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**DEVELOPMENT OF AN EXTRACTION PROCESS FOR
REMOVAL OF HETEROATOMS FROM COAL LIQUIDS**

FINAL REPORT

prepared for
**The U. S. Department of Energy
Pittsburgh Energy Technology Center**

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prepared by
**UOP
Des Plaines, Illinois**

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1.0 INTRODUCTION

Over the last two decades, the United States Department of Energy (DOE) has funded research for the advancement of several coal liquefaction processes as a strategy to develop an alternate source of liquid fuels and to reduce the Nation's dependence on imported oil. Coal-derived liquids from these processes contain a significant amount of aromatic compounds and oxygen and nitrogen containing polar compounds as compared to petroleum crude. These coal liquids need to be upgraded before they can be used as transportation fuels. The degree of upgrading required for these coal liquids has changed considerably over the last few years. For example, following the Clean Air Act of 1990, which places a strong emphasis on reducing automotive emissions, gasoline reformulation has become a priority throughout the refining industry. Conventional gasoline has been linked to the emission of carbon monoxide (CO), nitrogen oxides (NO_x), photoreactive unburned hydrocarbons, and airborne toxic chemicals. Refiners have introduced new gasoline formulations that are designed to minimize the emission of these pollutants. Reducing aromatics, olefins, and butane from gasoline to meet the new environmental regulations significantly lowers the octane of the gasoline pool. Alternate high-octane blending components are required to replace them. For coal liquids to be viable as alternate fuel feedstocks, they need to be upgraded to the same degree as the new gasoline formulations.

Other important issue that need to be addressed is the hydrogen requirement. With the tightening environmental regulations, the demand for cleaner hydrogen-rich fuels will increase. Alternate refinery configurations will be required to meet these specifications and yet maintain the gasoline octane requirements. The hydrogen consumption of a typical petroleum refinery could increase by as much as 30% depending on the refinery configuration. This increased hydrogen requirement may be overcome by new processes, or may require the addition of a costly hydrogen production plant.

In parallel to the development of the coal liquefaction processes, extensive research has been completed on the upgrading of coal liquids. Hydrotreating has been the principal method for removal of sulfur, nitrogen, oxygen, and metal containing compounds. These contaminants, if not reduced, would contribute to increased levels of air pollution, equipment corrosion, and down-stream catalyst poisoning. Hydrotreating is a catalytic hydrogenation method used to

upgrade distillate fractions. The removal of contaminants involves the controlled breaking of hydrocarbon molecules at the point where the sulfur, nitrogen, and oxygen atom are joined to carbon atoms. This breaking is accomplished by a reaction with hydrogen producing hydrogen sulfide, ammonia, or water. Most metal removal is accomplished by binding of the metal to the catalyst surface. A small amount of cracking may occur depending on the severity of the operation. Some of this work carried out by DOE and several companies, including UOP, has focused on integrating coal liquids into existing petroleum refineries. Research at UOP found that coal liquids could be converted to transportation fuels at the expense of high hydrogen consumption¹. Chevron studies report similar findings^{2,3}. The cost of the hydrogen production has been estimated to be 25% to 40% of the total refining cost for these coal liquids². In summary, upgrading of coal liquids by traditional methods would result in a larger hydrogen deficit as compared to a petroleum refinery.

Due to the high aromatic and heterocyclic content of coal liquids, alternative methods of heteroatom removal rather than direct hydrotreating may be more efficient. The removal of a significant portion of the polar compounds prior to hydrotreating could reduce the hydrogen consumption and render hydrotreatment somewhat easier. In addition, it may reduce the capital and operating costs for hydrotreating and possibly reduce the overall cost of refining coal liquids. Technologies that could preserve the state of these polar compounds are especially interesting. The phenols, cresols, and pyridines in coal liquid could be valuable byproducts if produced in a purified form. An appropriate extraction technique could produce these valuable products in an environmentally sound manner and reduce the amount of polar aromatic compounds.

1.1 Objective of the Research Program

The main goal of this research program is to evaluate and develop an extraction process for the upgrading of coal liquids. The process has the potential to reduce the hydrogen requirements in downstream upgrading processes and yield valuable byproducts. During the processing of hydrogen deficient coals, carbon dioxide is produced. The proposed program is based on an extraction process that can utilize the excess carbon dioxide at the liquefaction refinery.

1.2 Process Background

In an extraction process, two immiscible or partially soluble liquid phases are brought into contact to facilitate the transfer of one or more components from one phase to another (solvent) phase. The processes taking place are primarily physical, since the solutes being transferred are ordinarily recovered without any chemical change. However, the physical equilibrium relationships on which such operations are based depend mainly on the chemical characteristics of the solutes and the solvents. The liquid phase from which the soluble material has been extracted is called the raffinate and the solvent phase (containing the solute) is called the extract. A typical flow diagram of an extraction plant is shown in Figure 1.

Extraction may be carried out in various ways. In the simplest case the solvent is added to the liquid phase, causing a second liquid phase to form. Sometimes a third component is added to a mixture of two liquid phases to promote the transfer of solute from one phase to another. The third component may dissolve some solute and act as a cosolvent. In some cases the third component provides a convenient media for the transfer of the solute material and acts as an entrainer. In any case the successful operation of an extraction process requires that the solvent phase and the phase being treated be brought into intimate contact so the mass transfer can occur.

The amount of solute transferred to the solvent phase depends on the nature of the solvent, solubility of the solutes, and the operating conditions (pressure and temperature) of the extraction. A good solvent produces contrasting thermodynamic properties of the solute molecules in the extract and the raffinate phases. An appreciable difference in densities of the phase and a large interfacial tension are also desirable for easier phase separation.

Typical applications of solvent extraction include: removal of naphthenic and aromatic constituents from the paraffinic constituents of lubricating oil stocks, recovery of acetic acids from dilute aqueous solutions, the separation of unsaturated constituents from vegetable oils, purification of butadiene, and the recovery of penicillin⁴. Most solvent extraction applications for heavy hydrocarbon processing, such as coal liquefaction and related operations, are operated at high temperatures, required for good flow characteristics of the feed, and high pressures, necessary to maintain solvent power. For most of the commonly used solvents this high temperature and high pressure conditions fall in the supercritical region.

1.2.1 Application of Extraction Processes in Coal Liquefaction. The Wilsonville liquefaction pilot plant uses an extraction process to remove the insoluble solids from coal liquids. The process is called Critical Solvent Deashing (CSD) process and is based on the principles of the Residual Oil Supercritical Extraction (ROSE) process developed by the Kerr-McGee Refining Corporation⁵. The solids-containing coal liquid fraction is mixed with a light aromatic solvent such as toluene in 2.5/1 ratio under subcritical conditions, for example 550°F, 700 psi. Most of the coal liquids dissolve in the solvent, only the very high molecular weight fractions remain insoluble. The precipitated material, together with ash and the insoluble coal, settles quickly in the low-density low-viscosity fluid. The settled solids are removed, and are stripped to remove the solvent, leaving behind a free-flowing powder. The solution passing from the top of the settler is heated to supercritical temperatures (above 606°F) to reduce its density and to decrease the solubility of the coal liquids which separate out as the heavier phase. The recovery of the coal liquids is about 80%. The CSD process has been operated in conjunction with the 6 ton/day Wilsonville pilot plant.

