

## LIQUEFACTION CO-PROCESSING OF COAL AND SHALE OIL AT LOW SEVERITY CONDITIONS

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### ABSTRACT

Results are reported for a series of single stage batch reactor experiments in which Wyodak subbituminous coal and shale oil derived from medium grade Colorado oil shale were co-processed at low severity reaction conditions using CO/H<sub>2</sub>O as reducing agent. Distillate yields of over 85 wt% MAF coal with hydrogen equivalent consumptions of about 1.0 wt% MAF coal were obtained at 600°F reaction temperature. Results from blank shale oil runs at the same mild reaction conditions suggested that shale oil residuum reactivity was enhanced in the presence of coal or primary coal-derived products.

### INTRODUCTION

The possibility of liquefying coal at low severity reaction conditions ( $\leq 700^\circ\text{F}$ ) has intrigued researchers for many years. As early as 1921, Fischer and Schrader (1) reported production of an ether-soluble material from coal at 660°F using carbon monoxide and water as reducing agent. More recently other groups including the Pittsburgh Energy Technology Center (PETC) (2), the North Dakota Energy Research Center (3-4), SRI (5-7), and Carbon Resources, Inc. (8) have investigated various methods of utilizing H<sub>2</sub>, CO/H<sub>2</sub>O or CO/H<sub>2</sub>/H<sub>2</sub>O (syngas) in low severity liquefaction processes. Many incentives exist for converting coal at milder reaction conditions. The most important of these are listed below:

- 1) Reduced H<sub>2</sub> (or CO) consumption and hydrocarbon gas make
- 2) Better distillate and residuum product quality, since carbonization and other retrogressive reactions are suppressed to a large extent
- 3) Production of less refractory residuum which is more susceptible to hydrocracking in a conventional second stage hydrotreater or hydrocracker
- 4) Significant energy savings associated with lower operating temperatures
- 5) Less severe slurry handling and materials of construction problems

A number of studies have been reported in which coal and non-coal-derived heavy oil have been co-processed at severe reaction conditions to obtain valuable distillable liquid products (9-11). In some cases, larger distillate yields were obtained by co-processing coal and heavy oil than by processing each feed separately. Shale oil has been identified as a particularly promising feed, due in part to the high heterocyclic basic nitrogen content of the oil (12). In spite of the advantages of operating at milder conditions, little work on low severity co-processing has been reported.

The objective of this paper is to report yield and conversion data from a series of single-stage low severity co-processing runs using Wyodak subbituminous coal and shale oil derived from medium grade Colorado shale. Blank shale oil runs (no coal added) were also completed at low severity conditions to estimate the individual distillate yield contributions of coal and shale oil.

#### EXPERIMENTAL PROCEDURE

Wyodak subbituminous coal sample Wyo-3 was used as feed coal in the low severity liquefaction co-processing experiments. The ultimate analysis for this sample is presented in Table I. Sampling and preparation details of the coal have been reported elsewhere (13,14). Previous reactivity studies performed on four Wyodak subbituminous coals including Wyo-3 indicated that Wyo-3 was an extremely reactive coal at representative direct liquefaction reaction conditions (13,15). The high degree of reactivity was primarily attributed to the high organic sulfur and reactive maceral (vitrinite and exinite) content of Wyo-3 coal. Coal samples were dried to less than 1.0 wt% moisture content before use.

Two shale oil samples were used in low severity liquefaction co-processing runs. Solvent A-5 was a full boiling range sample of shale oil obtained from the Western Research Institute (formerly the Laramie Energy Technology Center of the Department of Energy). This sample was produced from thermal retorting of medium grade (29 gal/ton) Colorado oil shale. Solvent A-6 was prepared by mildly hydrotreating a portion of sample A-5 in a two liter batch Autoclave Magnedrive II reactor at 650°F for one hour with an initial cold hydrogen pressure of 2000 psig. Nalco 477 cobalt molybdate catalyst was used to hydrotreat the shale oil. Catalyst samples were thermally activated at 1000°F for two hours in a muffle furnace prior to use. Approximately 0.6 wt% hydrogen was consumed by the shale oil during hydrotreating. Properties of shale oil samples A-5 and A-6 are presented in Table II. Approximately 50 wt% of the nitrogen in these samples existed in quinoline-type or hydroquinoline-type molecular structures.

Runs were carried out in a 60 cm<sup>3</sup> stirred microautoclave reactor system designed and constructed at the University of Wyoming. This reactor was similar to larger Autoclave batch reactors except that heating was accomplished with an external high temperature furnace. At the end of each run, the reactor and its contents were quenched with an icewater batch. This reactor system provided the benefits of small tubing bomb reactors [quick heatup (~1 min. from room temperature to 650°F) and cooldown (~30 sec. back to room temperature)], while at the same time insuring sufficient mechanical agitation of the reactants with an Autoclave Magnedrive II stirring assembly to minimize hydrogen mass transfer effects. The system was also designed so that the reactor pressure was very nearly constant throughout an experiment. Two iron-constantan thermocouples attached to a Fluke 2175A digital thermometer were used for temperature measurements. One thermocouple measured the temperature of the reactor contents, while the other measured the temperature of the reactor wall. Reactor pressure was monitored using a 0 - 5000 psi Marsh pressure gauge.

In these runs, carbon monoxide and water were used as reducing agent, with hydrogen being produced via the aqueous phase water-gas shift reaction. Reaction conditions were studied in the range: 600-650°F

reaction temperature, 1000-1500 psig initial cold carbon monoxide pressure, and 15-60 minutes reaction time. Distilled water is an amount equal to 50 wt% of the dry feed coal was charged to each reactor run. Iron sulfate (5 wt% dry feed coal) was used as a disposable catalyst.

Gaseous products were analyzed using gas chromatography. Water and distillate yields were measured by distilling portions of the combined liquid-solid product mixture to an 850°F endpoint in a micro-distillation apparatus. Additional portions of the liquid-solid product mixture were extracted in a Soxhlet extraction apparatus using cyclohexane, toluene, and pyridine. Details of the experimental procedures used in this work have been reported (9).

## RESULTS AND DISCUSSION

Using data collected with the analytical procedures described, detailed yield and conversion results were computed for each liquefaction co-processing run. Details of the computational methods used in this study have been described previously (9). For purposes of the present discussion, process performance will be monitored using the following two parameters:  $C_4$ -850°F distillate yield (wt% MAF coal basis), and pyridine conversion (wt% MAF basis). Pyridine conversion is defined as a measure of the extent of conversion of all feeds (coal and non-coal-derived heavy oil) to pyridine soluble products. However, since both A-5 and A-6 shale oil samples were completely soluble in pyridine and negligible coking of the shale oil occurred at low severity reaction conditions, pyridine conversion values reported in this paper are direct measures of the extent of coal conversion in the co-processing runs.

### Effect of Shale Oil Prehydrotreatment

Figure 1 shows distillate yield results from co-processing runs completed using Wyo-3 coal and either A-5 or A-6 shale oil at 600°F and 1500 psig initial cold CO pressure. This data clearly shows that mild hydrotreatment of the shale oil greatly enhances co-processing performance. Coal conversion also increased significantly when A-6 shale oil was used in place of A-5 shale oil. Distillate yields of over 85 wt% MAF coal (58 wt% MAF coal and 850°F+ shale oil) and pyridine soluble coal conversions of nearly 60 wt% MAF basis were obtained with A-6. Previous high severity co-processing studies using Wyo-3 and A-6 also demonstrated the beneficial effect of prehydrotreatment. The enhancement at low severity conditions can be attributed to: 1) increased hydrogen donor ability of the hydrotreated shale oils and 2) increased concentration of partially hydrogenated basic nitrogen compounds such as tetrahydroquinoline and piperidinopyridine in the shale oil. These compounds are known to promote coal dissolution and catalyze the aqueous phase water-gas shift reaction.

### Effect of Reaction Temperature

Figures 2 and 3 present yield and conversion results for co-processing runs completed with Wyo-3 and A-6 at 600°F and 650°F. These data show that process performance improved at lower reaction temperature. This effect can be at least partially attributed to the favorable thermodynamic equilibrium of the water-gas shift reaction at lower temperatures.

### Effect of Initial Carbon Monoxide Pressure

The effect of varying the initial CO pressure is illustrated in Figure 4. At 600°F reaction temperature, increasing the CO pressure from 1000 to 1500 psig more than doubled the distillate yield over the entire range of reaction times studied. These data indicate that relatively high pressure is required to achieve sufficient CO solubility in the aqueous phase for the water-gas shift reaction to proceed at a satisfactory rate.

