has been given to potential use of supercritical gases as solvents for the separation of heavy oils. A general review of this field is given by Funk and Irani (1). This paper addresses the important question of selectivity and in particular examines the selectivity differences which one can obtain with supercritical gases versus conventional liquid solvents.

New experimental data are presented for the supercritical extraction of heavy oils using carbon dioxide and CO<sub>2</sub>/solvent mixtures and also phase-equilibrium data for extraction with liquid solvents to allow rational interpretation of differences in selectivity.

This paper also presents a non-analytical, statistically based technique for interpretation of experimental data which can complement the numerous analytical models (2,3,4) available for analysis of supercritical extraction data.

### DEASPHALTING -- LIQUID SOLVENTS AND SUPERCRITICAL GASES

Table 1 presents a summary of the properties of typical heavy oils which are separated by solvent deasphalting using paraffinic solvents. This extraction aims to produce an oil which is free of the very high molecular weight asphaltenes, lower in metals content (Ni, V, Fe), and with minimal quantities of heteromolecules (N, S, O).

Figure 1 shows a schematic diagram of a typical solvent deasphalting process. It is basically a countercurrent liquid-liquid extraction. The paraffinic solvent is recovered by vaporization or advanced heat-integrated schemes which recover the solvent as a supercritical fluid (5).

Selectivity in this extraction shows very interesting behavior. It is completely predictable, and predictable over a wide variety of liquid solvents. Figure 2 shows this "universal" curve for vanadium with Athabasca bitumen as the heavy oil. One sees that the fraction of vanadium in the oil fraction is a simple function of the yield of extract. Other similar curves hold for other major properties (S, N, O) and this behavior is found with a variety of other heavy oils (Arabian Long, Tia Juana Resid, Jobo).

Figure 2 doesn't just include extraction with paraffins but a variety of other solvent types (ketones, alcohols, amines, aldehydes, etc.). It also holds for mixed solvent systems (6). These data were obtained at ambient temperature and with a solvent/oil ratio of 10.

A key question in the field of supercritical extraction is whether supercritical gases can show selectivity behavior which deviates from the type of universal curve shown in Figure 2.

A detailed study of the use of supercritical propane (1) showed that there are no differences in selectivity when the extraction is compared at the same yield (the correlating factor in Figure 2). The experimental data presented in Figure 3 illustrate this point. First, simple comparison of liquid propane at 60°C and 7.72 MPa with supercritical propane extraction at 115°C ( $T_c$  for propane = 97°C) does show very different behavior. The yield curves are shown in Figure 3 and the extraction at supercritical conditions gives metal concentrations 20-25% of those obtained with liquid propane. However, pressure is a key variable in the supercritical extraction and increasing the pressure increases the DAO solubility; at a pressure of 10.34 MPa, the yield curve matches the curve for extraction with liquid propane. For these conditions (115°C, 10.34 MPa), the extracted DAO has extremely similar properties (Ni, V, Fe, S, O, N) to the extraction at sub-critical conditions.

This study with propane suggests that for paraffins, there is no inherent selectivity to extracting with the solvent as a supercritical gas although it may appear so if results are not compared at equal yield of DAO.

#### EXTRACTION WITH SUPERCRITICAL CO<sub>2</sub> AND CO<sub>2</sub>/SOLVENT MIXTURES

Figure 4 presents a schematic diagram of the extraction unit used for these experimental studies. The gas goes from the cylinder to a compressor which brings it to the system pressure. The extractor is stainless steel and the gas enters the bottom of the extractor and is dispersed by a stainless steel grid. The extractor contains the feedstock oil, which is distributed over glass beads to provide good contact between gaseous solvent and the oil. The extracted material and solvent leave the top of the extractor, the pressure is reduced and extracted material is collected for analysis. The basic design of the unit is similar to that proposed by Reid (7) and Eckert (8).

Figure 5 presents experimental data on the extraction of a heavy Boscan crude with supercritical CO<sub>2</sub> at 40°C ( $T_c$  for carbon dioxide = 31°C) from 5 to 25 MPa. Carbon dioxide was selected for this study because it is widely used in supercritical extraction and also because it may give selectivity (weakly acidic and with a quadruple moment). The results in Figure 5 show that CO<sub>2</sub> is a very poor solvent for heavy oils compared to propane. Even pressures of 24 MPa give only 2% oil in the extract phase (comparable results with propane (1) give 20-30% oil in the extract phase).

The selectivity results are very interesting and are summarized in Table 2. These data show a high selectivity for basic nitrogen compounds such as pyridines and quinolines. For example, the  $\beta$ (extract/feed) of the pyridines is 85. This is a very high selectivity and is very different for the low selectivities shown in the universal curve (Figure 2). It does seem expected that the acidic CO<sub>2</sub> would tend to preferentially extract the basic compounds. It is also interesting that some other classes of compounds (thiophenes and phenols) were also preferentially extracted. On the other hand, CO<sub>2</sub> shows no selectivity for saturated or aromatic hydrocarbons. The data in Table 2 were obtained by GC-MS analysis of the feed and extract samples.

Limited experimental studies examined the use of entrainers

(ethanol, heptane) to increase oil yield during the supercritical extraction with CO<sub>2</sub>. For these studies the solvents were added to the oil feedstock in the extractor. For both ethanol and heptane, 10% solvent added to the oil gave a 3-5 times increase in yield, however the type of selectivity shown in Table 2 disappeared and for each compound type, selectivities were less than 5 (similar to Figure 2). Thus for CO<sub>2</sub> extraction, entrainers may be used to dramatically increase yield but at the price of selectivity.

#### DATA ANALYSIS FOR SUPERCRITICAL EXTRACTION OF HEAVY OILS

There are presently available very powerful statistical techniques to design experiments in such a way that the data can be reduced to provide quantitative measures of key variables and interactions between variables (9). These statistical techniques are used in a wide variety of other technologies which deal with complex systems but have not found application in the area of supercritical extraction. This type of statistical analysis could complement the more traditional analytical modeling of supercritical phenomena.

#### ACKNOWLEDGEMENTS

I would like to acknowledge the advice of C. A. Eckert (University of Illinois) on experimental design and P. Palmese of Signal Research Center, who was responsible for overall design and construction of the experimental unit.

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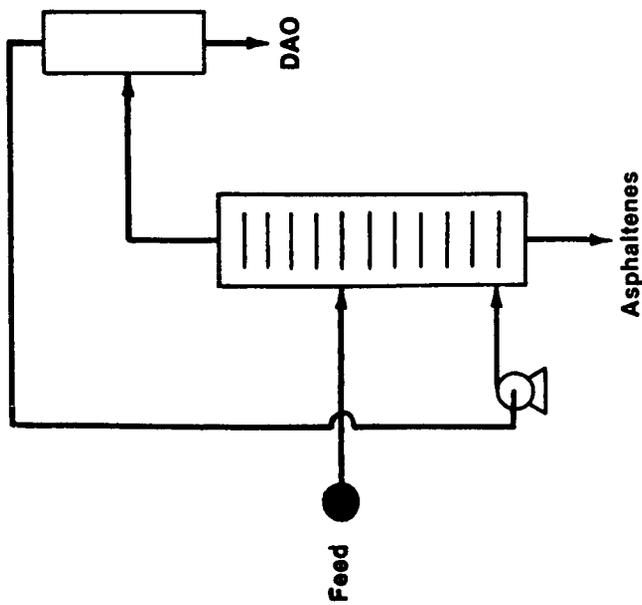
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**Table 1. Properties of Typical Heavy Oils**

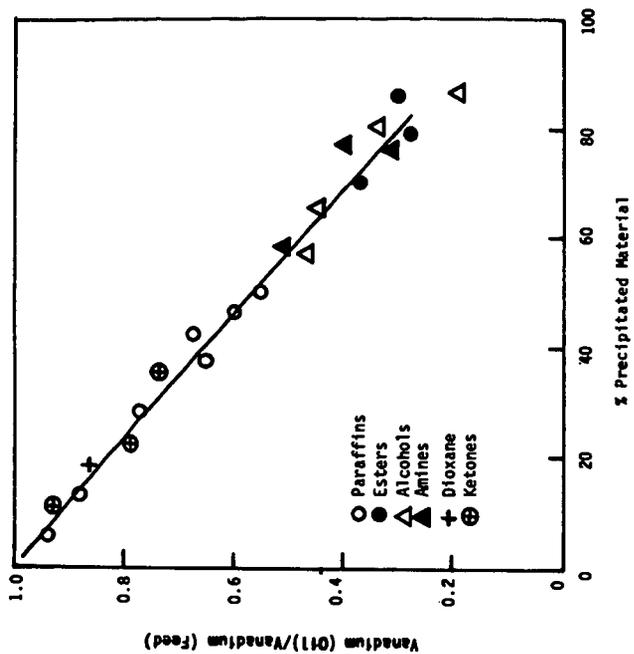
	<b>Athabasca Bitumen</b>	<b>Cold Lake Crude</b>	<b>Jobo Crude</b>
<b>Composition, Wt. %</b>			
Sulfur	4.9	4.29	3.87
Nitrogen	0.45	0.46	0.68
Oxygen	0.9	0.5	0.57
<b>H/C Atomic Ratio</b>	1.52	1.49	1.49
<b>Metals, WPPM</b>			
Nickel	80	61	90
Vanadium	250	180	455
<b>Asphaltenes, Wt. %</b>	14.2	17.9	17.7
<b>1050°F+, Wt. %</b>	47.3	45.2	49.4