UOP's Demex process, like the ROSE process, uses solvent extraction to separate vacuum residues from a refinery in three fractions: oils, resins, and pitches. The oils are asphaltene-free and have a metals concentration of only 15% to 20% of that in the charge. Quality and amount of resins produced are dependent on the desired qualities of the demetallized oil and pitch. Both processes recover solvent from the demetallized oil at supercritical conditions, and in general use the same unit operations. However, the unit operations are conducted differently and as a result, Demex process has operating advantage over the ROSE process. This advantages translate in terms of lower utility requirements for the Demex process. It is conceivable that a variation of the Demex process could be used in place of the CSD process (which is a variation of the ROSE process) for deashing coal liquids.

Several processes that use supercritical CO₂ or other acid gases for extraction of coal or coal liquids are described in literature⁶⁻¹⁴. Extraction of the chloroform-soluble fractions of coal pyrolysis pitches by supercritical CO₂ showed that paraffinic structures and light aromatic hydrocarbons were preferentially extracted and polar compounds were only partially extracted⁷. A german patent describes a three-step process for the separation of indole, quinoline bases, and

phenol derivatives from coal tar by extraction with supercritical CO_2 and C_3 - C_8 alkane or alkene stream^{9,12}. In the first step neutral oils are separated, followed by indole and quinoline bases in the subsequent steps.

The effect of an entrainer or a cosolvent with an extracting agent is difficult to predict because entrainers and cosolvent change the phase behavior of the system. The reason behind using entrainer or cosolvent is to enhance the extraction and/or to reduce the temperature and pressures at which the extraction is carried out. When diethylene glycol was used as an entrainer in the supercritical extraction of a coal liquid (boiling range 356°F to 662°F), the selectivity of extraction of polar and nonpolar compounds was significantly improved and it was possible to separate the polar compounds (phenol and cresols) from the nonpolar compounds¹¹. In absence of the entrainer, negligible selectivity for the extraction of paraffins was observed, even though the paraffins have a higher solubility in CO_2 than the aromatic compounds.

Other acid gases including SO_2 have also been used for the extraction of coal liquids and shale oils¹³. Basic nitrogen compounds were removed from a coal liquid containing a stoichiometric amount of water (based on nitrogen content) by contacting it with gaseous SO_2 . A salt complex containing the nitrogen compound, SO_2 , and water is precipitated. The salt is then separated from the stream and decomposed by heating. The liberated SO_2 is recycled¹³. In a test the nitrogen content of a coal liquid was decreased from 8.6 wt. % to 1.43 wt. %. Liquefied H_2S was used to treat an asphalt-containing mineral oil¹⁴. Extraction results in the formation of two liquid phases: an upper viscous oil phase dissolved in the H_2S solvent and a lower asphalt phase containing some oil and solvent. The results of this extraction compared quite well with those given by deasphalting the crude oil with pentane or heptane.

A liquefaction process based on the supercritical extraction of coal was developed by the U. K. National Coal Board⁸. The process involves extraction of coal by an aromatic solvent to extract up to 50% of the coal followed by separation of the solvent from the extract. The extract is then hydrocracked to produce gasoline and diesel fuel. The undissolved solids, called coal char, are divided into two parts. One part is gasified with steam to produce hydrogen for the process together with plant fuel gas, and the other part is burned to generate power and steam. Developers claim that the advantage of this extraction-liquefaction process is that the solvent recovers the lower molecular weight fractions of coal decomposition products, which are better

suited, and require less of the expensive hydrogen for conversion to the premium fuels. The more carbonaceous part of coal is left behind for gasification and combustion.

The work proposed in this study is based on an invention patented by the Phillips Petroleum Company¹⁵. It was observed that when a shale oil was extracted with an aqueous phase containing CO₂ at pressures and temperatures in the subcritical and supercritical CO₂ range, significant quantities of the heteroatoms N, S, and arsenic were extracted from the oil. The key feature of this invention is the use of water as an entrainer (or cosolvent) to facilitate and promote the extraction of the coal liquids by CO₂. As discussed above, the role of an entrainer or a cosolvent in extraction is not very clear. Water may dissolve some of the heteroatom compounds and may help reduce the severity (particularly pressure) at which the extraction is carried out. In the following sections, the principle behind supercritical extraction are reviewed and the details of the subject invention are discussed.

1.2.2 Extraction with Supercritical Fluids. The driving force behind the use of supercritical fluids (SCF) for extraction is the combination of properties that a solvent has in its supercritical fluid state. A typical pressure-temperature phase diagram for a pure component is illustrated in Figure 2. The SCF region is in the upper right portion where temperature and pressure conditions are above their critical values. In this region, the properties of the fluid are between those of a liquid and those of a gas. Density and solvent power are like those of a liquid, whereas transport properties and compressibility are like those of a gas. In addition, and importantly, one may vary the properties over wide ranges by making modest changes in temperature or pressure. The region of greatest importance is near the critical point, $0.9 < T_r < 1.2$ and $1.0 < P_r < 3.0$, where T_r and P_r are reduced temperature and pressure, respectively ($T_r = T/T_{\text{critical}}$, $P_r = P/P_{\text{critical}}$). In this region, relatively small changes in temperature and pressure produce large changes in density.

SCF properties, particularly the ability to control solvent power, are important in extraction processes. One can initially boost the solvent power of a fluid to that required for a selective separation, then reduce the power to extract a desired component and recover the solvent. SCF solvents penetrate substrates and approach equilibrium better than normal liquids because they have higher diffusivities and lower viscosities than those of liquids. In addition, a SCF solvent

presents no surface tension or wetting problems. In general, the following observations are made for a SCF:

- SCFs have solute loadings approaching liquid solvent loadings as densities approach liquid densities. In many cases, SCF loadings exceed liquid loadings because the higher temperatures at supercritical conditions result in higher solute vapor pressures.
- Solubility increases with increasing pressure. A dramatic increase in solubility occurs near the critical point as a result of large change in solvent density.
- Solubility may increase, remain constant, or decrease with increasing temperature depending on whether solute vapor pressure or solvent density is the dominant factor. At constant solvent density, solubility increases with increasing temperature.
- Solubility increases with increasing solvent density.

Carbon dioxide ($T_c = 88^\circ\text{F}$, $P_c = 1070$ psi, critical density = 0.47 g/cc) is widely used as a solvent in supercritical extraction of natural products, food, and as illustrated above, coal liquids. Reasons for the wide use of CO_2 in supercritical extraction are: critical temperature (very close to room temperature), easy availability, non-flammable nature, non-toxicity, and good solvent property for several organic compounds. Francis reports the mutual solubility of near-critical liquid CO_2 with some 261 organic substances¹⁶. These data can be used as a rough guide for estimating the magnitude of solubility in supercritical CO_2 .