### Results from Blank A-6 Shale Oil Runs

In an attempt to estimate the amounts of distillate derived from coal and from shale oil, several blank shale oil runs (no coal added) were completed. Results from both high severity and low severity blank runs are shown in Figure 5. These data were then used to estimate the amount of distillate attributable to the shale oil feed in each co-processing run. Estimates of the coal-derived distillate production were computed by assuming that half of the total coal-derived cyclohexane soluble product was distillate. Results of these calculations are shown in Figure 6. Both low severity and high severity runs are included in this figure for comparison purposes. In each co-processing run, additional distillate in excess of that predicted by the blank shale oil runs was obtained. Thus, it appears likely that the reactivity of shale oil residuum towards distillate production is enhanced in the presence of coal or primary coal-derived products.

### CONCLUSIONS

A series of low severity liquefaction co-processing runs has been completed using Wyodak subbituminous coal and two shale oil samples. Results indicated that prehydrotreatment of the shale oil, lower reaction temperature, and higher initial CO pressure all contributed to enhanced process performance. Distillate yields in excess of 85 wt% MAF coal were obtained at 600°F, 1500 psig CO pressure, and 60 minute reaction time. Results from blank shale oil experiments suggested that overall distillate yield could be maximized by co-processing coal and shale oil rather than processing the two feeds separately.

### ACKNOWLEDGEMENTS

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Table I

Ultimate Analysis of Wyodak  
Subbituminous Coal Wyo-3

Ultimate Analysis, wt% dry basis

Carbon	58.2
Hydrogen	4.3
Nitrogen	0.8
Sulfur	2.9
Sulfate	0.8
Pyrite	0.9
Organic	1.2
Oxygen (difference)	13.9
Ash	19.9

Table II  
Properties of Shale Oil Samples

Sample	<u>A-5</u>	<u>A-6</u>
<b>Wt% Distilled</b>		
Water	0.7	0.1
350°F	4.2	10.3
350°F-500°F	9.6	18.3
500°F-650°F	18.8	22.5
650°F-850°F	39.0	29.8
850°F+	27.7	19.0
<b>Ultimate Analysis, wt% dry basis</b>		
Carbon	83.3	84.7
Hydrogen	12.1	12.9
Nitrogen	1.4	1.2
Sulfur	0.5	0.4
Oxygen (difference)	2.7	0.8
Ash	0.0	0.0

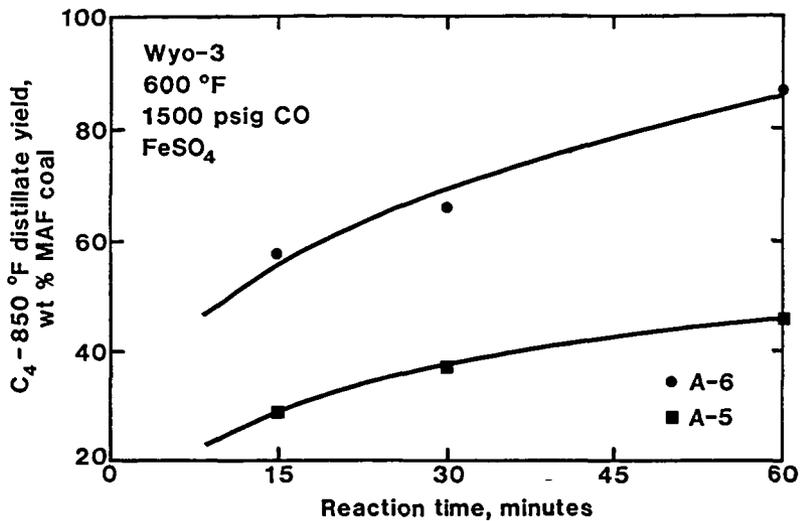


Figure 1. Distillate Yield as a Function of Reaction Time and Shale Oil Feed

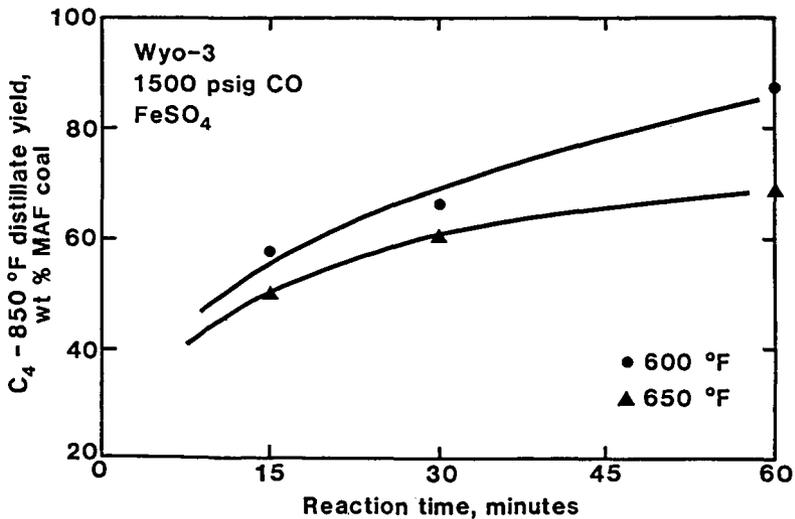


Figure 2. Distillate Yield as a Function of Reaction Time and Temperature

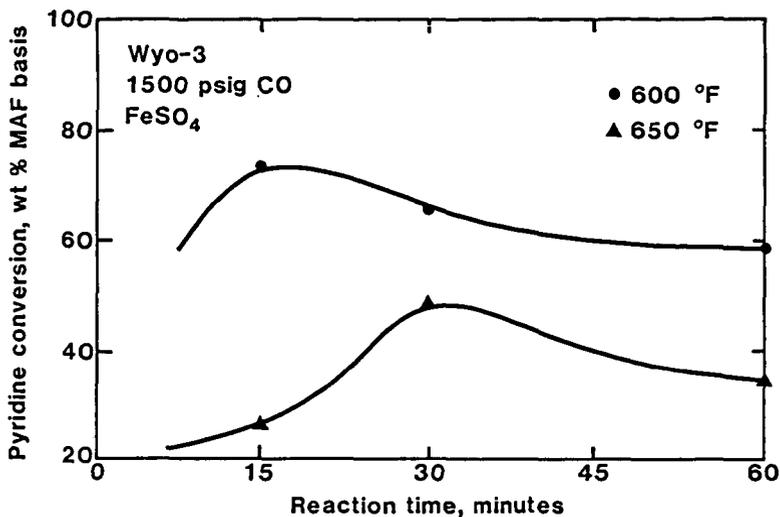


Figure 3. Pyridine Conversion as a Function of Reaction Time and Temperature

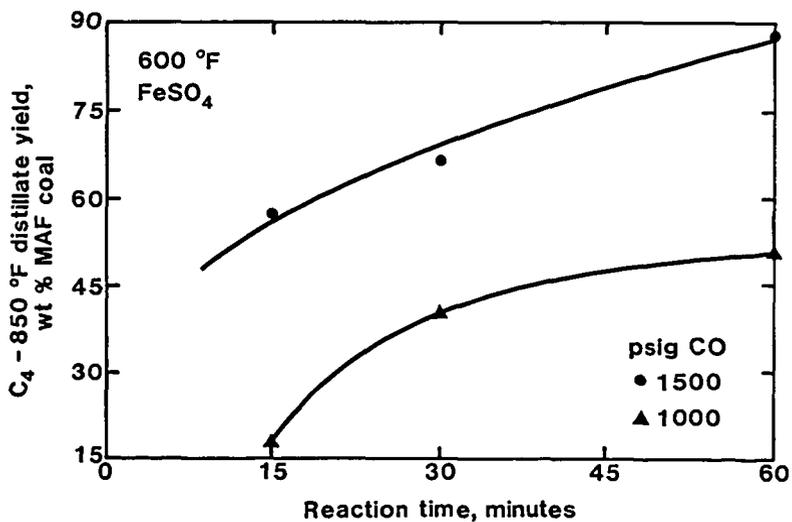


Figure 4. Distillate Yield as a Function of Reaction Time and CO Pressure

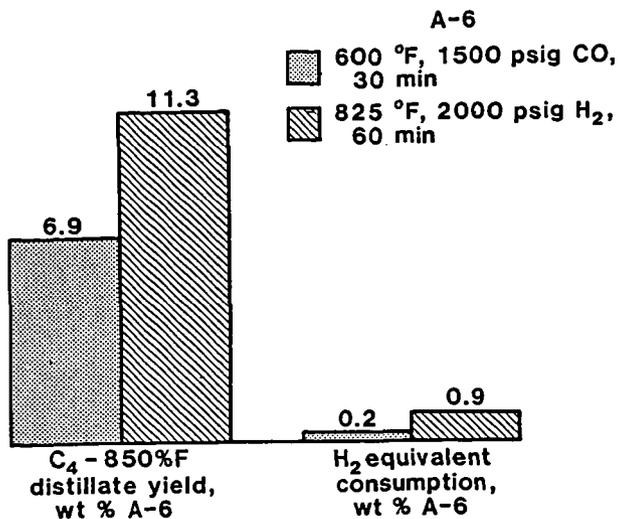


Figure 5. Results from Blank Shale Oil Runs at Low and High Severity Reaction Conditions