**Table 2. Analysis of Oil Extracted With  
Supercritical Carbon Dioxide at 40°C**

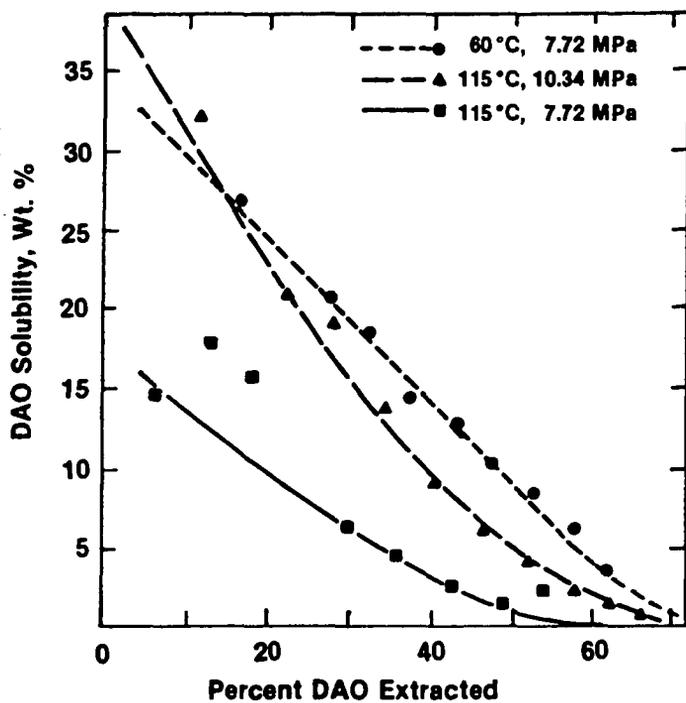
<b>Compound Type</b>	<b>Feed</b>	<b>100, atm</b>	<b>150, atm</b>	<b>200, atm</b>
Pyridines	0.02	1.69	1.31	0.56
Quinolines	0.41	1.55	1.54	1.51
Thiophenes	0.001	0.39	0.48	0.66
Phenols	0.01	0.63	0.52	0.26
Saturated Hydrocarbons	42.94	41.35	41.21	40.37
Aromatic Hydrocarbons	23.34	26.25	26.85	27.15



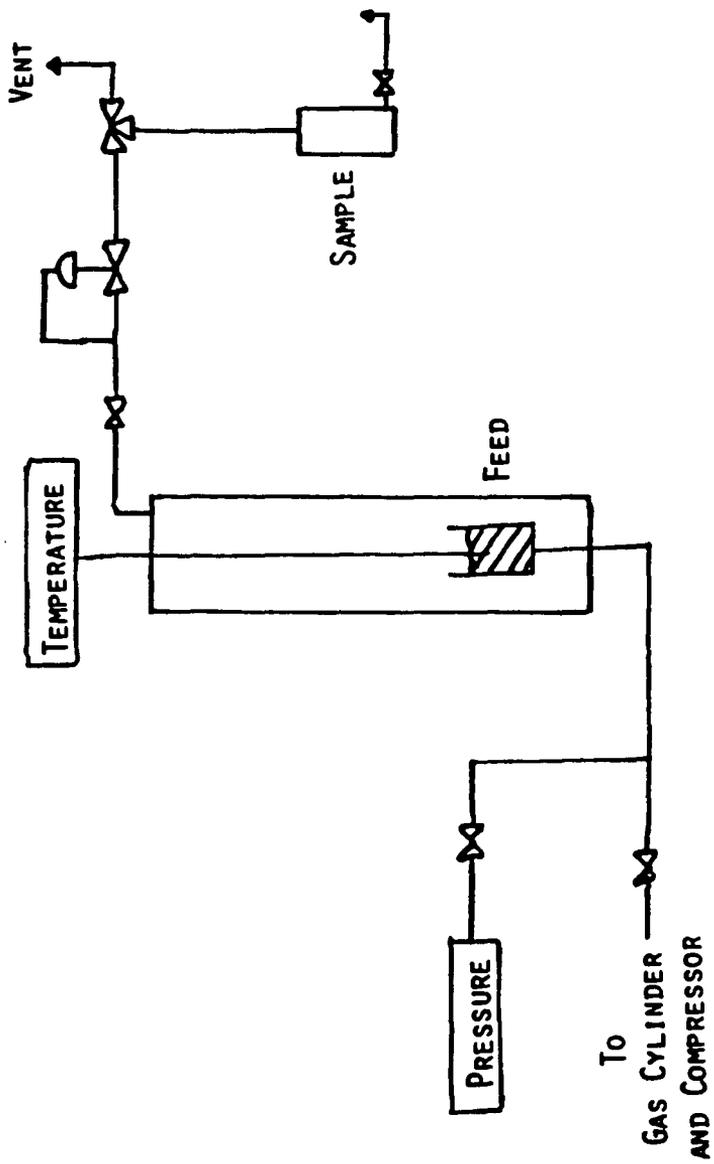
**Figure 1.** Schematic Diagram of a Solvent Deasphalting Process



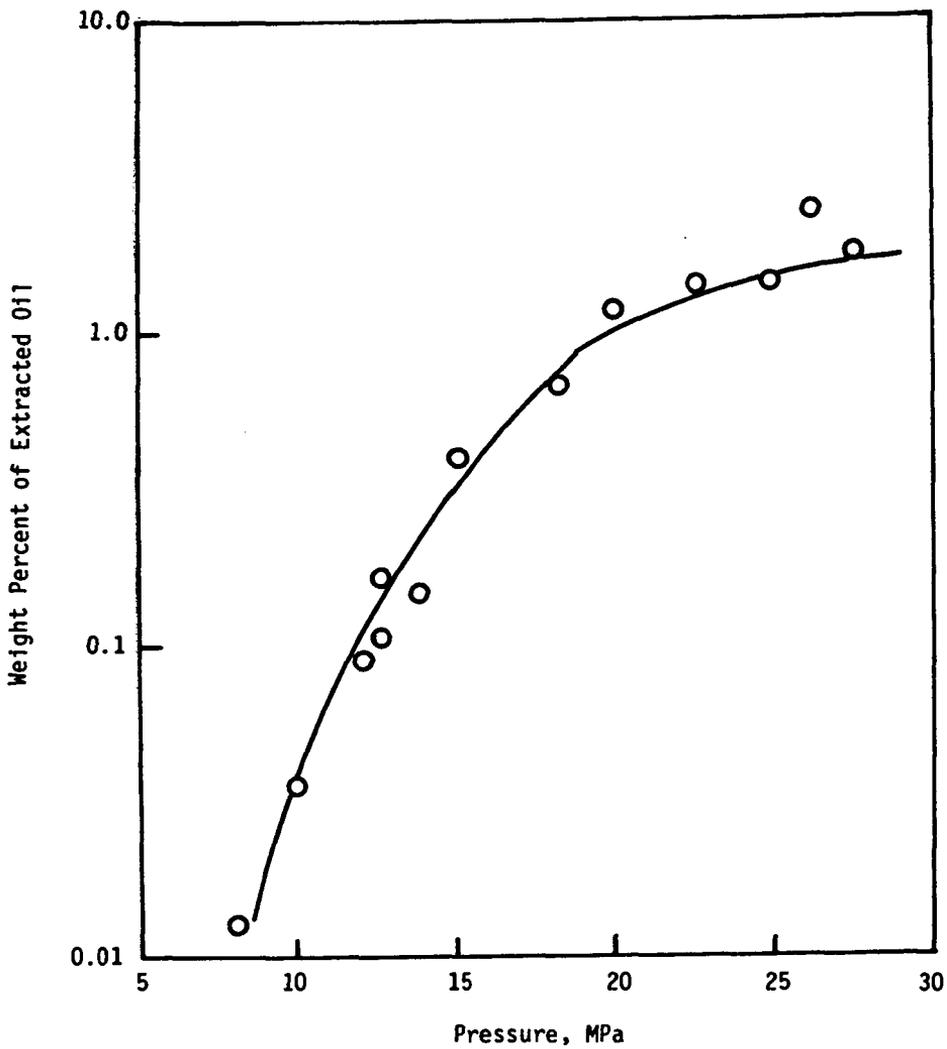
**Figure 2.** Correlation of Vanadium Content With Extraction Yield



**Figure 3.** Extraction of Arabian Long Heavy Oil With Liquid and Supercritical Propane



**Figure 4.** Experimental Unit for Supercritical Extraction With CO<sub>2</sub> and CO<sub>2</sub>/Solvent Mixtures



**Figure 5.** Supercritical Extraction of Boscan Crude With CO<sub>2</sub> at 40°C

# IDENTIFICATION OF POLAR MATERIAL VIA SUPERCRITICAL FLUID CHROMATOGRAPHY-FOURIER TRANSFORM INFRARED SPECTROMETRY

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## INTRODUCTION

In the past several years, a great amount of interest has been generated in Supercritical Fluid Chromatography (SFC) among separation chemists. The physical properties of a supercritical fluid, namely low viscosity, high diffusivity, and good solubility, give the mobile phase characteristics intermediate to those demonstrated in high performance liquid chromatography (HPLC) and gas chromatography (GC).(1) This situation has allowed for the separation via SFC of additional compounds which are not separable by HPLC or GC. Thus, SFC offers much promise in the separation of certain complex mixtures.

Detectors that are used for HPLC and GC, ultraviolet absorption and flame ionization, are also successfully used for SFC detection. However, as in the past when dealing with more conventional chromatographic methods, the need for higher information detectors in SFC exists. The success of Fourier Transform Infrared spectrometric detection with GC(2) and HPLC(3) has led to the obvious extension of this technique to SFC. The most commonly used mobile phase in SFC is CO<sub>2</sub>. It has relatively good solubility for many compounds, is nontoxic and inexpensive. Yet, both supercritical and subcritical CO<sub>2</sub> intensely absorb infrared radiation around 3600 cm<sup>-1</sup> and 2400 cm<sup>-1</sup>. Although these regions are opaque to any analyte which might absorb in the same region, excellent infrared spectra can be obtained in the regions of mobile phase IR transparency.

One problem in extending FTIR detection to SFC is insufficient detector sensitivity. An obvious means of improving the sensitivity in the IR is through an increase in the pathlength of the flow cell. This increase should enhance the signal-to-noise ratio of the spectra obtained. However, too great a pathlength may lead to a decrease in the width of the IR window region, a substantial drop in the IR throughput, and/or a decrease in overall resolution and integrity of the on-line spectra. In this paper we present a comparison of two flow cells, differing in length and flow geometry and two mobile phases (CO<sub>2</sub>, Freon 23) with UV-254 and FTIR on-line detection. In doing so, we show the eluting characteristics of basic nitrogen compounds on a packed bonded-phase silica column and compare retention characteristics of a polar model separation using two different supercritical mobile phases. A sensitivity study with a weak IR absorbing compound employing more nearly optimal chromatographic parameters than spectrometric parameters is discussed wherein the two cells are compared.