1.2.3 Heteroatom Removal by Extraction with CO_2 -Water. As discussed above, the removal of heteroatoms from coal liquids is an important step in their upgrading to produce transportation fuels. The commercially available methods for heteroatom removal, among other things, are big consumers of hydrogen, and development of alternate technologies for heteroatom removal is highly desirable. The CO_2 -water extraction technology proposed here has demonstrated removal of N, S, and As from mineral oil, and literature review indicates that such processes could separate polar (oxygen-containing) compounds from nonpolar compounds¹¹. So there is a potential to develop a single process that could remove all the undesirable heteroatoms from a coal liquid and thereby facilitate easier and more economical upgrading of the coal liquids.

Data from the extraction of total Paraho shale oil and fractions of it obtained by distillation are shown in Table 1. All of these runs were made at 500 psig and at a temperature between 81°F and 99°F. Water to oil ratio was maintained at 5:1. Carbon dioxide was supplied to the reactor on demand. Samples of the oil were analyzed for N, S, and arsenic. In the table, N, S, and As content of the oils before extraction and percent of each element removed by extraction is shown. No analysis for the oxygen content of the oil or the extracted fractions was carried out.

The following observations are made from Table 1:

- Reduction in N, S, and As were as high as 71%, 22%, and 50%, respectively.
- Tests were carried out at subcritical CO₂ pressures. As discussed above, increasing the pressures further to operate in supercritical CO₂ range may further increase the solubility of various undesirable compounds in the solution, which can subsequently be removed. In fact it was observed that the effectiveness of the separation of basic nitrogen-containing compounds is proportional to the partial pressure of CO₂ up to about 1300 psig.
- No attempts were made to optimize any of the operating conditions and only single-stage experiments were carried out.
- The role of water in this extraction process is not clear. Dissolution of CO₂ in water forms carbonic acid, which may be assisting in the separation of the heteroatom compounds. It is likely that the carbonic acid formation favors the extraction of polar compounds in the extract, and oxygen-containing compounds may be concentrating in the aqueous phase. However, this can not be verified directly because oxygen content of the oils were not measured.
- All of the arsenic that was extracted from the oil appeared in water.

The research program carried out under this contract is outlined in detail in Section 2.0.

TABLE 1
Data for the Extraction of Shale Oil*

Run No.	Oil Fraction	weight %		As ppm	% reduction		
		N	S		N	S	As
I	Total Paraho	1.89	0.83	37.7	25.1	8.0	26.0
II	200-300°F frac.	0.36	0.93	7.6	71.0	22.2	50.0
III	400-500°F frac.	1.41	0.52	31.1	32.9	2.4	16.0
IV	650-1000°F frac	2.25	0.40	22.3	5.6	4.7	35.0
V	650 + °F frac.	2.07	0.60	28.0	10.4	(21)*	2.0

* Apparent increase in sulfur content may be due to experimental error.

* Data is extracted from U.S. Patent No. 4,518,489.

FIGURE 1
Schematic Diagram of an Extraction Plant

FIGURE 2
Pressure-Temperature Phase Diagram

2.0 CONTRACT OBJECTIVE AND SCOPE OF WORK

2.1 Contract Objective

The main goal of this contract was to develop an extraction process for upgrading coal liquids; and in doing so, to reduce the hydrogen requirement in downstream upgrading processes and to yield valuable byproducts. This goal was to be achieved by developing a novel carbon dioxide extraction process for heteroatom removal from coal-derived naphtha, diesel, and jet fuel. The research plan called for the optimization of three critical process variables using a statistically-designed experimental matrix. The commercial potential of the new process was to be evaluated by demonstrating quantitatively the effectiveness of heteroatom removal from three different feedstocks and by conducting a comparative economic analysis of alternate heteroatom removal technologies.

2.2 Contract Scope of Work

The original scope of work under this contract was divided into the following six tasks:

2.2.1 Task 1.0 Project Work Plan. The objective of this task was to prepare a Project Management Plan covering the entire period of performance of the contract. The Plan was to present, in detail, all activities that were to be performed to successfully complete the work outlined in Tasks 2.0 through 6.0.

2.2.2 Task 2.0 Feed Procurement and Analysis. The objective of this task was to acquire, with DOE Project Manager's concurrence, enough quantities of the coal liquids to test the feasibility of the extraction process. Detailed analysis of the distillation fractions was to be carried out. The selection of feedstock is very important for this study because the objective is to determine the general feasibility and attractiveness of the CO₂-water extraction technology for heteroatom removal.

2.2.3 Task 3.0 Process Variables Screening Studies. The objectives of this task were (a) to assemble the extraction test facility, and (b) to conduct preliminary extraction experiments to determine the range of variables that were to be investigated in the experiments with coal-liquid fractions.

This task was divided into two subtasks: Subtask 3.1. Experimental Setup, and Subtask 3.2. Screening Experiments.

2.2.4 Task 4.0 Process Characterization and Optimization. Under this task of the contract, systematic statistically-designed experiments were to be carried out and the characteristics of the process in treating different feedstocks was to be determined. Bulk of the testing was to be carried out with coal-derived naphtha and enough information on the product streams was to be obtained to estimate the downstream process requirements in the design of an integrated plant for the production of the transportation fuels. As a minimum, detailed analysis of all the product streams was to be carried out for the tests run at the most desirable operating conditions. The test data were to be analyzed statistically and optimum operating conditions for desirable process performance was to be determined.

A reduced experiment statistically-designed matrix was to be conducted to test the coal-derived diesel and jet fuel fractions. Some two-stage experiments were to be carried out under this task with naphtha as the feedstock. The purpose of these experiments was to study the feasibility of multi-stage experiments and to obtain an experimental estimate for the quality of product from a multi-stage operation. Raffinate oil from first-stage extraction experiment was to be used as feed for the second-stage experiment. The overall effectiveness of two-stage process was to be determined.

This task was further divided into four subtasks: Subtask 4.1. Extraction of Naphtha, Subtask 4.2. Extraction of Diesel, Subtask 4.3. Extraction of Jet Fuel, and Subtask 4.4. Two-Stage Experiments.

2.2.5 Task 5.0 Process Assessment. In this task, the technical and economic attractiveness of the CO₂-water extraction process for heteroatom removal from various feedstocks was to be assessed.

This task was divided in two subtasks: Subtask 5.1. Technical Assessment, and Subtask 5.2. Economic Assessment.

2.2.6 Task 6.0 Administration and Reporting. The objective of this task was to provide all of the necessary reports as required by the contract.

2.3 Revised Scope of Work

After the project was initiated and some proof-of-the-principle extraction experiments were carried out, the scope of the work was revised. Tasks 4.0 and 5.2 were eliminated from the contract in their entirety. The reasons for this revision will be discussed at length in the following sections of this report.

3.0 RESULTS AND DISCUSSIONS

In this section, results of the work performed under various tasks will be presented and the implications of the experimental findings will be discussed. Tasks 1.0: Project Work Plan and Task 6.0: Reports and Documents of the program are project management and administrative tasks and these will not be discussed any further.