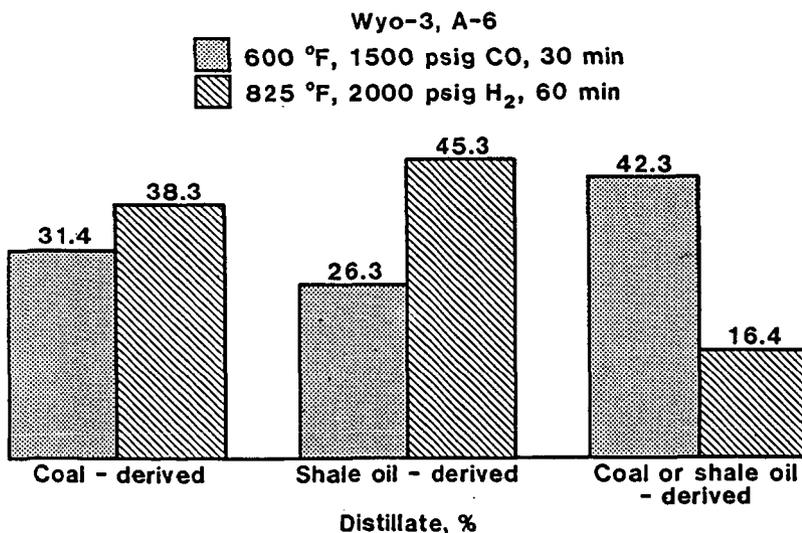


Figure 6. Estimated Distribution of Distillate Production from Wyo-3 Coal and A-6 Shale Oil at Low and High Severity Reaction Conditions

The Roles and Importance of Hydrogen  
Donation and Catalysis in Coprocessing

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The roles and relative importance of hydrogen donation and catalysis in producing an upgraded product slate from coprocessing are explored. These effects are examined in two types of systems: the upgrading of residuum and the coprocessing of coal with residuum. In these experiments, the reactions were performed both thermally and catalytically in the presence and absence of tetralin (TET) to elucidate possible synergetic interactions between the catalyst and TET for increased coal conversion and an improved product slate.

Catalytic coprocessing which has been extensively reviewed by Monnier (1) generally produces an improved product slate and a higher degree of upgrading than does thermal coprocessing. Previous work performed by Curtis et al. (2,3) has shown the necessity of having highly accessible catalysts for coprocessing. Catalyst accessibility affects both the amount of coal conversion and the degree of upgrading of liquefied coal to soluble products and of petroleum asphaltene to pentane solubles. In this work, two highly accessible catalysts are investigated: an oil soluble catalyst, Mo naphthenate, and a presulfided commercial NiMo/Al<sub>2</sub>O<sub>3</sub> hydrotreating catalyst which was ground to -200 mesh to increase its accessibility and, hence, its activity. Mo naphthenate is a metal salt of an organic acid that is thought to be converted to an active catalyst under typical coprocessing conditions of high temperature and hydrogen atmosphere with a partial pressure of hydrogen sulfide. The active species is believed to be a noncolloidal metal sulfide (4,5).

The effect of hydrogen donor compounds on the products obtained from coprocessing has been examined by Curtis et al. (6). They concluded that hydrogen must be available for upgrading reactions to occur in coprocessing and that the hydrogen can be present either as molecular H<sub>2</sub> or donable hydrogen. The type of donor present affected the product slate; tetrahydroquinoline promoted coal conversion while tetralin and dihydrophenanthrene promoted the production of lighter products. When reacted in either a H<sub>2</sub> or N<sub>2</sub> atmosphere, concentrations of donable hydrogen at the 0.5 wt% level or higher were required to substantially affect coal conversion.

The objective of the current work is to investigate the effect of hydrogen donor addition in conjunction with catalytic hydrotreatment on the products obtained from upgrading residuum and coprocessing coal with petroleum residuum. The reaction products are evaluated in terms of solubility fractions, coal conversion to solubles in the solvent extraction scheme used and oil production. Oil production is defined as the amount of pentane solubles after reaction minus the initial pentane solubles divided by the upgradeable materials which are the pentane insoluble materials from maf coal and the residuum. In addition, the amount of hydrogen transferred to the products via gas-phase molecular hydrogen and donation by hydrogen donors is examined. The efficacy of donable hydrogen in promoting coal conversion and producing a high quality product slate is evaluated in thermal and catalytic coprocessing.

## Experimental

Upgrading and Coprocessing Reactions. Upgrading and coprocessing reactions were conducted in 50 ml stainless steel reactors, charged with 1250 psig H<sub>2</sub> cold (giving ~3000 psi at reaction temperature), 3g mf coal and 6g solvent. In the catalytic experiments, the catalyst charge was 1g of presulfided Shell 324 NiMo/Al<sub>2</sub>O<sub>3</sub> (0.044g Mo/g mf coal) ground to -200 mesh from 1/16" inch extrudates or, when using Mo naphthenate, the charge was 0.002g Mo/g mf coal. Reaction conditions were 30 minutes at 400°C for the thermal reactions and at 400° and 425°C for the NiMo/Al<sub>2</sub>O<sub>3</sub> and Mo naphthenate reactions. The reactors were agitated at 700 cpm with 2 steel balls as agitation aids. Maya topped long resid (TLR) was used in the upgrading reactions and as the solvent in the coprocessing reactions. For coprocessing, Western Kentucky 9/14 bituminous coal was used. In the reactions using TET, one weight percent donable hydrogen was introduced; the TET composed about one-third of the solvent. Each upgrading or coprocessing reaction was, at least, duplicated and some were triplicated or quadruplicated. The activity of the NiMo/Al<sub>2</sub>O<sub>3</sub> was tested by reacting naphthalene in H<sub>2</sub> at 300°C. Naphthalene (NAPH) was nearly totally hydrogenated forming TET and decalin (DEC), producing the expected amount (7). The activity of the Mo naphthenate was also tested using naphthalene hydrogenation.

Product Analysis. The liquid products obtained from the upgrading and coprocessing reactions were analyzed using solvent extraction. The product fractions obtained were PS - pentane soluble; BS - benzene soluble, pentane insoluble; MCMS - methylene chloride/methanol soluble benzene soluble; THFS - tetrahydrofuran (THF) soluble, methylene chloride/methanol insoluble; IOM - insoluble organic matter, insoluble in THF. In the coprocessing reactions, coal conversion was calculated on the basis of the amount of material converted to soluble products and was corrected for the amount of IOM formed in the upgrading reactions with equivalent reaction conditions. The weight of the gas after reaction was measured and the hydrogen consumption was determined using PVT methods. The hydrogen consumption was calculated for each reaction.

The PS and BS fractions of the reaction products were analyzed by temperature programmed gas chromatography using a Varian Model 3700 equipped with a FID and a 60 m DB-5 J and W fused silica capillary column. The PS and BS fractions were analyzed for TET, DEC and NAPH to determine the amount of hydrogen transferred by TET to coal and the petroleum solvent. An internal standard, p-xylene, was used. Dihydronaphthalenes were not detected at detectability levels of  $2.4 \times 10^{-11}$ g.

Solvent extraction analysis of Maya TLR showed that the residuum before reaction was composed of 77.6% PS and 22.4% BS. TET, NAPH, and DEC were not observed in the chromatograms of the extracted residuum at the detectability levels of  $2.4 \times 10^{-11}$  g. Western Kentucky 9/14 coal was nearly insoluble at room temperature with less than 3% MCMS and 1% THFS being present.