## EXPERIMENTAL

A Hewlett-Packard (Avondale, PA) Model 1082B liquid chromatograph modified for supercritical fluid chromatography and equipped with a high-pressure Model 79875A variable wavelength UV detector was used in these investigations. Anaerobic grade CO<sub>2</sub> (Airco, Bluefield, WV) and Freon 23, CHF<sub>3</sub> (Dupont Co., Wilmington, DE) were used for the experiments. A Nicolet Model 6000C FTIR was used to collect time-resolved, 4 cm<sup>-1</sup> resolution spectra. A Model 7010A narrow-band (5000 - 700 cm<sup>-1</sup>) mercury-cadmium-telluride (MCT-A) detector was used in all experiments. Schematic diagrams of the flow cells employed in this study are shown in Figures 1 and 2. The internal surface of the 5 mm pathlength cell was a solid gold insert which had been polished longitudinally to give maximum infrared reflectivity. The internal cell dimensions were 1 mm ID x 5 mm pathlength. The cell windows were 13 mm diameter x

2 mm thick ZnSe disks, and were sealed in place with polyperfluorinated elastomer Kalrez O-rings (DuPont). The main body of the flow cell was 304 stainless steel with 0.010" ID x 1/16" OD SS inlet and outlet tubing silver-soldered in place. The second flow cell (Figure 2) was the high-pressure UV cell provided by Hewlett-Packard (1 mm ID x 10 mm). It was modified for FTIR by replacing the quartz windows used for UV detection with CaF<sub>2</sub> windows.

## RESULTS AND DISCUSSIONS

### Flow Cell Comparison

Each of the two cells has been evaluated in the same separation of a model mixture containing five basic nitrogen components. The optimum chromatographic conditions were determined via UV (254 nm) detection. The Gram-Schmidt reconstructed chromatogram arising from the optimized separation with the 5 mm cell showed only four components, while the UV trace (in-line after the FTIR) revealed all 5 components. Naturally with a UV detector, the elution order of a 5 component mixture could only be identified by single injections of each material. Employing an FTIR, interpretation of individual file spectra afforded immediate identification. The GSR for the 10 mm cell showed the fifth component and over-all better signal-to-noise for the same amount injected than that for the shorter pathlength. In the same respect, the coadded file spectrum of each component was much sharper, and the match to the spectrum in the EPA vapor-phase library was improved.

A detection limit study was carried-out by varying the amount of N-methylaniline injected under the same chromatographic and spectrometric conditions used for the five component separation. The IR band of interest was 1608 cm<sup>-1</sup>. For each cell 4 scans/file (scan time = 0.45 sec/scan) were collected, and coaddition over 1.4σ of the Gram Schmidt Reconstructed peak was performed. The injected minimum detectable quantity (IMDQ) of N-methylaniline using the 5 mm pathlength cell was found to be 156 ng (3xN<sub>rms</sub>).

### Mobile Phase Comparison

Certain fluorocarbons possess rather moderate critical pressures and temperatures. Their use as a relatively IR transparent mobile phase in HPLC is well documented.(4) Freon 23 (trifluoromethane) which has a critical temperature of 25.9°C and a critical pressure of 701.4 psi, has been suggested to exhibit similar eluting characteristics as CO<sub>2</sub>.(5) The IR windows of CO<sub>2</sub> have been found to complement very well the IR windows of Freon 23. A seven component mixture of phenols, alcohols and esters has been separated on a bonded-phase phenyl derivatized silica packed column under identical chromatographic conditions using supercritical CO<sub>2</sub> and Freon 23. Initially the separations were optimized with UV-254 nm detection. Afterwards sequential FTIR-UV-254 nm detection was employed. Injection of approximately 30 μg/each component yielded the Gram Schmidt reconstructed chromatograms shown in Figure 3. The solvent in each case was carbon tetrachloride which consistently eluted first. With UV-254 detection this peak is a minor one, however, with FTIR detection the peak is quite intense which reflects the high infrared absorbance of CCl<sub>4</sub>. The seven components eluted in the same order regardless of the mobile phase. The solvent strength of CO<sub>2</sub> appears to be slightly greater since each component has a lower retention time. This is notably the situation with benzyl benzoate, phenol, phenyl acetate and benzyl alcohol, the latter of which never eluted over a reasonable time period with Freon 23.

Examination of the on-line IR spectrum of several common components from the CO<sub>2</sub> and Freon 23 separations illustrates the complementary nature of IR information obtainable. For example while the O-H stretching mode of 2,6-di-tert-butyl phenol is obscured with CO<sub>2</sub>, it is readily observable with Freon 23. Although the remainder of the Freon 23 spectra is useless, it is those regions that are

transparent with CO<sub>2</sub>. Consequently continuous information is available through the mid-infrared region except for the triple-bonded absorbances around 2100 cm<sup>-1</sup>. The on-the-fly spectra of o-nitrophenol in CO<sub>2</sub> and Freon 23 are shown in Figure 4. A relatively weak, broad bonded O-H stretching mode is observed in both mobile phases for o-nitrophenol. There is a loss in sensitivity at this frequency when using Freon 23 relative to CO<sub>2</sub> due to decreased IR throughput to the detector windows.

In summary, both lightpipe cells offer very good S/N spectra obtained on-line during a chromatographic run. Although CO<sub>2</sub> seems to be an adequate mobile phase for SFC-FTIR, the regions of total absorbance may hinder the identification of a component in a complex mixture. Freon 23, although relatively opaque in the IR, does have reasonable transparency from 4000 cm<sup>-1</sup> to 2500 cm<sup>-1</sup>. The seemingly similar elution characteristics to CO<sub>2</sub> make method development with Freon 23 fairly easy and inexpensive. Thus CO<sub>2</sub> and Freon 23 make a good mobile phase pair for SFC-FTIR allowing for more complete identification of analyte species.

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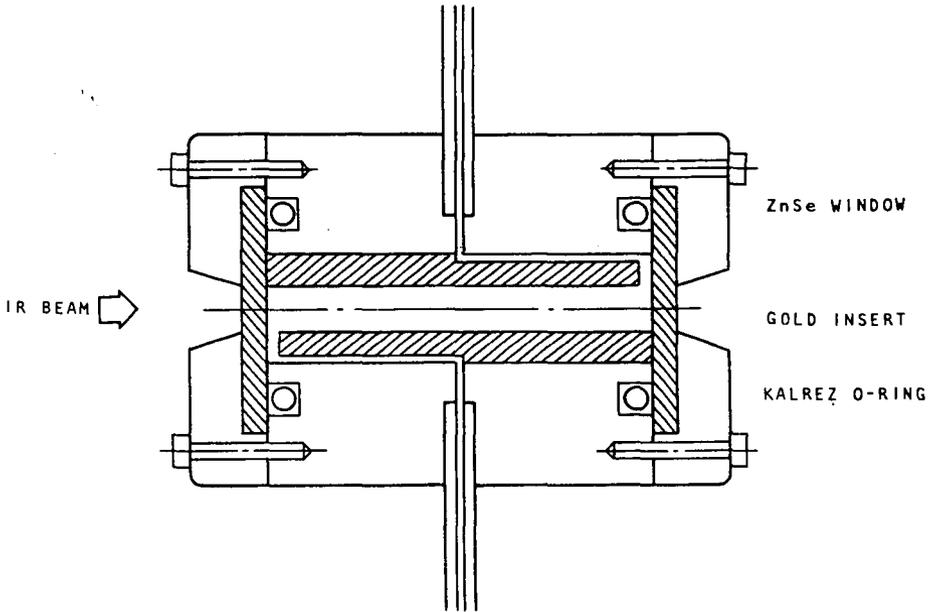


Figure 1

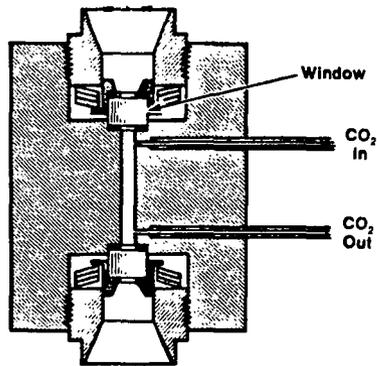


Figure 2

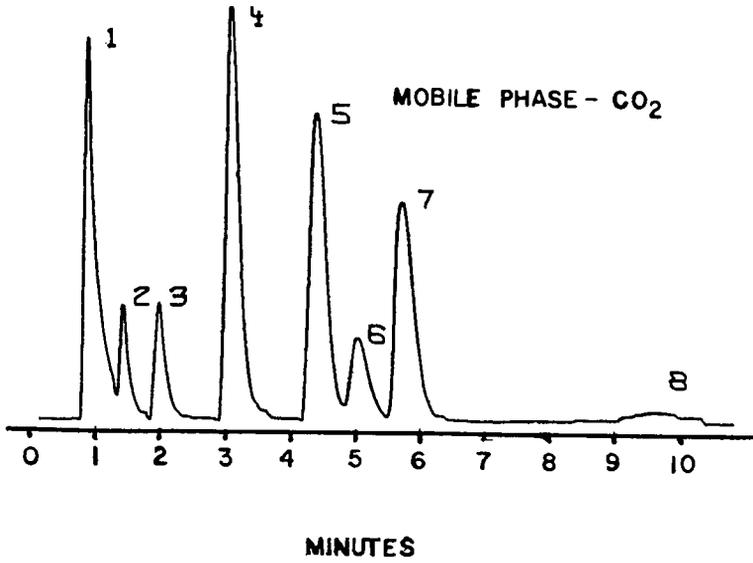
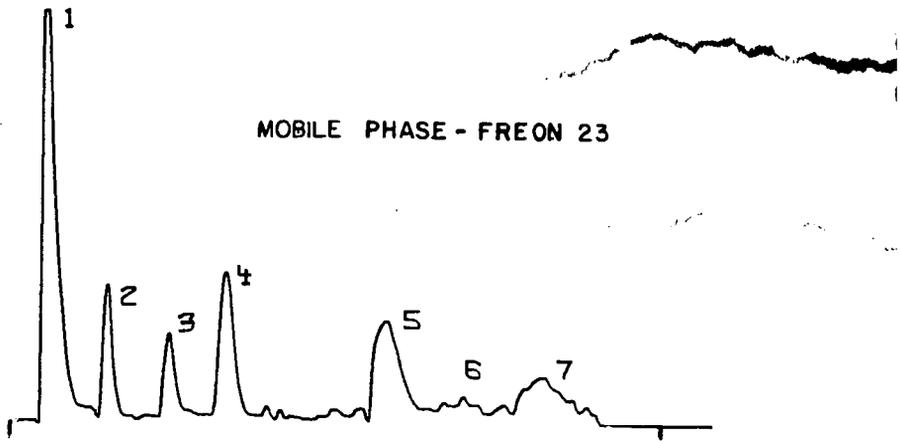