3.1 Task 2.0 Feed Procurement and Analysis

Two different coal liquids were procured for this program. Selection of these samples was based mainly on their availability. Though one of the important criteria for the selection of the coal liquids for this program was identified as the heteroatom content of the coal liquids. Typically the sulfur and nitrogen content of the coal liquids is expected to be high and this high heteroatom content was noted to be a problem in the PRDA solicitation for this contract¹⁷. For example, the naphtha fraction resulting from liquefaction of a Wyodak coal from the Wilsonville pilot plant was described to contain 2,500 ppm sulfur and 2,200 ppm nitrogen.

3.1.1 Wilsonville Coal Liquids. The feedstocks for this program were made available to UOP by the Pittsburgh Energy Technology Center (PETC) of the DOE. The first coal liquid feedstock that was sent to UOP was sample V178 from Wilsonville Run 257H¹⁸. The elemental analysis of this sample is presented in Table 2. This sample in its original form was not usable by UOP for the current program, so DOE's Project Manager coordinated the fractionation of this sample into naphtha, jet fuel, and diesel cuts at the Pittsburgh Applied Research Center (PARC). The fractionated samples were collected in three drums and were sent to UOP. Each of the cuts received at UOP was analyzed in detail. The results of these characterizations are shown in Table 3. The sulfur content of the fractionated samples varied from 463 ppm to 725 ppm and the nitrogen content varied from 3000 ppm to 8500 ppm (basic nitrogen varied from 630 ppm to 5550 ppm). Sulfur contents of these samples were much less than that expected.

A brownish aqueous layer was observed at the bottoms of the drums in which the three coal liquid samples were sent to UOP. This aqueous layer suggests that the coal liquids may have been partially degraded in storage and shipping prior to their arrival at UOP. The two suspected

degradations are oxidation by air leakage into the drum, and extraction of water-soluble compounds by water leakage into the drums. Adequate precautions were taken at UOP to assure that further degradation of the coal liquids is prevented.

Most of the experimental work was carried out on the coal-derived naphtha sample.

3.1.2 HRI Coal Liquids. With DOE Project Manager's concurrence, a second coal liquid feedstock sample was procured from a DOE contractor, namely HRI, Inc. of Princeton, New Jersey. This new feed for the program comprised of distillates from HRI's catalytic two-stage liquefaction CTSL™ Process. The distillate samples from the separator overhead (SOH) and atmospheric still overhead (ASOH) of HRI's Bench Run 227-78 (CMSL-2) Periods 14, 15, and 17 were consolidated in four samples and analyzed. Sample 8033-12 was ASOH from Period 17, 8033-13 was SOH from period 17, and 8033-14 and 8033-15 represent composites from period 14 and 15. The blended samples were tested "as-is" and no attempts to further fractionate these samples in a specific cut were made.

Analytical results for the four blended samples are presented in Table 4. Nitrogen for these samples ranged from 633 ppm (basic nitrogen 430 ppm) for composite sample 8033-15 to 1606 ppm (basic nitrogen 1180 ppm) for ASOH sample 8033-12. Sulfur content varied from 232 to 479 ppm. In comparison, to the Wilsonville coal liquid feedstock, both sulfur and nitrogen content of the HRI coal liquid samples is low.

3.1.3 Characteristics of Coal Liquid Feedstocks. The coal liquid feedstocks obtained for this program are from coal liquefaction processes that have been developed over a number of years and hence are much more advanced than the first generation coal liquefaction processes. As a result, the coal liquid samples obtained from these processes are quite different than the first generation coal liquids. These advanced processes incorporate a much efficient hydrogen transfer and do some "upgrading" while processing. This upgrading effect is reflected in the relatively lower heteroatom contents of this advanced coal liquefaction products as illustrated in Table 5, which shows the comparison of the Wilsonville coal-derived naphtha and HRI ASOH coal liquid with two similar cuts from some "less advanced" coal liquefaction processes. Data for the Solvent Refined-Coal I (SRC I), Two-Stage Liquefaction (TSL), and Solvent Refined-Coal II (SRC II) processes were obtained from reference 19.

As discussed earlier, though higher heteroatom content was desired for coal liquid samples for this program, this criteria was not met. The program was initiated with the *readily available* coal liquid samples supplied by PETC.

3.2 Task 3.0 Process Variable Screening Studies

The overall objective of this task was to do some preliminary proof-of-the-principle experiments, assess the effectiveness of the extraction process, and screen the process variables in a systematic manner. To accomplish these objectives, and as discussed in Section 2.2.3, this task was divided into two subtasks. Each of these subtasks are discussed in detail below.

3.2.1 Subtask 3.1 Experimental Setup. For the preliminary proof-of-the-principle experiments, a simple mini-autoclave was set up. This mini-autoclave consisted of a jurguson flask and was connected to a source of nitrogen and carbon dioxide. The autoclave was provided with an agitator to mix the autoclave contents -- which could be withdrawn from the bottom of the jurguson flask.

The experimental procedure for the proof-of-the-principle experiments in the jurguson flask consisted of several steps. First, a specified volume of coal-derived liquid and de-ionized (DI)-water was placed in the mini-autoclave and then the autoclave was closed and pressurized to a pre-determined pressure with the appropriate test gas (CO₂ in this case). After the plant pressure was stabilized, the autoclave contents were vigorously mixed with an internal mixer for a specified time. After mixing, the autoclave contents were allowed to settle for a pre-determined settling time. With this autoclave, it was possible to visualize the autoclave contents and to observe the interphase between the aqueous and the hydrocarbon phase. This helped in withdrawing the separated aqueous and the hydrocarbon phases. Product hydrocarbon phase was sampled and analyzed for sulfur and nitrogen. The hydrocarbon and the aqueous phase samples were drawn while the autoclave was still under operating pressure.

In the mini-autoclave plant, the amount of liquid that can be introduced was limited to 50 ml. It was realized that to get a better handle on the total and component material balances, it was necessary to treat a larger volume (500 ml) of the liquids. For tests with relatively larger liquid

volume, an autoclave assembly was used. The experimental procedure for these tests was similar to that for the mini-autoclave tests.

3.2.2 Subtask 3.2 Screening Experiments. Most of the screening experiments were carried out with the Wilsonville coal-derived naphtha sample because it was the lightest cut among all of the coal liquid samples available to UOP. Based on the patent data, the lightest cut from the Paraho Shale oil showed the most promise in terms of heteroatom removal by the CO₂-water extraction process¹⁵.

A total of 25 screening experiments were completed under this task. Run Nos. 1 and 2 were plant shake-up runs. The objective of these two runs was to establish the experimental procedures and to test the system components. These runs will not be discussed in any further detail.