## Discussion of Results

Upgrading of Residuum. The results from the thermal and catalytic upgrading reactions performed in the presence and absence of tetralin are given in Table 1. After Maya TLR was thermally upgraded in H<sub>2</sub>, the product solubility fractions obtained deviated only slightly from the unreacted residuum. The major change observed was the decrease of the BS fraction and the formation of lighter and heavier fractions. Hydrogen consumption during the reaction was 17.7 mmole of H<sub>2</sub> per 6 g charge of residuum. No TET, NAPH, or DEC was observed in the upgraded residuum. When TET was added at the one percent donable hydrogen level, the product analysis was similar to that without TET except that the IOM was greater

and the oil fraction was slightly less (Table 1). Both hydrogenation and dehydrogenation reactions involving TET were observed in the reaction system:



The dehydrogenation reaction was predominant and produced  $\text{H}_2$  while the hydrogenation reaction occurred to a lesser extent and consumed  $\text{H}_2$ . The net amount of hydrogen transferred was calculated by subtracting the  $\text{H}_2$  consumed by reaction 2 from that produced from reaction 1.

Table 1  
Upgrading of Residuum

Product	Thermal 400°C		NiMo/Al <sub>2</sub> O <sub>3</sub>			Mo Naphthenate		
	Maya TLR	Maya TLR + TET	Maya TLR	Maya TLR + TET	Maya TLR	Maya TLR	Maya TLR	Maya TLR + TET
Gas	1.9	2.0	2.1	2.4	3.7	1.3	2.7	1.7
PS	80.0	79.1	85.4	88.1	86.0	80.5	86.7	85.2
BS	17.1	17.4	7.7	5.3	4.5	15.9	9.9	11.0
MCMS	0.4	0.3	0.7	1.2	0.4	0.6	0.2	0.9
THFS	0.5	0.4	0.7	1.1	0.2	0.2	0.1	0.6
IOM	0.1	0.8	3.4	1.9	5.2	1.5	0.4	0.6
H <sub>2</sub> (g) Consumed, mmoles	19.5	14.2	31.3	28.5	44.3	23.1	19.5	12.82
H <sub>2</sub> Transferred, mmoles	NA*	2.6	NA	0.5	NA	NA	NA	0.62
Total H <sub>2</sub> Used, mmoles	19.5	16.8	31.3	29.0	44.3	23.1	19.5	13.44
Oil Production, %	11.4	10.2	39.6	53.5	44.1	16.0	43.6	39.5

NA: Not Applicable

In the thermal upgrading reaction with TET, 2.6 mmoles of  $\text{H}_2$  were transferred from TET to the residuum and an average of 14.2 mmoles of molecular hydrogen were consumed; therefore, the total hydrogen utilized by the residuum was 16.8 mmoles. Although the total amount of  $\text{H}_2$  transferred to and consumed by the residuum was greater in the reaction without TET, the increased hydrogen utilization by the residuum did not result in higher conversion of BS to PS; both reactions had nearly equivalent oil production.

**Catalytic Upgrading.** In the catalytic upgrading of Maya TLR with NiMo/Al<sub>2</sub>O<sub>3</sub>, two-thirds of the original BS were reacted, forming both lighter and heavier products (Table 1). A substantial amount of IOM, 3.4%, was produced compared to 0.1% in the thermal reaction. Catalytic hydrotreatment increased oil production to ~ 40% compared to 11.4% in the thermal reaction and hydrogen consumption was doubled. With NiMo/Al<sub>2</sub>O<sub>3</sub>, trace but measurable quantities of DEC, TET, and NAPH were observed in both the PS and BS product fractions. These results indicate that while substantial upgrading, i.e., high oil production and hydrogen consumption, occurred, coking also occurred, producing heavy products from the residuum.

In Table 2, the hydrogen contents of the PS and BS fractions from the upgrading reactions are given. Comparing the hydrogen content obtained from

catalytic to the thermal hydrogenation shows increases in the hydrogen content in both PS and BS fractions with NiMo/Al<sub>2</sub>O<sub>3</sub>. Thus, it appears that the increased hydrogen consumption resulted in a direct increase of the hydrogen content of the products. Comparison of the gas chromatograms obtained from both the PS and BS fractions prior to the reaction to that obtained after the thermal and catalytic reactions, however, did not show any visible changes in the product fingerprint. Changes in the compounds present or the addition of new compounds to these product fractions was not discernible in the chromatograms.

Table 2  
Elemental Composition of PS and BS Fractions from Upgrading Fractions

Reactants	Temperature °C	Catalyst	PS		BS	
			% C	% H	% C	% H
Maya TLR	No Reaction		84.7	11.5	NM*	NM
			84.7	11.4	NM	NM
Maya TLR	400	None	85.7	11.2	82.8	7.0
			85.6	11.4	83.1	7.0
Maya TLR	400	NiMo/Al <sub>2</sub> O <sub>3</sub>	87.1	12.0		
			86.8	11.8	83.9	8.5
Maya TLR	400	Mo Naphthenate	84.9	11.3	82.7	6.5
			84.6	11.2	82.9	7.6
Maya TLR	425	Mo Naphthenate	86.1	11.8	85.3	7.4
			88.0	12.1	85.3	7.3
Maya TLR	No Reaction		86.9	10.0	NM	NM
+ TET						
Maya TLR	400	None	86.6	10.2	83.6	7.3
+ TET			86.7	10.3	83.6	6.8
Maya TLR	400	NiMo/Al <sub>2</sub> O <sub>3</sub>	87.9	10.9	79.3	8.7
+ TET			87.6	10.8	78.2	8.4
Maya TLR	425	Mo Naphthenate	86.8	10.3	84.9	7.3
+ TET			87.0	10.3	84.3	7.4

\*NM: Not measured

When TET was added, a higher oil production (53.5%) and a decrease in BS were observed, although the total amount of heavy products (MCMS, THFS, and IOM) was similar to the reaction without TET. In these reactions, the catalyst and TET were both positive factors in producing PS materials. The molecular hydrogen consumed by the residuum was nearly equivalent to the reaction without TET. Only 0.39 mmoles of NAPH were produced which was approximately one-sixth that produced in the thermal reaction, indicating that hydrogenation of NAPH formed during the reaction to TET occurred in the presence of NiMo/Al<sub>2</sub>O<sub>3</sub>.

The catalytic upgrading reactions with Mo naphthenate were performed at 400 and 425°C. Compared to the thermal reaction, only a small change in product slate was observed with Mo naphthenate at 400 °C. At an increased reaction temperature of 425°C, the activity of the Mo naphthenate catalyst appeared to be enhanced since substantial increases in the upgrading of Maya TLR were observed; BS was converted to PS and only small amounts, <0.4%, of IOM were formed. An oil production of 43.6% was achieved yielding a substantial increase over that (16%) observed at 400°C. When TET was added, the product slate was very similar to that without TET although the total mmoles of H<sub>2</sub> utilized by the residuum was slightly less (Table 1). Only 0.44 mmoles of NAPH were produced, again indicating the rehydrogenation of NAPH to TET in the presence of Mo naphthenate.

Coprocessing of Coal with Residuum. In thermal coprocessing, Maya TLR and Western Kentucky 9/14 coal were reacted in the presence and absence of TET at a one percent donable hydrogen level (Table 3). The reaction without TET achieved 47.9% coal conversion which was corrected to account for the IOM produced from the reaction using Maya TLR alone. The thermal coprocessing reactions utilized 12.3 mmoles of H<sub>2</sub> and achieved an oil production of 12.6%. When TET was added, coal conversion increased to 69.7%; however, oil production was lowered to 4.1%. Although the consumption of molecular hydrogen in the reaction with TET was ~2 mmoles less than in the reaction without TET, an additional 6.5 mmoles of H<sub>2</sub> was transferred from TET to the coal/petroleum system, yielding the total of 16.6 mmoles of H<sub>2</sub> utilized by the coal/residuum system. The increased H<sub>2</sub> utilization by the coal/residuum/TET system resulted in increased coal conversion and in the production of the heavier product fractions but not in increased oil production.