Figure 3

2,8-DI-TERT-BUTYLPHENOL W/ FREON 29

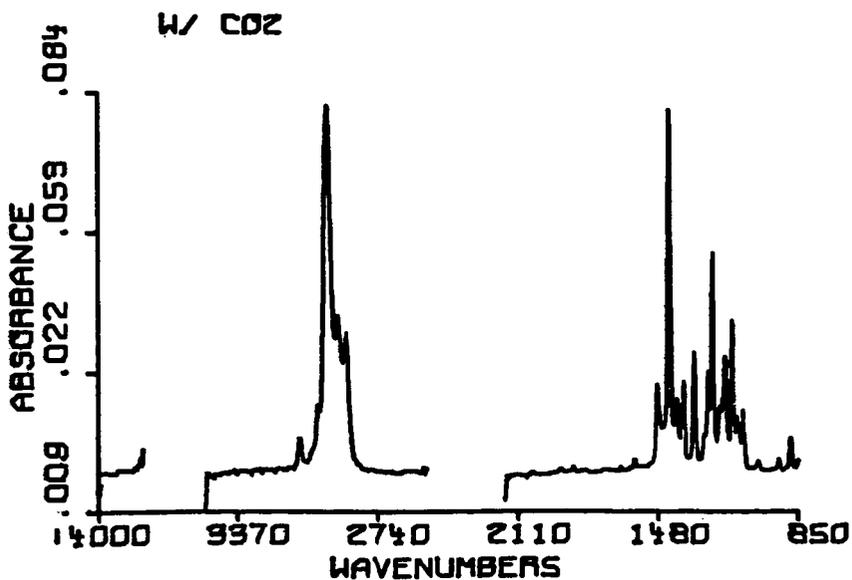
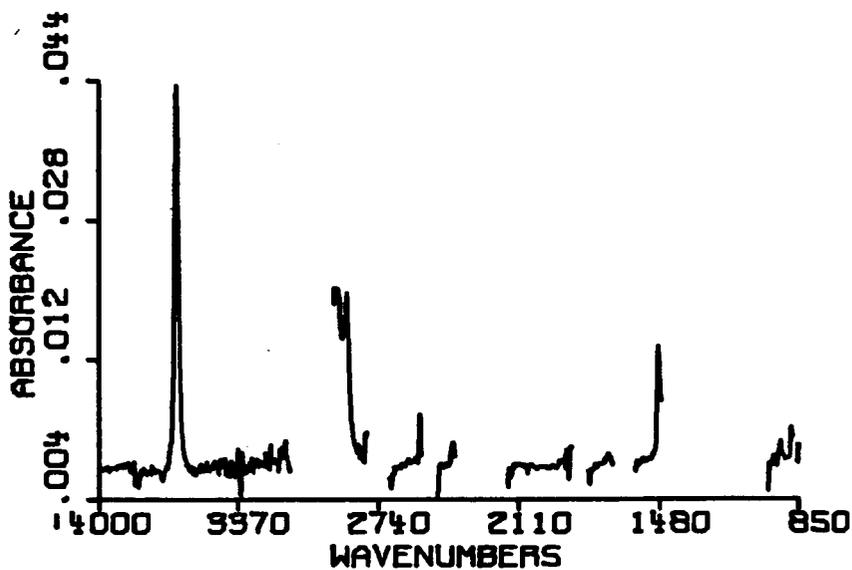
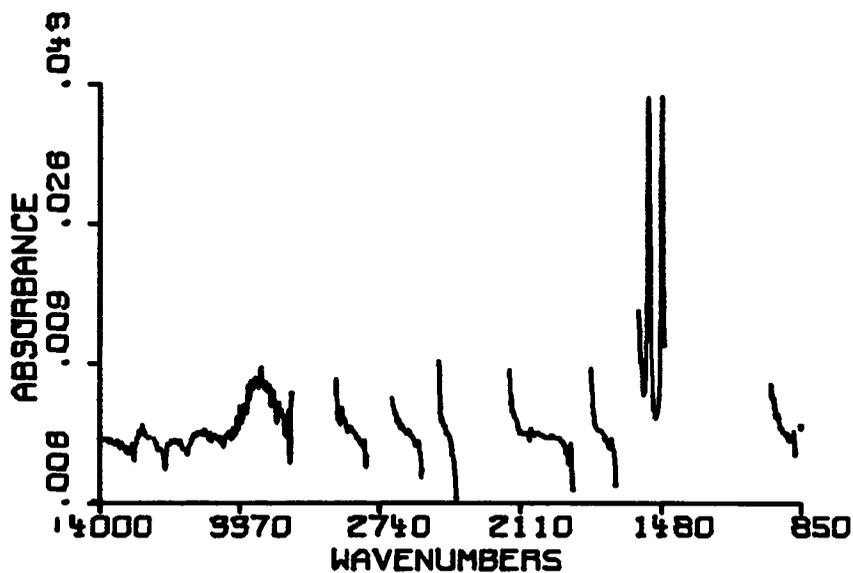


Figure 4

O-NITROPHENOL W/ FREON 29



W/ CO2

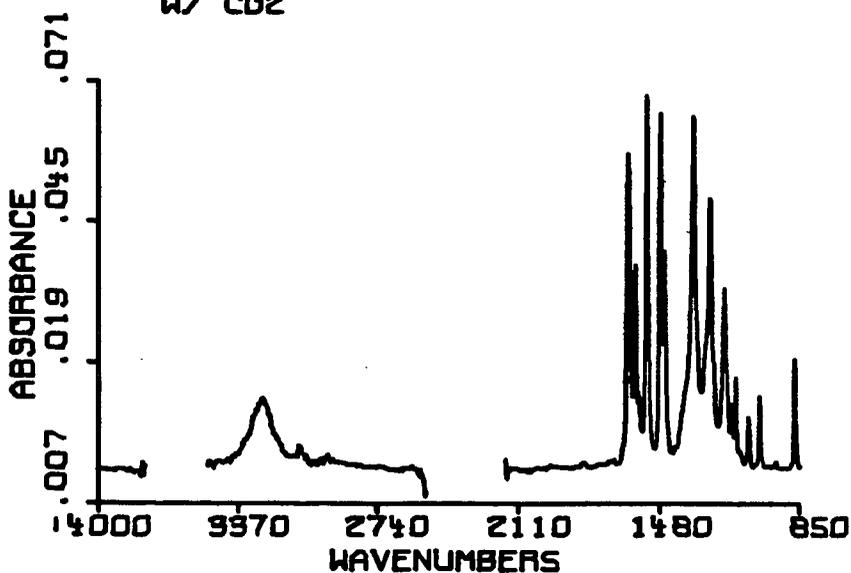


Figure 5

## HYDROTREATING IN SUPERCRITICAL MEDIA

by

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### INTRODUCTION

In recent years, supercritical fluid extraction has been a very popular technique for separations. The food and drug industries have used this technique for years on a commercial scale. Recently the energy industries have extended this application to coal liquefaction and oil shale extraction.<sup>(1-5)</sup> We, at Phillips, have also found that supercritical extraction of oil shale has improved the oil yield but produced a lower quality liquid product than those from insitu or above ground retorts. We were interested in developing an upgrading technology to upgrade the supercritically extracted (SCE) shale oil to synfuel or clean motor fuels. One of our upgrading projects was to investigate hydrotreating in the presence of the supercritical fluid which is used in the extraction step. If the hydrotreating step can be integrated with the supercritical extraction step, perhaps one can take advantage of, among other things, the pressure and heat available in the extraction step.

Our investigation consisted of essentially two parts. The first part involved the feasibility study of catalytic hydrotreating in the presence of supercritical fluid (in short, supercritical hydrotreating). If hydrotreating in the presence of supercritical media is possible, then we would like to extend the feasibility studies to other heavy feeds, such as topped crude and coal liquids. The second part of our investigation involved the parametric studies to see how reaction parameters effect supercritical hydrotreating.

### CONCLUSIONS

From our extensive investigation of the potential of hydrotreating of shale oil under supercritical conditions of the solvent used and then the reaction parameter effects, we would like to make the following conclusions:

A high nitrogen, heavy oil such as shale oil can be hydrotreated under supercritical conditions to yield very low nitrogen fuels and syncrude in one step, depending on the conditions used;

The presence of a light solvent gives a better product and reduces coke formation on the catalyst surface;

- . A non-aromatic solvent such as heptane improves nitrogen removal and reduces hydrogen consumption (from 2600 scf/bbl of shale oil to 1200 scf/bbl);
- . With Arabian topped crude, the solvent loses its enhancement effect for nitrogen removal if the solvent is less than 50 weight percent of the feed;
- . From parameter studies, for an extensive nitrogen removal, a relatively long residence time (30 minutes or longer) is required at 850°F and 1400 psig;
- . And the sulfur was almost completely removed even with the mildest reaction conditions studied.

## EXPERIMENTAL

### A. Hydrotreating System

A bench scale hydrotreating unit was used for these experiments as shown in Figure 1. The reactor is a 316 stainless steel tube with an inner diameter of one inch and a length of 27.5 inches. The total volume is about 290 ml. The reactor was equipped with a thermocouple well (a 1/4" x 25" stainless steel tube) for temperature measurements. The reactor was first filled with about 90 ml of inert packing, 100 ml of catalyst and the rest with an inert packing again to serve as the preheating zone for the oil and hydrogen. The temperatures were measured by thermocouples placed in the middle of each of the inert beds and the catalyst bed.

### B. Feeds

During the course of the investigation the following feeds were used: supercritical extracted coal liquid, supercritical extracted shale oil, Paraho shale oil, and Arabian topped crude (650°F+). Their properties are given in Table 1. To make the feed mixture, the heavy oil was usually dissolved in a solvent such as toluene or n-heptane.

### C. Catalysts

The Ni-Mo catalyst was commercially available from Nalco.

### D. Catalyst Presulfurization

The catalyst was generally heated to 300°F with nitrogen purging, and then the nitrogen atmosphere was replaced with a flow of 10% H<sub>2</sub>S in hydrogen. At the same time, the temperature was slowly increased to 600°F and was kept at this temperature until the catalyst was completely sulfided. The reaction usually takes four hours at 600°F and 100 liter of 10% H<sub>2</sub>S in H<sub>2</sub>.