3.2.2.1 Baseline Extraction Runs. Run Nos. 3, 4, and 5 were base case water-only extraction runs and were carried out under a nitrogen atmosphere. Data from these three runs are summarized in Table 6. The feedstock for these runs was Wilsonville naphtha. In these runs, 25 ml of naphtha was mixed with 25 ml of DI water and the autoclave contents were pressurized to 50 psig with nitrogen. The contents were mixed for 5 (Run No. 3) to 120 (Run No. 5) mins and then allowed to settle for 10 minutes. Two distinct phases (hydrocarbon and aqueous) were formed at this time and were separately collected. The sulfur and nitrogen content of the hydrocarbon phase is shown in Table 6. The S and N removal reported in Table 6 is based on the disappearance of the sulfur and nitrogen from the product relative to the feed and is defined as follows:

$$\% \text{ S Removal} = [(\text{Feed S} - \text{Product S}) / \text{Feed S}] * 100$$

$$\% \text{ N Removal} = [(\text{Feed N} - \text{Product N}) / \text{Feed N}] * 100$$

Following observations are made from these data:

- The nitrogen content of the feed is reduced by up to 41 % with water extraction.
- No increase in nitrogen removal is apparent after 30 minute of mixing time.
- There is an apparent increase in the sulfur content of the product.

The exact reasons for the apparent increase in the sulfur content of the hydrocarbon products were not investigated in any detail; however, two sources were suspected for this observed increase. The sulfur content of the hydrocarbons was measured by LECO analyzers. Though this analytic technique has been found to be reliable for various petroleum feedstocks, difficulties were encountered with the coal-based feedstocks and different numbers for sulfur contents of the same sample were obtained over a short period of time. These numbers differed by 30-40%, which in some cases is greater than the differences observed between the feed and the product samples. Also for this set of data, the feed sulfur was assumed to be the same as the head sample and individual sulfur data for each different feed sample was not collected. Because of these reasons, the sulfur removal numbers may not represent the process performance and hence, no rational decision can be made on the effect of water extraction on sulfur removal.

3.2.2.2 Proof-of-the-Principle Extraction Runs. Runs 6 through 16 were carried out by the same procedure as that described above for Runs 3 through 5. Wilsonville coal-derived naphtha was used as the feedstock. Data from this set of runs are presented in Table 7. The hydrocarbon to water ratio for these runs was 1:1. The range of variables investigated were: CO₂ pressure: 50 to 800 psig, mixing time: 5 to 120 minutes, and settling time: 10 to 60 minutes. All the runs were carried out at ambient temperature (20 to 27°C). Feed samples were not individually analyzed for Runs 6 through 12, and the feed sulfur and nitrogen content for these runs was assumed at 734 ppm and 3400 ppm, respectively. Table 7 also includes sulfur and nitrogen removal data which are calculated by the formula listed under Section 3.2.2.1.

Figure 3 shows the effect of mixing time on the removal of nitrogen compounds from the Wilsonville naphtha and a comparison of Wilsonville naphtha extraction with CO₂-water (Runs 6-9) and water only (Runs 3-5). Following observations are made:

- Mixing time of more than 30 minutes does not seem to have any advantage for nitrogen removal from Wilsonville naphtha.
- At 50 psig pressure, extraction of naphtha with CO₂ offers only a marginal advantage over extraction with water (under an inert -- N₂ atmosphere).

Following this set of tests (Runs 3 through 8), the mixing time for the subsequent tests was set at 30 minutes. Analysis of data from Runs 6 through 16 is presented in the following paragraphs.

In Runs 17 through 24, the mixing time and the settling time were set at 30 minutes each. The operating procedure was slightly modified. The aqueous phase was sampled from the mini-autoclave under operating pressure and was mixed with a paraffin and allowed to settle to separate the paraffin and the aqueous phase. The paraffin phase was analyzed for sulfur and nitrogen. Except for Runs 17 to 19, the aqueous sample obtained after mixing with paraffin was also analyzed for sulfur and nitrogen. Data for nitrogen and sulfur removal for these runs are presented in Table 8. Runs 17 through 21 used Wilsonville naphtha as the feedstock. Run 22 was carried out with Wilsonville diesel, Run 23 with Wilsonville Jet Fuel and Run 24 with a high-sulfur petroleum-based diesel. The CO₂ pressure for these runs was varied from 100 to 600 psig. Efforts were also made during these runs to do a material balance. Data from the material balance analysis are reported in Table 9. The sulfur and nitrogen removal for Wilsonville naphtha as a function of CO₂ pressure are shown in Figure 4. Only those runs for which the mixing time is 30 minutes or more are plotted in this figure. Following observations are made from the data shown in Tables 7, 8, and 9 and Figure 4:

- Except for a few cases, the overall and component material balance are in the low- to high-90 percent range (Table 9). This closure on the overall and component mass balance is reasonable for a batch experiment of this nature.
- The nitrogen removal results are quite reproducible for a number of experiments carried out at identical operating conditions (See Tables 7 and 8). For example, in Runs 16, 19, and 21 carried out at 600 psig CO₂ pressure, the nitrogen removal was 38.9%, 37.5%, and 35.5%, respectively.
- Based on the patent claims¹⁵, one would expect that with increasing CO₂ pressure the removal of nitrogen and sulfur from the naphtha will increase. However, as shown in Figure 4, no effect of increasing CO₂ pressure on nitrogen removal was observed. The data for sulfur removal are very erratic. The possible reasons for the erratic nature of the sulfur removal data are discussed above in Section 3.2.2.1.
- The nitrogen removal from Wilsonville diesel and jet fuel was 11% and 8%, respectively (Table 8, Runs 22 and 23). This is not surprising because one would expect lower heteroatom removal from these heavier cuts than that obtained for naphtha.

- Even with the best heteroatom removal results obtained in this series of tests, the naphtha product had a nitrogen content of 1700 ppm (Run 17) and a sulfur content of 513 ppm (Run 12). This heteroatom levels are quite high for any subsequent upgrading of this product stream.

3.2.2.3 Autoclave Extraction Run. Run 25 with feed sample 8033-12 was completed in the autoclave assembly. The operating procedure was slightly modified and the run was conducted at ambient temperature and with a 1:1 hydrocarbon to DI-water volume ratio. The experimental procedure consisted of several steps. First, 250 ml each of the coal liquid and the DI-water were placed in the autoclave and then the autoclave was pressurized to 600 psig with CO₂. After plant pressure was stabilized, the autoclave contents were vigorously mixed with an internal mixer for 30 minutes. After mixing, the autoclave was allowed to settle for 30 minutes. Samples of the hydrocarbon, aqueous phase and the interphase were taken. The interphase was then mixed with n-hexane to separate aqueous and organic phases. All four samples were then characterized.

Table 10 shows the analysis of each of the four phases. The numbers highlighted in this table are estimated. Various material balance and heteroatom rejection calculations are shown in Exhibit 1. The feed, hydrocarbon phase, and interphase hydrocarbon were analyzed by the ASTM D2887 chromatographic distillation technique. Results from these analyses are shown in Figure 5.

Overall material balance for this run was quite good as all of the material fed to the reactor was recovered. Also, the nitrogen balance was good, but the sulfur balance was poor. The hydrocarbon product yield was quite low at 77.1%; however, this was the result of the way in which the experiment was conducted. The interphase level in the autoclave was not visible and operator judgement was used to separate the aqueous phase, interphase, and hydrocarbon phase. When reasonable assumptions were made about the recovery of hydrocarbon phase in the interphase, all of the hydrocarbon was accounted for. Based on the combined hydrocarbon product, 23.2% of nitrogen (24.2% basic nitrogen) and 25.5% of sulfur was rejected. The combined hydrocarbon phase still contains 828 ppm nitrogen and 342 ppm sulfur. This level of heteroatoms in the hydrocarbon phase is still quite high and further heteroatom removal will be necessary before this hydrocarbon stream can be upgraded. The implications of these data are discussed in detail under Section 3.4.