Table 3  
Coprocessing of Coal with Residuum at 400°C

Product Distribution, %	Thermal		NiMo/Al <sub>2</sub> O <sub>3</sub>		Mo Naphthenate
	Maya TLR + Coal	Maya TLR Coal + TET	Maya TLR + Coal	Maya TLR + Coal + TET	Maya TLR + Coal
Gas	1.7	1.9	1.8	1.7	1.9
PS	53.2	48.3	63.6	60.1	54.7
BS	17.3	18.6	17.9	22.3	18.4
MCMS	5.8	9.9	3.1	5.5	8.6
THFS	5.9	9.0	1.6	1.9	8.6
IOM	16.1	12.3	12.0	8.5	7.8
H <sub>2</sub> (g) Consumed, mmoles	12.3	10.1	30.2	45.7	26.7
H <sub>2</sub> Transferred, mmoles	NA*	6.5	NA*	0.6	NA*
Total H <sub>2</sub> Used, mmoles	12.3	16.6	30.2	46.3	26.7
Corrected Coal Conversion, %	47.9	69.7	68.9	81.8	78.5
Oil Production, %	12.6	4.1	23.3	29.2	3.8
BS Production, %	5.6	12.9	7.7	22.1	9.7

NA: Not Applicable

Catalytic Coprocessing. Catalytic coprocessing of Western Kentucky coal with Maya TLR was performed in the presence of NiMo/Al<sub>2</sub>O<sub>3</sub> and Mo naphthenate catalysts and also with and without TET. Analysis of the products achieved from these reactions are given in Tables 3 and 4. Catalytic treatment with NiMo/Al<sub>2</sub>O<sub>3</sub> achieved 68.9% coal conversion which was greater than thermal coprocessing (47.9%) and nearly equivalent to thermal coprocessing with TET (69.7%). The oil production from catalytic coprocessing was more than double that of the thermal reactions with and without TET. In addition, higher hydrogen consumption and lower yields of the MCMS and THFS fractions were obtained, indicating a more highly upgraded product. The combined effect of hydrogen donation from TET and hydrotreatment from NiMo/Al<sub>2</sub>O<sub>3</sub> synergetically promoted coal conversion since the addition of TET produced a higher coal conversion (81.8%) than did the catalyst alone (68.9%) or the thermal reaction with TET (69.7%). High quality products were produced during

the reaction with oil production reaching nearly 30%, higher BS and lower levels of MCMS and THFS fractions were also observed. A higher consumption of molecular hydrogen occurred with TET addition than without. During the reaction, three times more NAPH was produced than DEC; however, the NAPH production of 0.53 mmoles in the catalytic reaction was low compared to 3.4 mmoles produced in the thermal reaction. As in the upgrading reactions, the presence of NiMo/Al<sub>2</sub>O<sub>3</sub> caused NAPH to be rehydrogenated to TET and a consumer of H<sub>2</sub>. The total amount of H<sub>2</sub> utilized by the coal/resid/TET system was 46.3 mmoles which was higher than the thermal reaction or the NiMo/Al<sub>2</sub>O<sub>3</sub> reaction without TET. A small increase in the hydrogen content of the PS was observed compared to the thermal reaction as shown in Table 5.

Table 4  
Coproducting of Coal with Residuum at 425°C

Product Distribution, %	Thermal	NiMo/Al <sub>2</sub> O <sub>3</sub>	Mo Naphthenate	
	Maya TLR + Coal	Maya TLR + Coal	Maya TLR + Coal	Maya TLR + Coal + TET
Gas	4.1	3.5	4.0	3.6
PS	55.1	61.8	66.8	61.9
BS	15.0	19.8	19.3	21.8
MCMS	3.4	2.8	4.8	6.0
THFS	3.1	2.0	1.6	2.1
IOM	19.4	9.6	3.5	4.6
H <sub>2</sub> (g) Consumed, mmoles	29.8	41.6	57.5	49.9
H <sub>2</sub> Transferred, mmoles	NA*	NA	NA	2.6
Total H <sub>2</sub> Used, mmoles	29.8	41.6	57.5	52.5
Corrected Coal Conversion, %	52.4	80.6	89.5	89.3
Oil Production, %	6.6	22.8	31.4	32.0
BS Production, %	-1.8	11.3	12.6	19.5

\*NA: Not applicable

When Mo naphthenate was used in coprocessing at 400°C, coal conversion increased compared to the thermal reaction but little other effect was observed (Table 3). When the temperature was increased to 425°C (Table 4), substantial increases in coal conversion, hydrogen consumption, and oil production were observed in the reactions using Mo naphthenate. Since in these reactions both a catalyst was added and the temperature was increased, the effect of the temperature increase on the reaction must be ascertained. This effect can be evaluated from the data given in Table 4, by comparing the products produced during the thermal reaction at 425°C to those produced with Mo naphthenate. Since both coal conversion and oil production were low in the thermal reaction at 425°C, the high levels of coal conversion and oil production can then be attributed to the catalytic activity of Mo naphthenate not the temperature increase. Comparing Mo naphthenate to NiMo/Al<sub>2</sub>O<sub>3</sub> at 425°C, shows that Mo naphthenate is more active in terms of oil production and coal conversion even though the concentration level of Mo in the NiMo/Al<sub>2</sub>O<sub>3</sub> reaction was 22 times that in Mo naphthenate reaction.

Table 5  
Elemental Composition of PS and BS Fractions from Coprocessing

Reactants	Temperature °C	Catalyst	PS		BS	
			% C	% H	% C	% H
Maya TLR	400	None	84.5	11.4		
+ Coal			84.0	11.3	82.8	7.1
Maya TLR	400	NiMo/Al <sub>2</sub> O <sub>3</sub>	84.8	10.9	84.6	7.4
+ Coal			84.8	10.9	86.8	7.3
Maya TLR	400	Mo Naphthenate	84.3	10.8	83.6	7.2
+ Coal			84.3	10.8	84.1	7.2
Maya TLR	425	Mo Naphthenate	85.7	11.0		
+ Coal			84.6	10.6	86.3	6.4
			84.9	10.7	85.1	6.8
			85.1	10.6		
Maya TLR	400	None	86.3	10.1	83.8	6.9
+ Coal + TET			86.4	10.1	83.5	7.0
Maya TLR	400	NiMo/Al <sub>2</sub> O <sub>3</sub>	87.8	10.5		
+ Coal + TET			87.1	10.5	86.0	7.0
			85.7	10.3	84.7	7.1
			87.4	10.5		
Maya TLR	425	Mo Naphthenate	86.9	10.5	85.6	6.6
+ Coal + TET			86.5	10.3	85.7	6.6

The presence of TET in the coal/resid/Mo naphthenate system did not substantially change the product slate. Coal conversion, hydrogen consumption and oil production were the same as the reaction without TET. The total amount of NAPH formed during the reaction was 1.5 mmoles which fell between that for the thermal and NiMo/Al<sub>2</sub>O<sub>3</sub> reactions. Ten times as much NAPH was formed as DEC. The H<sub>2</sub> utilized by the Mo naphthenate systems, 57.5 mmoles without TET and 52.5 mmoles with TET, was high compared to the other reactions performed. The product slates from these Mo naphthenate reactions show the effective utilization of H<sub>2</sub> in terms of coal conversion and oil production.

Effect of the Catalyst Compared to Tetralin on the Product Slate. The addition of catalyst in the residuum upgrading reactions increased the amount of oil production achieved and, in the case of NiMo/Al<sub>2</sub>O<sub>3</sub>, substantially increased the IOM formed. The presence of TET had varying effect; but only in the reaction with NiMo/Al<sub>2</sub>O<sub>3</sub> did TET improve the oil production. In all upgrading reactions, the BS fraction was reduced during the reaction forming both lighter and heavier products. The catalytic reactions with NiMo/Al<sub>2</sub>O<sub>3</sub> and Mo naphthenate at 425°C reduced the BS fraction the most. The combination of TET plus NiMo/Al<sub>2</sub>O<sub>3</sub> resulted in the greatest reduction of the BS fraction and subsequent increase in the PS fraction.

In the coprocessing experiments, both the addition of catalyst and the addition of tetralin promoted coal conversion. For the NiMo/Al<sub>2</sub>O<sub>3</sub> reactions, the combination of catalyst and tetralin synergetically promoted coal conversion. With Mo naphthenate, coal conversion was high (89.5%) without TET addition and no change was observed with the addition of TET. Thus, with a highly accessible and active catalyst, additional hydrogen donation from the solvent had little influence on coal conversion. Therefore, coal conversion in coprocessing appears to be dependent upon both catalyst and hydrogen donation except in the case of a highly active catalyst where catalytic activity predominates.

TET did not promote the production of PS materials in either the thermal or catalytic reactions. In fact, in the thermal reactions the presence of TET was detrimental to oil production.

The effect of TET and catalytic treatment on BS production is also instructive in examining the roles and relative importance of these two factors in coprocessing. BS production is defined as the difference between the final BS and the initial BS divided by the upgradeable material which is maf coal. Compared to the thermal reaction at 400°C, the addition of TET increased the amount of BS production (Table 3). Catalytic treatment at 400°C did not increase the BS production; however, the addition of TET to reaction system with NiMo/Al<sub>2</sub>O<sub>3</sub> at 400°C did enhance BS production. At 425°C, the presence of NiMo/Al<sub>2</sub>O<sub>3</sub> and Mo naphthenate increased the BS production as shown in Table 4. The addition of TET to the Mo naphthenate reaction again increased the BS production. Since all of these reactions showed positive oil production, the increases observed in the BS production were directly related to the upgrading of liquefied coal to BS products. Thus, the presence of TET assisted in the production of BS but not in the production of PS. The presence of a hydrotreating catalyst was required for oil production in the coprocessing reactions.