## RESULTS AND DISCUSSION

In this report the results from the investigation of hydro-treatment of shale oil, Arabian topped crude, and lignite extract (under supercritical conditions) are being discussed. These experiments were carried out to investigate the potential of hydrotreatment in the presence of a light solvent under supercritical conditions for shale oil upgrading and the effect of reaction parameters in supercritical hydrotreating. In other words, these experiments are mainly exploratory in nature to find whether hydrotreatment under supercritical conditions has any advantage in the upgrading of high nitrogen heavy crudes, and if so, how do the major parameters affect the hydrotreatment under these conditions. The first few experiments were carried out with shale oil obtained from supercritical extraction. This shale oil is a very waxy grease and almost fits the definition of a solid. It has a very high nitrogen content (2.3%) and a sulfur content of 0.9%. The hydrogen content in the shale oil is relatively high with H/C atomic ratio of 1.48, equal to that of some petroleum crudes. Only a limited amount of this material was available, so only a few experiments were performed with this shale oil.

### A. Supercritical Hydrotreatment of SCE Shale Oil

SCE shale oil was hydrotreated at high severity because of its high nitrogen content and extremely high viscosity (Table 1). The experimental results are shown in Table 2. Based on the shale oil fed, the product distribution is the following: 12% gases, 52% boiling less than 300°F (calculated by difference) and 36% in the heavy oil fraction (>300°F). The elemental analyses of the heavy oil fraction have indicated that better than 99% of the nitrogen was removed. The sulfur removal was equally high. The actual heteroatom removal may even be higher because part of the nitrogen and sulfur found in the heavy oil could be contributed by the presence of dissolved ammonia and hydrogen sulfide gases. No attempt was made to wash out the ammonium sulfide before the elemental analyses were carried out.

For runs 2, 3, 4, and 5 the feed entered the hydrotreater directly from the supercritical extraction unit. The extract contained about 4% shale oil in toluene. Runs 2 and 3 were carried out at 842°F, and Runs 4 and 5, at 750°F. At the lower reaction temperature (750°F), the yield of gases dropped to less than 2%, and the yield of heavy oil fraction increased by about 10%. The extent of nitrogen removal was reduced significantly at the lower temperature. However, the sulfur removal seemed to be unaffected by the lowering of reaction temperature from 842 to 750°F. Thus these experimental results suggest that the supercritically extracted shale oil can be processed to yield very low nitrogen and sulfur fuels or syncrudes.

### B. Supercritical Hydrotreatment of Arabian Topped Crude

A series of experiments were performed with Arabian topped crude (650°F+) to investigate the hydrotreatment of high sulfur crudes in the presence of a light solvent under supercritical conditions. The experimental results obtained are summarized in Table 3. The overall results are comparable to those obtained from the supercritical hydrotreatment of SCE shale oil (Run 1). The sulfur removal is

very extensive (about 99% removal, reduced from 3.3% to 0.02%). The nitrogen content in the heavy oil fractions are relatively low, less than 60 ppm for runs with total liquid hourly space velocity (LHSV) of 0.5 (Runs 6 and 7) and about 770 ppm for Run 8 with an LHSV of 1.6. Thus, for extensive nitrogen removal, lower LHSV is needed.

Runs 9 and 10 were carried out to study the effect of an aliphatic solvent such as n-heptane in supercritical hydrotreating of topped crude. Comparing the results from Runs 6 and 7 in which toluene was used as the solvent, the nitrogen contents in heavy oil fractions are much lower for the heptane runs than the toluene ones. The sulfur contents are about the same. Thus, one can conclude that an aliphatic solvent is better solvent for hydrodenitrogenation than the aromatic solvent. The reason is that the aromatic solvent was competing for hydrogenation.

#### **C. Supercritical Hydrotreatment of Lignite Extract**

Lignite extract was hydrotreated in the presence of toluene under supercritical conditions (850°F, 1400 psig, 20 wt % lignite in toluene, a hydrogen GHSV of 300, and a LHSV of 1 or 1.6). The results are tabulated in Table 4. The elemental analyses of the heavy oil fraction have indicated the following changes (Runs 13 and 14): nitrogen, reduced from 0.91 to 0.14% and sulfur reduced from 4700 ppm to about 100 ppm.

Run 15 was carried out with a higher LHSV of 1.6, and the results are not too much different from Runs 13 and 14. The heteroatom removals are about the same. The heavy oil fraction, however, was increased to 43% from 30 and 36% (Runs 13 and 14). Thus the conclusion is that the lignite extract, a solid, can also be upgraded to yield a syncrude by the supercritical hydrotreatment process.

#### **D. Supercritical Versus Conventional**

A series of hydrotreating experiments were carried out under conventional conditions (without the use of a light solvent). The results are given in Table 5, along with some results obtained from a supercritical hydrotreatment experiment. The experiments performed were not under identical conditions, but they are close enough that the results obtained are valid enough for comparison.

The results from the supercritical hydrotreatment experiments are superior in almost every respect to conventional hydrotreatment experiments (without the use of solvent). Under similar conditions supercritical hydrotreating produced better products, for example: less gas yield (10% vs 25%), more of light oil fraction, <300°F, (55 vs 35%) and less coke formed on the catalyst surface (0.3 vs 3.8% based on the feed). For conventional hydrotreating we had encountered reactor plugging problems when the unit was running more than 196 hours. This problem was not found with supercritical hydrotreating.

#### **E. Reaction Parameter Studies**

Experiments were carried out with conventional shale oil (direct retorted Paraho shale oil) for the purpose of studying the

effects of reaction parameters in hydrotreating under supercritical conditions. In one group of experiments, the space velocity was varied (1.6, 3.2, and 5) while the other reaction parameters were kept constant. For temperature studies, the following reaction temperatures were investigated: 700, 750, 800, and 850°F. The pressure effect was examined at four levels -- 1000, 1400, 2000, and 2400 psig at 800°F. We have also studied the effect of solvent to feed ratio and solvent types (saturate vs aromatics).

The liquid hourly space velocities (LHSV, including the solvent) of 1.6, 3.2, and 5 were investigated at 850°F, 1400 psig, 20 wt % Paraho shale oil in toluene. The results are illustrated in Figure 2. With the LHSV of 1.6, the heavy oil fraction is only 34%, but when LHSV is increased to 3.2, the heavy oil fraction increased to 63% and did not change with further increase in LHSV. This seems to suggest that one third of the shale oil can undergo a molecular weight reduction more rapidly (a residence time of about 12 minutes) than the second third, which needs a residence time of up to an hour, while the last third survives longer than one hour.

For heteroatom removal, the results reveal that for a LHSV of 1.6 the nitrogen content in the heavy oil fraction, which is about 34 wt % of the total products, is 360 ppm (1.9% in the feed). Thus, the overall nitrogen removal is greater than 98%. For LHSV of 3.2 the nitrogen content in the heavy oil is increased to about 6,000 ppm. With a further increase in LHSV to 5, there seems to be very little change in the nitrogen removal. The sulfur removal is very rapid. Even with the LHSV of 5, there is only 53 ppm sulfur in the heavy oil.

Figure 3 illustrates the results from reaction temperature studies. The reaction temperatures used ranged from 700 to 850°F, with an increment of 50°F. The sulfur seems to be removed rather easily even at 700°F (from 7000 ppm in the feed to 200 ppm in the heavy oil fraction) or 97% removal. At higher temperatures the sulfur content in the heavy oil is much lower (~100 ppm). On the other hand, the nitrogen removal requires a much higher temperature. This, of course, is not surprising. For the purpose of obtaining relatively clean syncrude, we probably have to operate at high temperature (800°F) and low space velocity (<1.6).

The yield of heavy oil increases with a decrease of reaction temperature (Figure 3). For example, with the reaction temperature of 850°F, the heavy oil is only about 30% of the total products. While at the other extreme, that is, with the reaction temperature of only 700°F, the heavy oil fraction represents 90% of the whole products. Thus the higher temperature is necessary for the production of light products.

The effect of pressure on HDN and heavy oil yield in supercritical hydrotreating of shale oil is given in Figure 4. The experimental conditions used for these experiments are: 800°F, hydrogen GHSV of 600, LHSV of 1.6, 20 wt % shale oil in toluene, and reaction pressure of 1000-2400 psig. The nitrogen content in the heavy oil fractions have revealed that nitrogen removal increases with increasing reaction pressure. At the highest pressure studied (2400 psig), the nitrogen content in the heavy oil is only about 300 ppm. This is

about 98% nitrogen removal. The nitrogen removal decreased with the decrease in reaction pressure.

The effect of crude oil concentration in the feed was investigated with Arabian 650°F+ topped crude. Three concentrations (20, 50, and 80% of topped crude in toluene) were chosen, while the other experimental conditions were kept constant (see Figure 5 and Table 3). Both the nitrogen removal and heavy oil conversion are more extensive when the crude is hydrotreated at a more diluted level such as 20%. The heteroatom removal is reduced at higher crude concentrations and levels off at 50% or higher. The yield of the heavy oil fraction increases with increasing concentration of crude in the toluene.

The use of a non-aromatic solvent as the supercritical hydrotreating solvent was studied first with Arabian topped crude and then with Paraho shale oil in hope of reducing hydrogen consumption. The results are tabulated in Table 6. Run 16 used toluene as the solvent, and Runs 17 and 18 used n-heptane. The experimental results have shown that nitrogen removal is slightly higher with n-heptane than with toluene (a more significant difference was found with Arabian topped crude as the feed). The yield of heavy oil fraction is lower (37% for heptane and 47% for toluene) for the saturated solvent. This means hydrocracking was more extensive. The H/C atomic ratio of the heavy oil is also much higher for heptane than for toluene. Thus hydrogenation is deeper with heptane as the solvent. Hydrogen consumption is also significantly reduced, 1200 scf/bbl of shale oil for heptane versus 2600 scf/bbl for toluene. With everything considered, heptane is by far a better hydrotreating solvent than toluene.

To sum up, extensive research has been done to study the potential of supercritical hydrotreatment for the upgrading of shale oil and then the effects of major reaction parameters in supercritical hydrotreating. The experimental results have demonstrated that hydrotreatment in the presence of a light solvent and under supercritical conditions has some advantages over conventional hydrotreatment. Compared with conventional process, the supercritical hydrotreating process yields a better product (less gas, more distillates) and produces less coke on the catalyst. Supercritical hydrotreating appears to be a very versatile process which can be optimized for a variety of different products. This process can be applied equally well for upgrading other heavy oils, such as coal liquids and high sulfur petroleum topped crudes, to yield low nitrogen and sulfur syncrudes and transportation fuels.

Saturated solvent such as n-heptane has been examined as the process solvent. Saturated solvent seems to do better in terms of nitrogen removal and hydrogen consumption. With either solvent, sulfur removal was very extensive. From reaction parameter studies, a relatively high severity is required for extensive nitrogen removal.