3.3 Task 4.0 Process Characterization and Optimization

The objective of this task was to carry out systematic, statistically-designed experiments and to determine the characteristics of the process in treating different feedstocks. To meet this objective, this task was further divided into three subtasks to study process performance on three different coal liquids. The subtasks were: Subtask 4.1 Extraction of Naphtha, Subtask 4.2 Extraction of Diesel, and Subtask 4.3 Extraction of Jet Fuel.

In view of the results of the proof-of-the-principle experiments with Wilsonville naphtha (see Section 3.2), characteristics of the available feedstocks from the advanced coal liquefaction processes (Section 3.1), and the technical reasons discussed below in Section 3.4, it was decided, with DOE Project Manager's concurrence, that no further work be carried out under this task. As a result, Task 4.0 was eliminated from the modified statement of work for the contract.

3.4 Task 5.0 Process Assessment

The objective of this task was to assess the technical and the economic attractiveness of the CO₂-water extraction process. This task was further divided into Subtask 5.1 Technical Assessment and Subtask 5.2 Economic Assessment. Since detailed process characterization (Task 4.0) was eliminated from the modified statement of work, basis for a detailed cost estimate was not generated during this program and Subtask 5.2 Economic Assessment was also deleted from the contract.

3.4.1 Subtask 5.1 Technical Assessment. The overall objective of this program was to develop an extraction process (with CO₂ and water as the solvent) for the removal of heteroatoms from *coal-derived* naphtha, diesel, and jet fuel. As discussed in Section 1.2.3, this process has been demonstrated on Paraho Shale oil and has shown significant reduction of nitrogen content for various fractions, particularly of the lighter fractions¹⁵ (see Table 1). A secondary, but quite important from a commercial view point, objective of the program was to evaluate the benefits attained in terms of reduced hydrogen requirement for the upgrading of the coal liquids.

The proof-of-the-concept experiments demonstrated that the nitrogen removal from coal-derived naphtha (30-45%) is comparable to that reported for the somewhat heavier 400-500°F Paraho shale oil fraction (33%). Nitrogen removal from the HRI ASOH (23%) is comparable to the results reported for the Total Paraho sample (25%). In this respect the data collected in this program match quite well with that reported for the Paraho shale oil and its fractions¹⁵. However, there were two other findings in this program, one of which is different than that claimed by the patent. When the coal naphtha was treated with de-ionized water *only* (under a nitrogen atmosphere), the nitrogen reduction obtained (41%, Figure 4) was comparable to that obtained with CO₂-water as the solvent. Secondly, contrary to what is claimed in the patent, no effect of increasing CO₂ pressure was observed in this program up to a CO₂ pressure of 800 psig. This is illustrated in Figure 4, which shows that irrespective of the CO₂ pressure, the nitrogen reduction remained in a very narrow range between 30 to 45%. If one looked only at the results (without any statistical analysis), nitrogen reduction at 800 psig CO₂ pressure (30%) was lower than that obtained at 600 psig CO₂ pressure (38%). Because of the limited data, no statistical analysis of the data was attempted.

These data raise a very fundamental question: within the range of variables investigated and with the feedstocks studied, what is gained (in terms of nitrogen reduction) by using CO₂-water extraction compared to water-only extraction? Based on the data above, the answer to this question is that the water-only extraction is equally effective with the CO₂-water extraction for the feedstocks and the process conditions investigated in this program.

The secondary objective of this program was to reduce the hydrogen requirements for the upgrading of the coal liquids. As discussed under Section 1.0, hydrogen costs are one of the largest contributor (25% to 40%) to the total cost of refining coal liquids². If substantial heteroatom removal is achieved by the CO₂-water extraction than the cost of the coal liquid upgrading can be reduced significantly. UOP has done considerable amount of work on upgrading of coal liquids¹. Data on the hydrotreating of coal-derived naphtha and distillate are presented in Tables 11 and 12. For the upgrading of H-Coal naphtha and distillate, their sulfur and nitrogen content needs to be reduced to ppm level. As shown in these tables, H-Coal naphtha is hydrotreated to 0.5 ppm sulfur and 0.6 ppm nitrogen at a hydrogen consumption of 480 SCF/B. For H-Coal distillate severe hydrotreating is required to achieve the desired sulfur and nitrogen levels (Table 11). The hydrogen requirement in this case is 3640 SCF/B. If the proposed extraction process achieves the level of nitrogen and sulfur represented by mild

hydrotreating in Table 11, then it is probable that the hydrogen requirements for distillate upgrading can be reduced by 1100 SCF/B.

As shown in Tables 7 and 8, the best nitrogen and sulfur levels attained in the Wilsonville naphtha after extraction with CO₂-water were 1700 ppm and 513 ppm respectively. This heteroatom levels are much higher than that desired for subsequent processing and as a result, the hydrogen savings that will be attained by incorporating the extraction process will not be significant. In other words, the extraction process will not reduce the hydrotreating required for these products.

Based on this technical assessment of the process for the coal liquids tested under this program, it was decided that no further experiments should be carried out and that the program should be ended.

TABLE 2
Elemental Analysis of Wilsonville Coal Liquid
(Run 257H Sample V178)

Element	% by weight
Carbon	87.53
Hydrogen	11.80
Sulfur	0.02
Nitrogen	0.06
Chlorine	0.00
Oxygen (by difference)	0.59

TABLE 3
Characterization of Wilsonville Coal Liquid Fractions

	Naphtha	Jet Fuel	Diesel
Specific Gravity	0.7733	0.9601	0.9883
API Gravity	51.5	15.9	11.7
Distillation (Volume % ↓)	Temperature, °C		
IBP	42	190	288
5	64	201	295
10	74	205	297
20	87	210	299
30	95	216	300
40	105	223	301
50	114	228	304
60	123	235	309
70	133	241	314
80	142	248	322
90	152	254	334
95	167	260	348
EP	180	268	352
% Over at EP	96.4	98.5	98.3
Sulfur (wt-ppm)	725	463	552
Basic N (wt-ppm)	630	4290	5550
N by Chemil (wt-ppm)	3000	5600	8500
Arsenic (AAS wt-ppm)	<0.1	<0.1	0.11
Carbon (wt-%)	76.8	83.0	86.6
Hydrogen (wt-%)	11.8	9.4	9.6
Oxygen (wt-%)	2.5	6.3	3.1
Bromine Number	24.9	5.4	5.3
Paraffins (vol-%)	33.8		
Naphthenes (vol-%)	41.7		
Aromatics (vol-%)	15.5	74.4	77.7
Olefins (vol-%)		5.8	3.5
Naphthenic	4.7		
Paraffinic	2.4		
Polynaphthenes (vol-%)	1.7		