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## REACTIVITY SCREENING OF FEEDSTOCKS FOR CATALYTIC COAL/OIL CO-PROCESSING

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### ABSTRACT

HRI is currently conducting a four-party funded program to develop and demonstrate catalytic coal/oil co-processing using HRI's proven ebullated-bed reactor technology. The initial task in the research program was to determine reactivities of four coals (Illinois No. 6 and Ohio No. 5/6 bituminous, Alberta sub-bituminous and Texas lignite) and four petroleum residuums (Cold Lake, Maya, West Texas Sour, and Canadian IPL), both separately and in combination, using a 20cc microautoclave reactor. Experimental conditions and analytical procedures were developed to properly approximate ebullated bed conditions at the small, batch scale and to allow estimation of both coal and petroleum residuum conversions. Over 200 single-stage microautoclave tests were conducted studying severity, feedstock ratio, and catalyst effects. An interesting synergistic response was noted which indicates optimum performance at 50/50 coal/oil ratio for one particular feedstock pair. Initial results from a single-stage run in a continuous bench unit verified the trends noted in the microautoclave study.

### INTRODUCTION

Hydrocarbon Research, Inc. (HRI) has developed and commercialized ebullated-bed reactor technology for the catalytic hydroconversion of both coal and heavy oil. The H-Oil® Process has been commercially demonstrated in both single- and two-stage process configurations, and the H-Coal® Process has been successfully scaled up through the 200 ton/day Catlettsburg pilot plant. While economic conditions have prevented the commercial application of direct liquefaction technology, coal/oil co-processing has gained increasing attention as a more commercially viable, nearer term way to introduce coal-derived liquid fuels into the market place. HRI's COILS<sup>SM</sup> Process for co-processing was demonstrated on a bench unit scale as early as 1974<sup>(1)</sup>, and more recently a two-stage process configuration was demonstrated on a Canadian feedstock combination of potential commercial interest<sup>(2)</sup>. In 1985, a four-party funded program was started to further develop and demonstrate catalytic coal/oil co-processing using HRI's ebullated-bed reactor technology. The program sponsors, objectives and elements are listed in Table 1. This paper focuses on the results of the microautoclave reactivity screening program.

## MICROAUTOCLAVE DESCRIPTION AND PROCEDURES

With the recent increase in interest in co-processing, numerous investigators have reported results of batch reactor reactivity studies at various scales<sup>(3-6)</sup>. Many of these approaches tend to take a conventional coal liquefaction approach, by characterizing the effectiveness of petroleum oils as coal liquefaction "solvents". In coal/residuum co-processing, the oil is not a process solvent as such, but rather a reactant, and its reactions/conversions are of equal - or even greater, depending on specific conditions - importance than those of the coal. The opposite approach to this is to view co-processing as an extension of refining technology, treating the coal as an additive, usually in limited quantities<sup>(7,8)</sup>. HRI's program was set up to consider a broad range of potential applications using catalytic ebullated-bed co-processing. The microautoclave experimental and analytical procedures were specifically developed to reflect this, and are in many respects considerably different than those used by other workers. Some discussion is therefore necessary to explain the basis for these differences.

The 20cc microautoclave reactor used in these studies is shown in Figure 1. Solvent, coal, residuum, and catalyst are charged batchwise in the appropriate amounts prior to mounting the reactor. Following pressure-testing, the desired H<sub>2</sub> (or N<sub>2</sub>) pressure is established. Due to the volume of gas lines above the reactor itself, it is essentially an "infinite source" hydrogen system, and no adjustment of operating pressure due to temperature is usually required. The entire assembly is shaken vertically with approximately one-inch strokes at 460 rpm, with temperature control by immersion in a fluidized sand bath heater. Dual sand baths are available for simulation of two-stage, close-coupled processing. Two identical microautoclave reactors are always operated side-by-side. A cold trap is provided to collect any light liquids lost during operation or depressuring.

Following each run the reaction is quenched by immersion in a water bath, and slowly depressured. The reactors and cold traps are then removed, and the products are combined and subjected to the workup procedures described in Figure 2. The use of the catalyst basket allows separation of product solids from catalyst extrudates. Ash-balancing then allows calculation of coal conversion. If necessary, product ashes can be checked for catalyst metals to distinguish coal ash from attrited catalyst. TGA simulated distillation is used to estimate product residuum contents and calculate residuum conversions. For selected runs, solvent precipitation was used to calculate asphaltene and preasphaltene components in the product residuum, although this is of lesser utility in co-processing than in coal liquefaction since petroleum residua contains very low levels of insolubles.

As noted above, HRI's microautoclave operating procedures and conditions are specifically designed to most properly approximate the conditions of an ebullated-bed reactor, and are in many cases quite different than those "typically" used in the industry. Some specifics include:

- Catalyst Type and Loading - The ebullated-bed reactor operates with conventional extrudate catalysts at very high loadings (up to 50% of the reactor volume is occupied by catalyst). Our microautoclave experiments typically charged a catalyst/feedstock ratio of 1/1 to reflect this. Techniques such as grinding of catalyst are not representative. The catalyst used typically is process-presulfided in a pilot unit, and the use of the catalyst basket allows separation from reaction products. Some assumptions are necessary in calculation procedures to account for items such as IOM deposition on catalyst, catalyst attrition, etc. during an experiment.
- Feedstock Dilution with Distillate Products - The ebullated bed is a well-mixed reactor, due to the typically high ratio of internal recycle to fresh feed. As a result, reaction occurs in a concentration represented by the products. No batch reactor can properly model a CSTR from the standpoint of fundamental kinetics, so a compromise has to be made. Since the initial conversion reactions in coal liquefaction are critical, an attempt is made to simulate the reactor environment in which they occur. Thus, microautoclave reactor charges are made up with a high level of distillate diluent. An attempt is made to approximate, to the extent possible, the properties of the distillate materials which would be expected to be produced from the feedstocks and conditions of interest. The distillate solvents used are generally materials produced in substantial quantities from larger pilot plant operations on the feedstocks of interest.
- Product Analyses - Coal conversion to THF-solubles is calculated in a fairly typical manner. As noted above, conversions based on solubilities in other solvents are not considered to be especially meaningful for co-processing. A simulated distillation procedure was developed using a Perkin-Elmer TGS-2 Thermogravimetric Analyzer (TGA), which allows estimation of 975°F+ conversions. No attempt is made to generate data such as gas yields or distillate product distribution or quality. Such data are difficult to generate reliably on such a small scale. Even if this could be done, the results would not be meaningful for scaleup due to the large impacts of the distillate diluents and the major differences between batch and continuous units, on any scale.

#### SCREENING STUDY CONDITIONS

A five-point, low-to-mild severity condition matrix was used to screen each feedstock and combination of interest, as shown in Table 2. As noted, a 4/1/1 charge ratio of distillate solvent/reactant (coal and oil)/catalyst was used. Severities ranged from 2-20 STTU, based on HRI's conversion model developed for coal conversions. It is recognized that the time/temperature relationships for co-processing may not be truly represented by the STTU model, but it was used as a convenient way to express both severity parameters. The matrix used provides a comparison of three residence times at one temperature (800°F), and three temperatures at one residence time (30 minutes). All severities are lower than those typically encountered in larger scale operations. This serves to keep conversions low enough so that kinetic reactivity differences can be properly observed.

## FEEDSTOCK PROPERTIES

Some properties of the four coals and four oils studied are listed in Table 3. The Cold Lake feedstock was available as a deep-cut ASB from previous HRI H-Oil® studies, while the other three oils were provided as crude oils and were batch vacuum-distilled to approximately the same residuum content prior to the reactivity studies. All four coals were subjected to standard HRI bench unit preparation procedures (crushing, pulverizing to -70 mesh, drying to 2-10% moisture, and screening) and were further vacuum dried immediately prior to microautoclave testing. Three diluent solvents were also used, as shown. The Illinois-derived solvent was used for Ohio and Illinois bituminous coals, the Wyodak solvent for Alberta sub-bituminous coal and Texas lignite, and the Cold Lake solvent for all petroleum oils. Except for a few solvent-specific runs, solvents were blended in the same ratios as the feedstocks for each run.