**TABLE I**  
**FEED PROPERTIES**

Feed	Elemental Analyses				H/C
	C	H	N	S	
SCE Shale Oil <sup>1</sup>	84.5	10.4	2.3	1.0	1.48
Paraho Shale Oil <sup>2</sup>	84.5	11.7	1.9	0.7	1.66
Arabian Topped Crude <sup>3</sup>	84.9	11.3	0.18	3.3	1.60
Lignite Extract <sup>4</sup>	82.0	9.3	0.91	0.47	1.36

1. The SCE shale oil is a waxy black semi-solid.
2. Paraho shale oil has about 70 Vol % of 650<sup>+</sup> F material.
3. Totally 650<sup>+</sup> F material.
4. Hard solid at room temperature.

**TABLE II**  
**SUPERCRITICAL HYDROTREATMENT OF SCE SHALE OIL\***

Run No. <sup>a</sup>	Temp. OF	LHSV	Gases	Heavy Oil (>300 F)		
			(C <sub>1</sub> -C <sub>4</sub> )Wt%	Wt. %	N(ppm)	S(%)
1	842	0.5	12	36	52	0.03
2	842	1.6	--	46	150	0.03
3	842	1.6	--	44	150	0.02
4	750	1.6	<2	54	2300	0.08
5	750	1.6	<2	32 <sup>b</sup>	2000	0.04

\*A total operating pressure of 1400 psig and sulfided Ni-Mo/Al<sub>2</sub>O<sub>3</sub> catalyst were used in these experiments. The shale oil has the following elemental analyses: C, 84.5; H, 10.4; N, 2.3; S, 1.0.

<sup>a</sup>The feed for Run 1 consisted of 20 wt % shale oil in 80 wt % toluene, but for Runs 2 to 5, the feed was only 4% shale oil in toluene.

<sup>b</sup>In this run this fraction was distilled up to 400<sup>o</sup>F instead of 300<sup>o</sup>F as usual.

TABLE III

SUPERCRITICAL HYDROTREATMENT OF ARABIAN TOPPED CRUDE (ATC)  
(850°F, 1400 psig, H<sub>2</sub> GHSV 300, Nalco Ni-Mo Catalyst)

<u>Run No.</u>	<u>Feed<sup>A</sup></u> Wt % ATC in Solvent	<u>LHSV</u>	<u>Heavy Oil</u>		
			<u>Wt %</u>	<u>N (%)</u>	<u>S (%)</u>
6	20	0.5	34	0.006	0.02
7	20	0.5	34	0.004	0.02
8	20	1.6	59	0.068	0.04
9	20	0.5	33	2 ppm	0.02
10	20	0.5	36	3 ppm	0.03
11	50	1.6	64	0.094	0.17
12	80	1.6	72	0.094	0.13

<sup>A</sup>Solvent for Runs 9 and 10 was n-heptane; for others toluene was used.

TABLE IV

SUPERCRITICAL HYDROTREATMENT OF LIGNITE EXTRACT

<u>Run No.</u>	<u>LHSV</u>	<u>Heavy Oil Fraction (&gt;300°F)</u>		
		<u>Wt %</u>	<u>N(ppm)</u>	<u>S(ppm)</u>
13	1	30	1530	150
14	1	36	1400	90
15	1.6	43	1180	100

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Lignite Extract Feed                      100                      9100                      4700

---

Conditions: 850°F, 1400 psig, 300 H<sub>2</sub> GHSV, 20 wt %  
lignite extract in toluene, Nalco Ni-Mo catalyst.

**TABLE V**

**COMPARISON OF CONVENTIONAL AND  
SUPERCRITICAL HYDROTREATING**

(Conditions: 1400 psig, 850°F,  
H<sub>2</sub> GSHV=300, Nalco Ni-Mo)

<u>FEED</u>	<u>NO SOLVENT</u>	<u>WITH SOLVENT</u>
	<u>SHALE OIL (NEAT)</u>	<u>20% SHALE OIL IN TOLUENE</u>
LHSV	0.3	TOTAL = 1.6 SHALE OIL = 0.32
GAS YIELD (Wt %)	25	10
LIGHT (Wt %)	35	55
HEAVY OIL (Wt %)	35	35
COKE (Wt %)	3.8	0.3

**TABLE VI**

**SUPERCRITICAL HYDROTREATMENT OF SHALE OIL IN  
TOLUENE OR n-HEPTANE**

(850°F, 1400 psig, Nalco Ni-Mo catalyst,  
1.6 LHSV, 300 H<sub>2</sub> GSHV)

<u>Run No.</u>	<u>Feed</u>	<u>Heavy Oil (&gt;300°F)</u>				<u>H<sub>2</sub> Consumption</u>
		<u>Wt %</u>	<u>N(ppm)</u>	<u>S(%)</u>	<u>H/C</u>	<u>Scf/Bbl</u>
16	20% Shale Oil in Toluene	57	3149	<0.01	1.66	2600 ± 200
17	20% Shale Oil in Heptane	36	1595	<0.01	1.79	1200 ± 100
18	20% Shale Oil in Heptane	37	1890	<0.01	1.82	1200 ± 100

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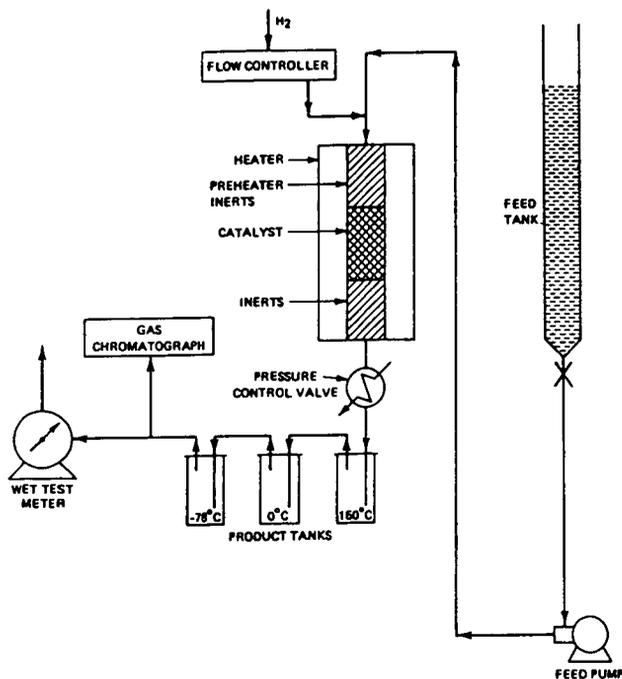


FIGURE 1  
SUPERCRITICAL HYDROTREATING SYSTEM

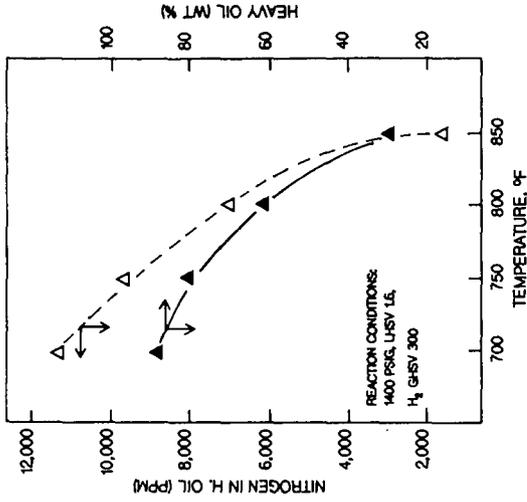


FIGURE 3  
EFFECT OF TEMPERATURE ON  
SUPERCRITICAL HYDROTREATMENT OF SHALE OIL

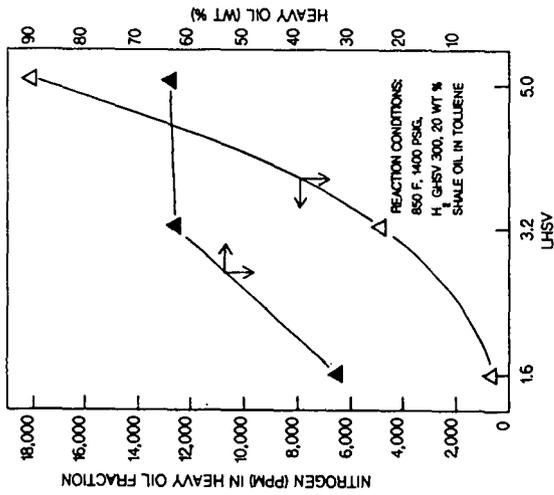


FIGURE 2  
SPACE VELOCITY EFFECTS ON  
SUPERCRITICAL HYDROTREATMENT OF SHALE OIL

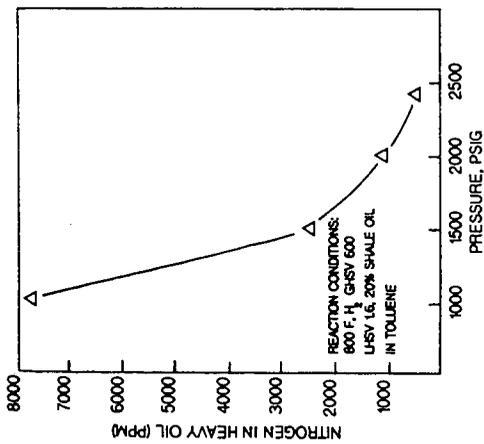


FIGURE 4

EFFECT OF PRESSURE ON  
 SUPERCritical HYDROTREATMENT OF SHALE OIL

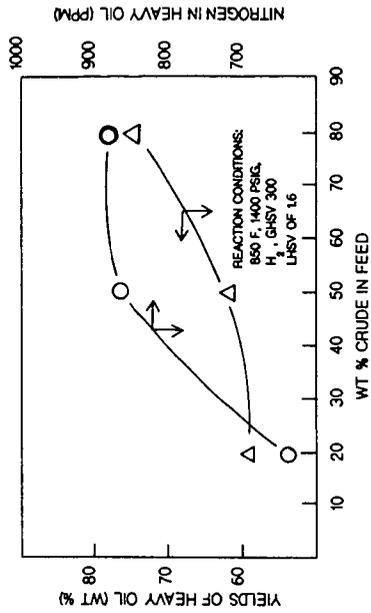


FIGURE 5

EFFECT OF OIL CONCENTRATION  
 IN SUPERCritical HYDROTREATMENT OF  
 ARABIAN TOPPED CRUDE

## EXTRACTION AND DESULFURIZATION OF CHEMICALLY DEGRADED COAL WITH SUPERCRITICAL FLUIDS

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### INTRODUCTION

In the systematic investigation of "Extraction and Desulfurization of Coal With Supercritical Fluids", it was found that sulfur materials in coal were removed selectively from the coal matrix, employing ethanol or methanol as the solvent. It is a well-known fact that a fluid under supercritical conditions exhibits an enhanced dissolution power which can increase the solubilities of various organic materials by several hundredfold. Depending upon the specific compounds and the solvent involved, solubility of each organic compound in a given solvent may vary at different temperatures and pressures. This differentiation of solubilities will allow selective removal of certain organic matter under supercritical conditions.