TABLE 4
Characterization of HRI Coal Liquids

	ASOH 8033-12	SOH 8033-13	Composite 8033-14	Composite 8033-15
Specific Gravity	0.9171	0.8669	0.8931	0.8810
API Gravity	22.8	31.7	26.9	29.1
Distillation - D86A (Volume % ↓)	Temperature, °C			
Initial Boiling Point	137	75	93	83
5	192	130	139	118
10	213	130	162	136
20	234	139	203	169
30	255	161	235	209
40	270	192	258	233
50	281	224	275	261
60	292	252	289	281
70	302	282	303	298
80	313	311	316	315
90	326	347	334	338
95	338	387	354	366
End Point	340	390	363	364
% over at EP	97.6	97.2	97.9	97.6
Sulfur (wt-ppm)	479	484	259	232
Basic N (wt-ppm)	1180	810	570	470
N by Chemil (wt-ppm)	1606	1121	754	633
Arsenic (AAS wt-ppm)	<0.1	<0.1	<0.1	<0.1
Carbon (wt-%)	87.3	85.9	86.9	87.0
Hydrogen (wt-%)	8.9	10.4	10.5	10.7
Bromine Number	6.6	5.6	4.6	5.1

TABLE 5
Sulfur and Nitrogen Contents of Coal Liquids

	Sulfur, ppm	Nitrogen, ppm
SRC - I C ₅ - 177° C cut	4500	4100
TSL C ₅ - 177°C cut	2000	3800
SRC - II C ₅ - 177° C cut	2700	7800
<i>Wilsonville Naphtha (42 - 180°C cut)</i>	725	3000
SRC - I 177 - 454° C cut	4100	6400
TSL 177 - 454° C cut	1600	5300
SRC - II 177 - 454° C cut	2900	12200
<i>HRI ASOH (137 - 340° C cut)</i>	479	1606

TABLE 6
Extraction of Coal-derived Naphtha with Water

Run Number →	3	4	5
Mixing Time, min	5	30	120
N ₂ Pressure, psig	50	50	51
Temperature, °C	24	25	26
Feed S, wt-ppm	734	734	734
Feed N, wt-ppm	3400	3400	3400
Product S, wt-ppm	918	751	740
Product N, wt-ppm	2200	2000	2000
Aqueous phase pH	9.2	9.2	9.1
S Removal, %	-25.1	-2.3	-0.8
N Removal, %	35.3	41.2	41.2

TABLE 7
Extraction of Coal-derived Naphtha with CO₂ and Water

Run Number →	6	7	8	9	10	11	12	13	14	15	16
Mixing Time, min	5	30	120	60	30	30	30	60	5	30	30
Settling Time, min	10	10	10	60	30	30	30	30	30	30	30
CO ₂ Pressure, psig	51	50	50	50	100	200	400	600	590	800	600
Temperature, °C	22	22	24	26	26	27	27	25	24	20	25
Feed S, wt-ppm	734	734	734	734	734	734	734	630	630	682	1100
Feed N, wt-ppm	3400	3400	3400	3400	3400	3400	3400	3500	3500	3300	3600
Product S, wt-ppm	NA	699	772	715	603	586	513	638	677	664	951
Product N, wt-ppm	2200	1900	1900	1900	2300	2200	2200	2200	2200	2300	2200
Aqueous phase pH	6.7	6.6	6.5	6.7	6.6	6.9	7.1	6.9	6.8	6.8	7.1
S Removal, %	NA	4.8	-5.2	2.6	17.8	20.2	30.1	-1.3	-7.5	2.6	13.5
N Removal, %	35.3	44.1	44.1	44.1	32.4	35.3	35.3	37.1	37.1	30.1	38.9

TABLE 8
Extraction of Coal Liquids with CO₂ and Water

Run Number →	17	18	19	20	21	22	23	24
Coal Liquids	Naphtha	Naphtha	Naphtha	Naphtha	Naphtha	Diesel	Jet Fuel	K-Diesel
CO ₂ Pressure, psig	100	300	600	300	600	600	600	600
Temperature, °C	23	25	25	23	26	25	24	26
Feed S, wt-ppm	596	910	924	922	786	281	325	4000
Feed N, wt-ppm	3100	3100	3200	3100	3100	8200	5000	600
Product S, wt-ppm	818	826	892	879	791	342	NA	4400
Product N, wt-ppm	1700	1900	2000	1900	2000	7300	4600	NA
Aqueous phase pH	6.7	6.5	8.8	6.8	6.7	6.3	6.6	5.6
S Removal, %	-37.2	9.2	3.52	4.7	-0.6	-21.7	NA	-10.0
N Removal, %	45.2	38.7	37.5	38.7	35.5	11.0	8.0	NA

TABLE 9
Material Balance for Runs 17 to 24

Run Number →	17	18	19	20	21	22	23	24
Weight Recovery, %								
Total	94.9	92.4	94.3	92.4	89.4	93.9	97.9	92.3
Aqueous phase	97.9	96.5	97.9	97.2	96.2	84.9	97.0	89.0
Hydrocarbon	91.0	86.8	89.4	86.1	80.3	102.9	98.9	96.2
Nitrogen, wt-ppm								
Feed	3100	3100	3200	3100	3100	8200	5000	600
Hydrocarbon phase	1700	1900	2000	1900	2000	7300	4600	NA
Paraffin	83	109	92	179	82	12	42	NA
Aqueous phase	NA	NA	NA	857	764	186	440	54
N Distribution, %								
Hydrocarbon phase	54.8	60.8	61.4	61.3	64.5	89.0	91.0	NA
Paraffin	2.4	3.6	2.7	7.8	2.9	0.1	0.7	NA
Aqueous phase	NA	NA	NA	36.2	33.1	2.3	8.8	NA
TOTAL	NA	NA	NA	105.3	100.6	91.4	100.5	NA
Sulfur, wt-ppm								
Feed	596	909	924	922	786	281	325	4000
Hydrocarbon phase	818	825	892	879	791	342	NA	4400
Paraffin	8	10	18	3	5	0	0	13
Aqueous phase	NA	NA	NA	60	38	4	1	NA
S Distribution, %								
Hydrocarbon phase	124.8	78.8	86.3	82.1	80.9	125.2	NA	105.8
Paraffin	1.2	1.1	1.8	0.5	0.7	0.1	0	0.4
Aqueous phase	NA	NA	NA	8.3	6.3	1.3	0.3	0
TOTAL	NA	NA	NA	90.8	87.8	126.5	NA	106.2

TABLE 10
Properties of Feed and Product Streams for Run 25

	Weight, g	Sulfur, wt-ppm	Nitrogen, wt-ppm	
			Basic	Total
Feed	214	461	930	1083
DI Water	243	0	0	0
Hydrocarbon Phase	165	422	830	974
Aqueous Phase	198	< 10	110	95
Interphase	95	40	256	230
Int. - Aqueous	45	< 10	230	105
Int. - Hydrocarbon	50	77	280	345

Note: Highlighted numbers are estimated.