## PROGRAM OUTLINE

Over two hundred tests were conducted under the program, as noted in Table 4. The co-processing feedstock pairs chosen for evaluation were based on program sponsors' concerns and represent meaningful commercial candidates. No work was done on the Illinois No. 6 coal, since it was being extensively studied in HRI's parallel DOE funded coal liquefaction program. Most of the discussion to follow centers on the Ohio coal/Cold Lake ASB pair, which was the most extensively studied in 1985 (including both single- and two-stage process variable studies in the continuous bench unit). This combination has been selected by OOSFC as the basis for a prototype commercial facility to be located in Ohio.

## INDIVIDUAL FEEDSTOCK REACTIVITIES

Figures 3 and 4 show STTU response curves for the Ohio coal and the Cold Lake ASB. Similar curves were generated for each of the other feedstocks. In order to provide a quantitative reactivity ranking, kinetic rate constants were back-calculated from the data assuming various batch reactor models. For the oils alone, a second order fit was found to be the most satisfactory, as shown in Figure 5. While it is unlikely that the conversion reactions are truly second order, in the sense of being bimolecular, such a model fit is not unusual in systems of this type, where the "reactant" is not a single component but rather a range of components with different reactivities. For the coals, a more complex model would be required to separate the effects of coal conversion to THF-solubles, the fraction of converted coal which forms 975°F+ residuum, and the kinetics of conversion of the residuum. Realizing these deficiencies, the coal data were force-fit to the same simplified second order 975°F+ conversion model so that a direct comparison of oils, coals, and co-processing pairs could be made. These results are shown in Table 5. As expected, the oils are considerably more reactive to total 975°F+ conversion at low severities than the coals. It is notable that the co-processing pairs do not necessarily fall in either the order or magnitude which would be expected from the individual feedstocks, indicating that synergistic interactions do occur. It is also notable that the feedstock pair (Ohio/Cold Lake) studied most extensively in the

program does not represent the "best" choice based on reactivities, but was chosen based on commercial considerations.

#### OHIO COAL/COLD LAKE ASB CO-PROCESSING

Figure 6 shows the reactivity curves for a 50/50 blend of Ohio coal and Cold Lake ASB. The drop off in 975°F+ conversion at 20 STTU may be indicative of some regressive reaction due to poor solvent quality, as this is the highest temperature point (825°F) in the grid. The STTU axis has been extended to include a point at a typical bench unit operating severity. It is notable that there was no problem in achieving high (90% plus) coal conversion to THF solubles. This was true of all the pairs studied, indicating that the inherently poor hydrogen donor properties of the petroleum oils can be overcome by catalytic, ebullated-bed co-processing.

Figure 7 shows the effect of coal to oil ratio on conversions in a low severity test (10 STTU). As expected, the THF conversion increases as the coal concentration increases, since a higher percentage of the solvent is then coal-derived as well. The 975°F+ conversion response is far less explainable. The individual feedstock points at 0 and 100% are connected, to represent expected conversions based on strict linear averaging. At coal concentrations up to 50%, conversions near or above this line occur, indicating a positive synergy. Surprisingly, at coal concentrations of 67-75%, a large negative interaction occurs, and 975°F+ conversions are actually lower than those for coal alone. Each of these points was found to be reproducible. The most likely explanation for this phenomenon is that the presence of the petroleum oils sufficiently reduces the solvent quality in this range to cause a large drop in the conversion of the coal residua. At the lower coal concentrations, this effect is offset by the improved conversions of the petroleum residua. Interestingly, this effect shows itself only in the 975°F+ conversions and not in the THF conversions. It should be noted here that coal/oil ratio studies with other feedstock pairs do not show this same negative behavior (at least not to this extent), but in all cases the response is non-linear.

Since this trend was interesting and unexpected, it was decided to repeat the coal/oil ratio studies at a higher severity, typical of bench unit process conditions. This was done to coincide with the single-stage bench run, which provided comparative results in the single-stage, integrated bench unit at 33, 50 and 67% coal. These results are shown in Figure 8. Note that the complex ratio response curve for 975°F+ conversion has been reproduced, although the extent of the negative deviations at 67-75% coal are reduced. The bench unit data, at 33 and 50% coal, provide excellent agreement with the microautoclave data. The bench data at 67% coal do show some negative effect, although not as pronounced as in the microautoclave. One key difference is that each bench data point represents several days of continuous, integrated operation with solvent quality equilibration, while microautoclave solvents are artificially composited. It should also be noted that the tie points at 0 and 100% coal were not determined on the bench unit, so that the extent of positive/negative synergy may not be directly comparable. The 50% coal case has been shown to be economically preferred at several severities at least in part due to synergistic reactivity effects.<sup>(9)</sup>

## CONCLUSIONS

HRI's microautoclave has been shown to be an effective tool for comparing reactivities of coals, oils, and combinations for catalytic coal/oil co-processing. Specific improvements in experimental and analytical procedures were implemented to expand the utility of the microautoclave from coal liquefaction into oil and co-processing. Data generated on the Ohio coal/Cold Lake ASB combination led to some unexpected results, which were later confirmed by continuous bench unit studies.

## ACKNOWLEDGEMENTS

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TABLE 4

## PROGRAM SUMMARY

Thermal Solvent Quality	NUMBER OF TESTS
Coal Reactivity - Ohio	12
Alberta	14
Texas	10
Oil Reactivity - Cold Lake	24
JPL	10
Maya	10
West Texas	5
Alberta/Cold Lake Co-Processing	18
Ohio/Cold Lake	34
Ohio/Maya	10
Ohio/West Texas	10
Texas Lignite/M. Texas	14
Hydrotreated Recycle Simulation	17
Two-Stage Simulation	8
	217

TABLE 3

## FEEDSTOCK PROPERTIES

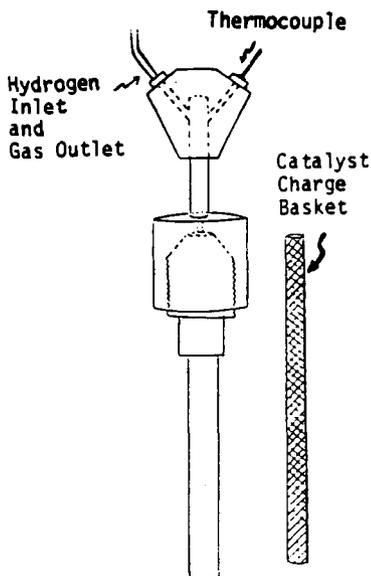
OILS Gravity, °API	COLD LAKE		MAYA		WEST TEXAS	
	JPL	14.5	4.1	14.7	SOUR	14.7
Carbon, W %	83.2	87.2	83.1	86.5		
Hydrogen, W %	10.2	11.0	9.7	11.4		
Nitrogen, W %	0.5	0.4	0.7	0.3		
Sulfur, W %	5.2	1.3	5.0	2.4		
975°F+, W %	70.0	67.9	84.5	65.0		
COALS	OHIO	ILLINOIS	ALBERTA	TEXAS		
Proximate, W % Dry	No. 5/6	No. 6	SUB-BITUMINOUS	LIGNITE		
Volatiles	39.8	35.2	39.7	43.5		
Fixed Carbon	53.4	52.8	52.1	44.5		
Ash	6.8	11.7	8.2	12.0		
Carbon, W %	75.3	69.9	67.9	63.3		
Hydrogen, W %	5.6	4.9	4.7	5.3		
Nitrogen, W %	1.6	1.4	1.4	1.2		
Sulfur, W %	3.0	3.7	0.5	1.2		
Ash, W %	6.8	11.7	8.2	12.0		
Oxygen, W %	7.7	7.8	17.3	17.0		
(by difference)						
SOLVENTS	ILLINOIS	H-COAL DERIVED	H-OIL DERIVED			
Source	11.5	15.8	24.4			
Gravity, °API	89.3	89.4	86.0			
Carbon, W %	9.4	10.1	11.8			
Hydrogen, W %	0.5	0.3	0.2			
Nitrogen, W %	0.1	< 0.1	1.6			
Sulfur, W %	21.8	24.4	63.8			

## REACTIVITY COMPARISON

Average Second Order Rate Constants for 975°F+ Conversion	OILS - West Texas	CO-PROCESSING PAIRS (50/50 Ratio)
	Maya	Alberta/Cold Lake
	JPL	Ohio/Cold Lake
	Cold Lake	Ohio/Maya
	Texas Lignite	Ohio/West Texas
	Illinois No. 6	Texas Lignite/West Texas
	Ohio No. 5/6	
	Alberta	