When ethanol or methanol is used as supercritical fluid, chemical reactions may be taking place between sulfur compounds in coal and the solvent in the presence of mineral matter. Pyritic sulfur may be reduced, and certain organic sulfur materials may be removed through chemical reactions. In this situation, the reactivity between organic sulfur in coal and supercritical alcohols is not only dependent on reaction conditions, but is also dependent on the distribution of sulfur functional groups in coal. That is to say, some forms of sulfur compounds are easier to be reacted and subsequently extracted than others. Therefore, the desulfurization potential with supercritical fluids may be affected by the coal types and sources, since various coals may have different sulfur functional groups in their respective structures.

In order to better understand the complex system of desulfurization of coal with supercritical alcohols, we have launched an extensive experimental study to achieve the following research objectives. They are: (1) to determine the selectivity of desulfurization of coal with supercritical alcohols, (2) to determine the effect of chemical pre-treatment on supercritical desulfurization potential, (3) to evaluate the gaseous and liquid product streams, and to characterize the desulfurized solid char for establishing the material and sulfur balances, and (4) to evaluate the physical and chemical transformation of coal during supercritical desulfurization.

### LITERATURE REVIEW

Most work on supercritical extraction of coal reported in the literature has as a primary objective the maximum conversion of coal to liquid products. A 1975 article by Whitehead (9) [one of the first references to supercritical

coal extraction presented in the literature] presented data on supercritical extraction of coal by coal tar or petroleum naphtha fractions. Tugrul and Olcay (8) reported in 1978 extractions yields and analytical results obtained by supercritical-gas extraction of 250 mesh lignite. They found extraction nearly complete after 30 minutes; extract yields of about 24% were reported. Gas chromatography/mass spectrometry analyses of several extract fractions indicated dozens of paraffins, alkylated hydrocarbons, phenolic and oxygenated compounds; however, no sulfur compounds were reported. A kinetic study of a high-volatile bituminous coal utilizing supercritical toluene was reported by Slomka and Rutkowski (7). A close fit of their experimental data on time dependence of extraction yield was found when a second order equation was used. The use of supercritical toluene extraction of coal in pilot plant studies supported by the British Coal Board was reported by Maddocks (3). The major objective of that study was also maximum conversion of coal to liquid products; reduction of sulfur in the unconverted solid was not reported.

Some work has been reported utilizing alcohols for supercritical extraction of coal. Makabe, et al. (4) reported extraction of coal with ethanol-sodium hydroxide with the objective of maximizing extraction yield; no sulfur data was reported. Methanol reaction with a low volatile Bituminous West Virginia coal at higher temperatures (460 - 600°C) was reported by Garner, et al. (2). Promotion of coal gasification was the objective of that study; sulfur content of the resultant char was not reported.

In contrast to the previous reported work utilizing supercritical solvent extraction of coal, where major objectives have been the conversion of coal to liquid or gaseous products, the major objective of our research effort is to study supercritical desulfurization of coal with alcohols. Researchers at Purdue University have studied the supercritical desulfurization of coal by using water as a solvent. Although their data have indicated that pyritic sulfur was effectively removed, the rate of removal of organic sulfur was found to be very slow.

The recent article by Amestica and Wolf (1) does compare results obtained with toluene and ethanol when used for the supercritical extraction of an Illinois No. 6 coal. The experimental apparatus employed appears similar to ours, and temperatures utilized for the ethanol extraction (350 - 450°C) are also comparable. The ethanol/coal ratio of 7/1 is greater than the 1/1 ratio that we normally utilize in the batch reactor system, and the reaction time of 30 minutes is less than the 1 or 2 hour reaction periods we normally employ.

In the article, it is reported that the "sulfur rejected" varied from 1.7% to 11.7% in the three runs reported. However, a footnote given in the table states these values were calculated as a "sulfur percentage of daf coal feed in the gas phase". The text indicates determination of the sulfur was accomplished by scrubbing of the uncondensed gases in a zinc acetate solution. No data are given in the article with respect to the sulfur content of the solid product, nor is mention made of sulfur analyses on the liquid product. To interpret the sulfur captured from the uncondensed gases by a zinc acetate solution as being a measure of the "sulfur rejected" from the coal during the supercritical extraction implies that all the sulfur removed was accounted for; this seems to be a risky assumption, based on the lack of appropriate data presented in the article.

The possibility of condensation reaction of solvent degradation products occurring during supercritical extraction of coal with ethanol and alkali-ethanol is supported by data given by Makabe and Ouchi (5, 6). However, as the discussion that follows will indicate, we have not found evidence that this occurs under the conditions we employ for supercritical desulfurization of coal with alcohols.

## EXPERIMENTAL

Most of the investigation was performed in two reactor systems. They are a semi-continuous reactor and a batch reactor. Their respective experimental set-ups are described in the following.

### Semi-Continuous Reactor Studies

The flow chart for the semi-continuous Berty gradientless reactor, equipped with a Magne-drive impeller and internal recirculation systems, is given in Figure 1. The ground coal is held in a basket within the reactor, while solvent is pumped continuously through the system. After cooling following a run, the solid product is removed from the reactor basket for weighing and analysis. It is possible to maintain a constant pressure in this system, in contrast to the batch system where pressure increases during the course of a run, final pressure being determined by the temperature and charge size of the reactor.

### Batch Reactor Studies

Figure 2 shows the flow diagram of the 300 cc batch reactor system that has been utilized in our experiments. The coal and solvent are charged to the reactor, heated to reaction temperature, and maintained at reaction temperature for a designated period; generally one or two hours. After reaction, the separation of products is accomplished by venting the fluid phase slowly from the reactor through the product collection system.

As shown in Figure 1, the product collection system consists of a water cooled condenser and primary liquid collection vessel, followed by a dry ice-acetone cooled cold trap coil and a series of three absorption vessels. The non-condensable gases are then discharged through a sample vessel and to a wet test meter for volume measurement. The first two absorbers contain ethyl alcohol; the third absorber contains an aqueous zinc acetate solution.

The total sulfur measurements were performed on a Fisher Total Sulfur Analyzer. The starting coal, the solid product resulting from the supercritical desulfurization reaction, the primary liquid product collected, additional liquid recovered from the cold trap (if any), and samples from each of the absorbers were analyzed.

## RESULTS AND DISCUSSIONS

### Semi-Continuous Reactor Results

Figures 3 and 4 show the data of sulfur removal and coal extraction for four different coal samples with supercritical ethanol at 325°C and 1750 psi. It can be seen that the percent of sulfur removed is much higher than the

percent coal extracted (weight loss of coal). A term called desulfurization selectivity ratio which is defined as the ratio of percent of sulfur removed to percent of coal extracted, varied between 2.96 to 4.38 under these conditions as shown in Table 1.

TABLE 1  
 SUPERCRITICAL ETHANOL DESULFURIZATION OF COAL  
 AT 325°C; 1750 psi  
 Desulfurization Selectivity Ratio

Extraction Time, Hours	Desulfurization Selectivity Ratio			
	Coal "A"	Coal "B"	Coal "C"	Coal "D"
0	2.81	3.40	4.09	12.0
1	3.29	2.98	3.40	7.36
2	3.81	2.88	3.10	5.49
4	3.39	2.96	3.49	4.38

A series of experiments were performed to evaluate whether or not a pre-treatment of coal with KOH solution will enhance the desulfurization efficiency. In the pre-treatment, 60 grams of coal particles were soaked in 180 grams of KOH in ethanol solution with a given concentration for five minutes, filtered, washed twice with 180 grams of ethanol and filtered again before its use. The results are presented in the following.

TABLE 2  
 THE EFFECT OF KOH PRE-TREATMENT  
 (275°C and 1800 psia)

	<u>% of Sulfur Concentration Removed</u>
No pretreatment	21.3
2% KOH	28.5
3% KOH	28.9
4% KOH	29.8
5% KOH	34.0

The data indicates that an improvement of desulfurization potential was realized with KOH pre-treatment.

In order to evaluate the degree of potassium ion incorporation into the coal structure during the pre-treatment, several experiments were conducted at 325°C and 1750 psia employing ethanol or methanol as solvent. In these experi-

ments, the soaking and washing solutions were collected, and were analyzed for potassium ion on a Perkin Elmer Atomic Adsorption Spectrometer. It can be seen in Table 3 that most of the potassium ion was found in the solution.

TABLE 3  
POTASSIUM ION BALANCE

KOH Pre-treatment	Ethanol		Methanol	
	% S Removed	% K <sup>+</sup> Recovered	% S Removed	% K <sup>+</sup> Recovered
None	27.0	--	30.2	--
5% KOH, soaking, rinsing	32.16*	102	39.1	99

\*Average of three experiments

#### Batch Reactor Results

Table 4 shows a summary of experimental data (elemental analysis) of the desulfurized coal samples for the batch reactor system under different operating conditions. The original coal has a total sulfur content of 4.27 percent, and 72.6 percent of the total sulfur is organic sulfur. Since the concentration of total sulfur in the solid product from the supercritical desulfurization is reduced nearly 50 percent or more for five out of nine cases, and the sulfur removals resulting from the supercritical desulfurization exceeds the pyritic sulfur content of the original coal, it is concluded that organic sulfur in this coal is being removed. The possibility that the selective removal of sulfur may be due to condensation reactions of the solvent, with subsequent incorporation in the coal matrix, may also be rejected by consideration of H/C ratio data in Table 4. If significant incorporation of -CH<sub>2</sub>- groups from the solvent were to occur, an increase in H/C ratio would be expected. As the data indicated, the H/C ratio actually decreases during the supercritical desulfurization.

Table 5 summarizes the sulfur balance information obtained on a series of batch reactor runs under a variety of conditions. Note that the sulfur determined in the liquid products and in the absorber total from 67.1% to 94.7% of the total sulfur removed from the coal during the supercritical desulfurization. When the sulfur content of the solid product is included, the overall sulfur balance ranges from 82.4% to 97.1% of the sulfur contained in the original coal.