TABLE 11
Hydrotreating of H-Coal Primary Naphtha

	Naphtha Feed	Hydrotreated Product
°API at 60°F	43.7	46.8
IBP, °F	132	153
EP, °F	396	393
Sulfur, wt-ppm	1289	0.5
Nitrogen, wt-ppm	1930	0.6
Oxygen, wt-ppm	5944	34
Chlorine, wt-ppm	23	4
MS Types, volume %		
Polar	4.2	-
Aromatics	18.6	17.6
Olefins	5.5	-
Naphthenes	55.5	63.4
Paraffins	16.2	19.0
Hydrogen Consumption, SCF/B	-	480

TABLE 11
Hydrotreating of H-Coal 400°F+ Distillates

	Distillate Feed	Hydrotreated Product (Mild)	Hydrotreated Product (Severe)
°API at 60°F	8.6	16.8	29.2
IBP-650°F, vol.-%	81	91	99
650°F-EP, vol.-%	18	5.5	-
EP, °F	769	710	670
Sulfur, wt-ppm	800	6.7	0.2
Nitrogen, wt-ppm	4100	856	2
Oxygen, wt-ppm	5200	--	--
Aromatics, vol.-%	90	73	12
Hydrogen Consumption, SCF/B	--	1130	3640

EXHIBIT 1
Calculations for Run 25

Material Balance

$$\text{Total In} = \text{Feed} + \text{DI water} = 214 + 243 = 457 \text{ g}$$

$$\text{Total Out} = \text{Hydrocarbon} + \text{Aqueous} + \text{Interphase} = 165 + 198 + 95 = 458 \text{ g}$$

$$\text{Material Recovery, \%} = (\text{out/In}) * 100 = 100.2$$

Nitrogen Balance

$$\begin{array}{ll} \text{Nitrogen In} = 214 * 1083 * 1\text{E-}06 = 0.2318 \text{ g} & \text{(Basic N)} \\ & (0.1990 \text{ g}) \end{array}$$

$$\text{Nitrogen Out} = (165*974 + 198*95 + 95*230) * 1\text{E-}06 = 0.2014 \text{ g} \quad (0.1831 \text{ g})$$

$$\text{Nitrogen Recovery, \%} = (0.2014/0.2318) * 100 = 86.9 \quad (92.0)$$

Sulfur Balance

$$\text{Sulfur In} = 214 * 461 * 1\text{E-}06 = 0.0987 \text{ g}$$

$$\text{Sulfur Out} = (165*422 + 198*10 + 95*40) * 1\text{E-}06 = 0.0734 \text{ g}$$

$$\text{Sulfur Recovery, \%} = (0.0734/0.0987) * 100 = 74.4$$

Rejection Efficiencies

$$\text{Total Hydrocarbons recovered} = 165 + 50 = 215 \text{ g}$$

$$\text{Hydrocarbon Phase Yield, \%} = (215/214) * 100 = 100.5$$

$$\text{N content of Total hydrocarbon phase} = (165*974 + 50*345)/215 = 828 \text{ ppm}$$

$$\text{Basic N content of Total hydrocarbon phase} = (165*830 + 50*280)/215 = 702 \text{ ppm}$$

$$\text{Sulfur content of Total hydrocarbon phase} = (165*422 + 50*77)/215 = 342 \text{ ppm}$$

$$\text{N Rejection, \%} = [1 - [(165*974 + 50*345)/(214*1083)]] * 100 = 23.2$$

$$\text{Basic N Rejection, \%} = [1 - [(165*830 + 50*280)/(214*930)]] * 100 = 24.2$$

$$\text{Sulfur Rejection, \%} = [1 - [(165*422 + 50*77)/(214*461)]] * 100 = 25.5$$

Figure 3

Comparison of CO₂-water and Water Extraction

@50 psig, 1:1 HC-to-water ratio

■ Nitrogen ▲ Carbon Dioxide

Figure 4

Effect of Pressure on N and S Removal

1:1 Hydrocarbon-to-water ratio
■ Nitrogen * Sulfur

4.0 REFERENCES

1. A.J. DeRosset, et al., "Upgrading of Coal Liquids", Annual Report for the Period January 31, 1978 to January 31, 1979 for Contract No. EF-77-C-01-2566, UOP Inc., May 1979.
2. R.E. Hildebrand, "Refining of Coal Derived Syncrude", U.S. Department of Energy Memorandum with Summary Report Attached, April 1980.
3. J.B. MacArthur, et al., "H-Coal Process Liquids - Upgrading Options for Fuels Production", paper presented at the 1982 NPRA Annual Meeting, San Antonio, March 21-23, 1982.
4. Brown, G. G., Unit Operations, John Wiley & Sons, New York, NY, 1950, pp. 297-321.
5. Williams, D. F., "Extraction with supercritical gases," Chemical Engineering Science, vol. 36, no. 11, pp. 1769-1788, 1981.
6. Hoyer, G. G., "Extraction with supercritical fluids: Why, how, and so what," ChemTech, pp. 440-448, July 1985.
7. Cagniant, D., et al., "Carbon dioxide supercritical extraction from coal and petroleum," Erdoel, Erdgas, Kohle, 106 (9), pp. 350-355, 1990.
8. Williams, D. F., "Getting the best out of coal - by gas," Spectrum, 13(4), pp. 53-54, 1975.
9. Beneke, H., Siegfried, P., "Three-step process for separation of indole, quinoline bases and phenol derivatives from coal tar oil by supercritical extraction with carbon dioxide," German Patent No. DE 3813636, 5 pp., 1989.
10. Barker, I. K., et al., "Separation of compounds from gasifier tars by extraction with supercritical carbon dioxide," Fuel, 68(5), pp. 601-606, 1989.
11. Yamasaki, A., et al., "Supercritical carbon dioxide extraction for coal liquid and the effect of diethylene glycol as an entrainer," Nenryo Kyokaishi, 68(2), pp. 153-157, 1989.

12. Siegfried, P., et al., "Method for separation of phenols and bases from coal-tar oils by extraction," German Patent No. 3610369, 6 pp., 1987.
13. Baset, Z., "Removal of basic nitrogen compounds from organic streams," U.S. Patent No. 4332675, 4 pp., 1982.
14. Dugan, J. J., Eng, J., "Deasphalting with liquid hydrogen sulfide," U.S. Patent No. 4054512, 4 pp., 1977.
15. Hitzman, D. O., "Oil Treatment," U.S. Patent No. 4518489, May 21, 1985.
16. Francis, A. W., "Ternary Systems of Liquid Carbon Dioxide," J. of Phys. Chem., vol. 58, pp. 1099-114, 1954.
17. Program Research and Development Announcement (PRDA) No. DE-RA22-91PC91035, Advanced Research Liquefaction, U.S. Department of Energy, February 15, 1991.
18. P. Zhou, Burns and Roe Services Corporation, Pittsburgh, Pennsylvania, Letter to J. Schauer, UOP, November 12, 1992.
19. Carson, T. C., Hastings, K. E., and Potts, J. D., "Two-Step Coal Liquefaction is a Hydrogen Efficient Route to Distillate Fuels," paper presented at the Annual Fall Conference of the Canadian Society for Chemical Engineering, Sarnia, Ontario, 9/30 - 10/3/1979.

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