The total materials balance of these experiments ranges between 92.4% to 100.6%.

#### CONCLUSIONS

It is concluded from experimental information obtained that sulfur, including organic sulfur in coal, is selectively recovered from coal matrix with supercritical alcohol. The effect of chemical pre-treatment with KOH soaking

and/or acid leaching is found to be significant. The pre-treatment step may help the depolymerization of coal structure which makes it easier for super-critical alcohol to reach the sites of sulfur compounds for extraction and conversion.

#### ACKNOWLEDGEMENTS

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TABLE 4  
ELEMENTAL ANALYSES OF SOLID PRODUCT FOR BATCH REACTOR SYSTEM

Solvent and Conditions <sup>a</sup>	C	H	N	S	H/C Ratio	% S Removed (Conc. Based)
Original raw coal	66.04	4.85	1.17	4.27	0.881	
MeOH	72.63	4.04	1.31	2.99	0.667	30.0
MeOH + 5% KOH	70.37	3.72	1.25	1.96	0.634	54.1
HCl refluxed; MeOH	77.17	3.05	1.32	2.16	0.474	49.4
MeOH + 5% KOH + CO 400 psi	69.60	4.15	1.18	2.58	0.716	39.6
Acid leached <sup>b</sup> ; MeOH + 5% KOH	71.91	3.96	1.23	1.53	0.661	64.2
Acid leached <sup>c</sup> ; MeOH + 5% KOH	73.32	3.07	1.30	1.88	0.502	56.0
MeOH + 5% KOH; Two stage	69.16	3.18	1.12	1.47	0.552	65.6
EtOH	75.82	3.95	1.39	2.75	0.625	35.6
EtOH + 5% KOH	73.90	3.32	1.24	2.60	0.539	39.1

<sup>a</sup>All run at 350°C

<sup>b</sup>Soaked for 48 hours

<sup>c</sup>Soaked for 4 hours

TABLE 5  
SULFUR BALANCE

Solvent	Rxn T C	% Reductn of Sulfur in Coal	% of Sulfur Removed as Found in			Overall Sulfur Balance
			Liq.	Absorber	Total	
EtOH	350	31.4	43.3	43.7	87.0	93.9
EtOH	375	36.8	13.2	81.5	94.7	97.1
MeOH + 5% KOH	350	53.9	12.4	64.3	76.7	85.7
MeOH + 5% KOH	350	56.1	7.2	74.0	81.2	88.2
MeOH	350	48.8	6.9	60.2	67.1	82.4

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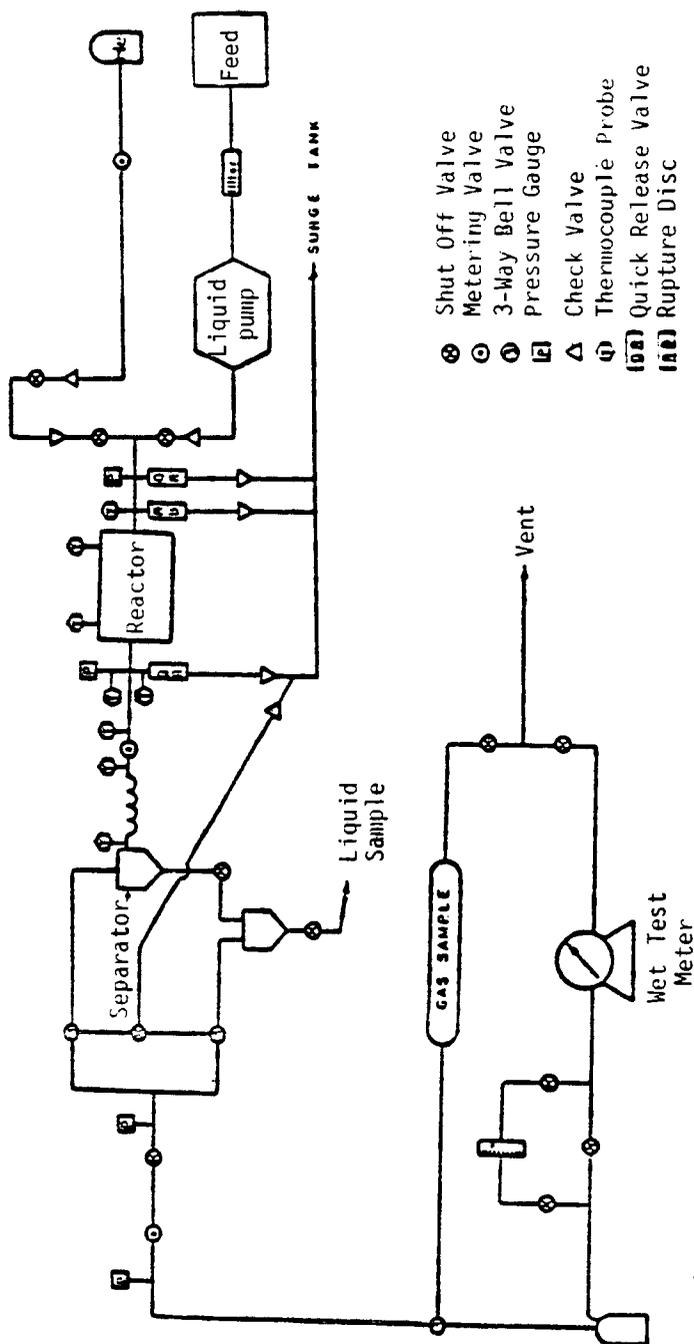


Figure 1. Flow Diagram of the Experimental Setup  
Semi-Continuous Reactor

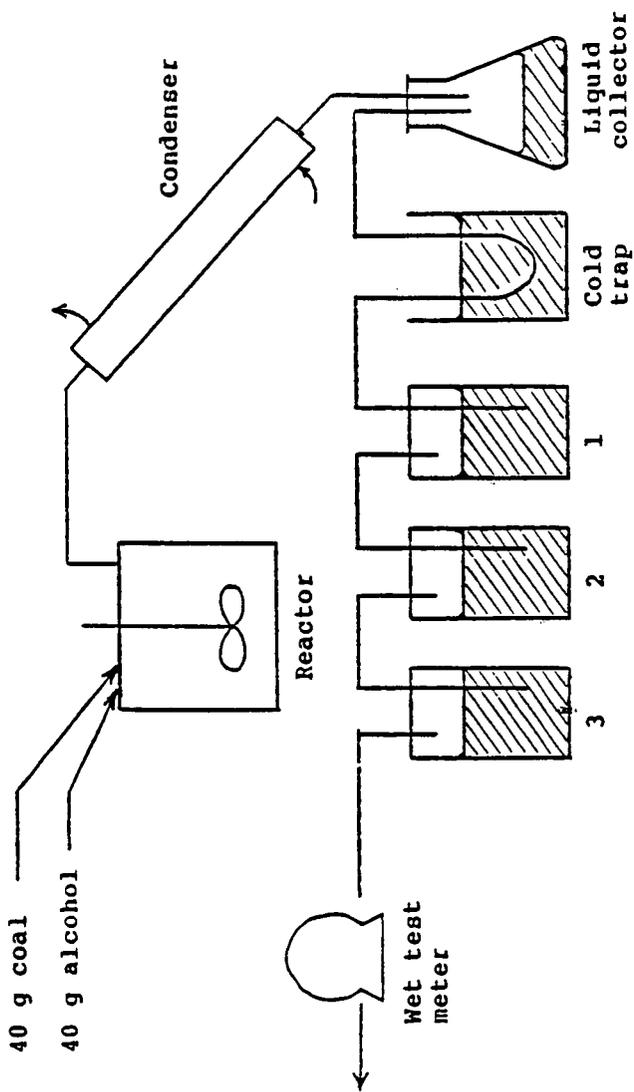


Figure 2. Batch Reactor Flow Diagram  
 Absorbers 1 and 2 contain ethanol, 3 contains aqueous zinc acetate solution.

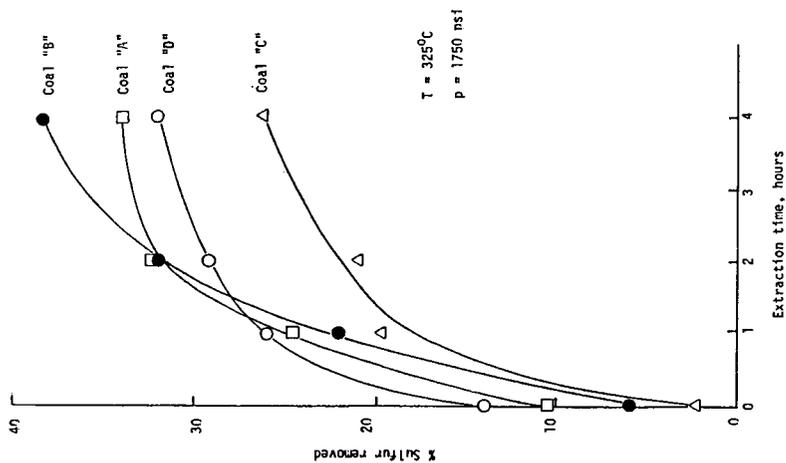


Figure 4. Percent of Sulfur Removed in Semi-Continuous Reactor

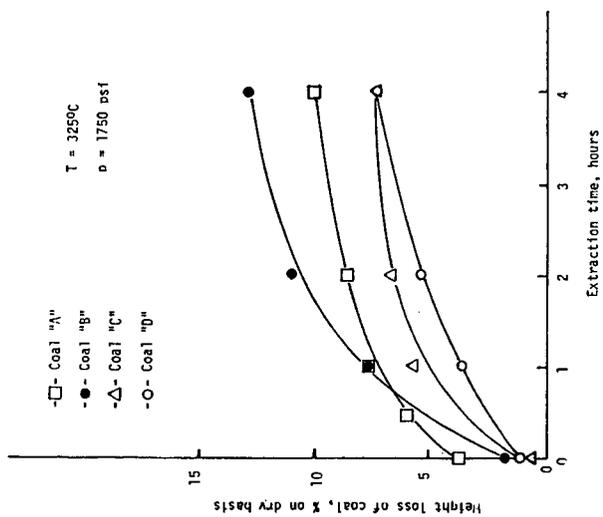


Figure 3. Percent of Coal Extracted in Semi-Continuous Reactor