# MICROAUTOCLAVE REACTOR

FIGURE 1



## MECHANICAL DESIGN

- 20cc Internal Volume
- Maximum Inlet Hydrogen Pressure 3000 psi
- Operations to Liquefaction Temperature
- Thermal and Gas Inlet Coupling
- 347ss Material of Construction
- External Cap Threads
- Reactor Cap Redesign
- Cold Traps
- Catalyst Basket
- Utilizes Whole Extrudate Catalyst

## TESTING CAPABILITIES

- Thermal Tests Varying Charge, Feed Ratios, Temperature, Time
- Catalytic Tests Varying Charge, Feed Ratios, Temperature, Time

FIGURE 2

## PRODUCT WORKUP PROCEDURES

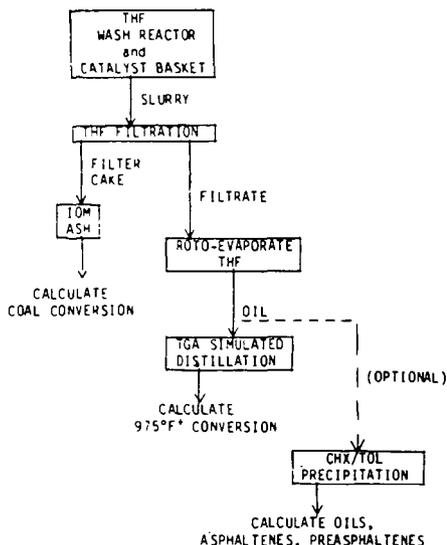


FIGURE 3

CATALYTIC REACTIVITY OF OHIO No. 5/6 COAL

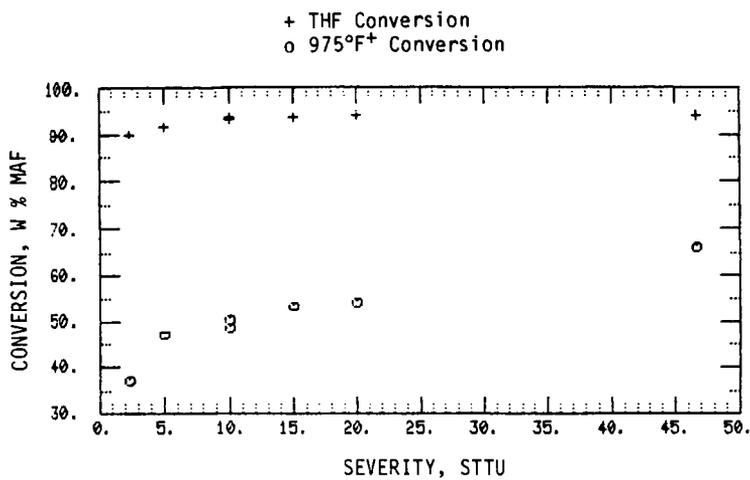


FIGURE 4

CATALYTIC REACTIVITY OF COLD LAKE ASB

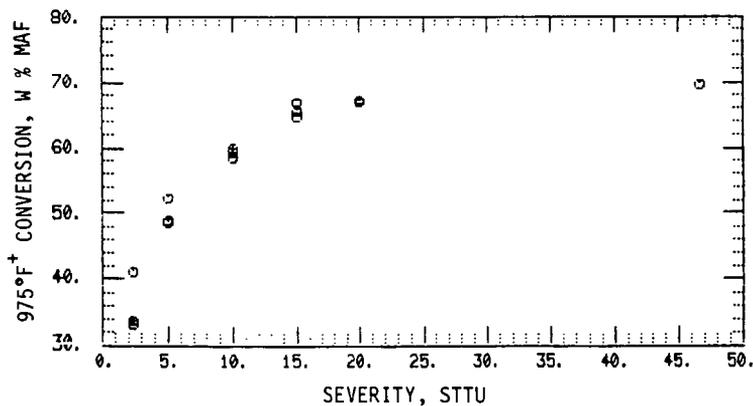


FIGURE 5

CALCULATED SECOND ORDER RATE CONSTANTS FOR  
975°F+ CONVERSION OF OIL FEEDSTOCKS

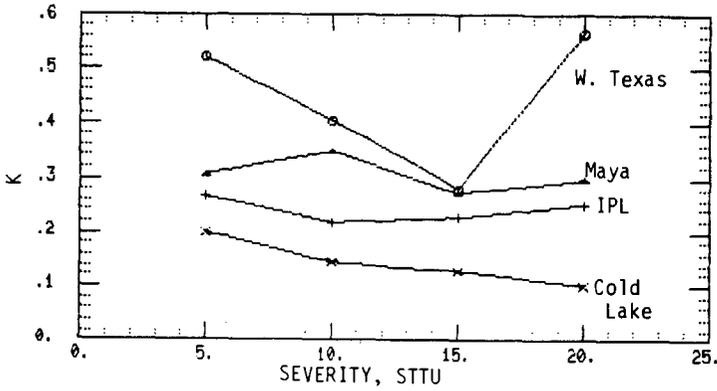


FIGURE 6

CATALYTIC CO-PROCESSING OF 50/50 BLEND OF  
OHIO NO. 5/6 COAL AND COLD LAKE ASB

+ THF Conversion  
o Total Feed 975°F+ Conversion

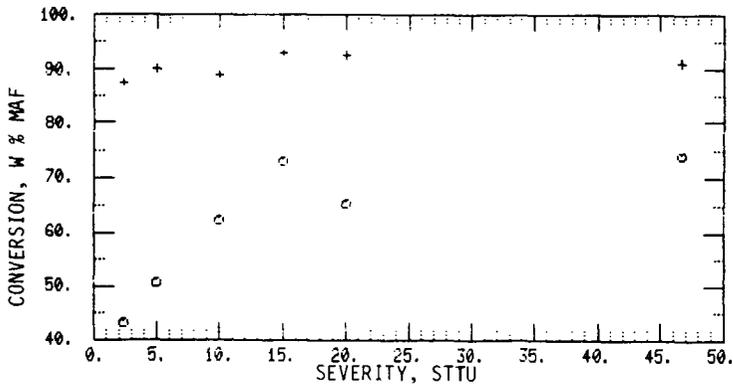


FIGURE 7

CATALYTIC CO-PROCESSING OF OHIO NO. 5/6 COAL AND COLD LAKE ASB  
EFFECT OF COAL CONCENTRATION

(SEVERITY: 10 STTU)

+ THF Conversion  
 o Total Feed 975°F+ Conversion

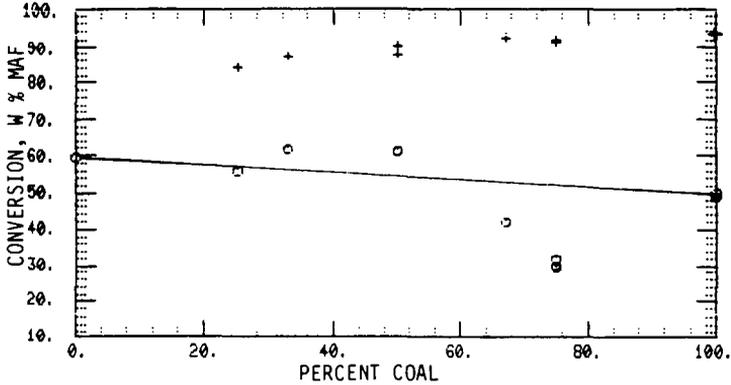
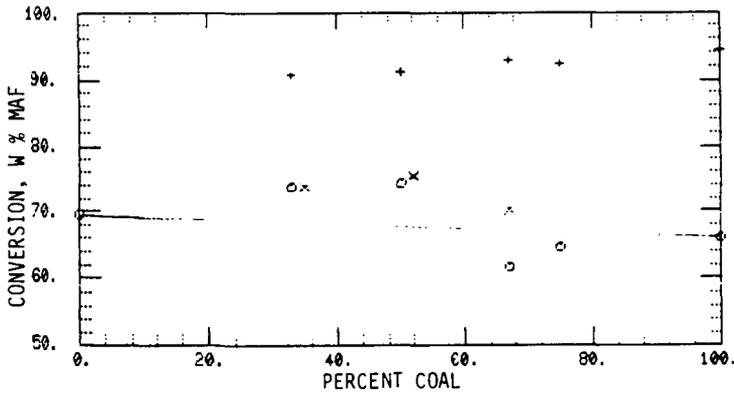


FIGURE 8

CATALYTIC CO-PROCESSING OF OHIO NO. 5/6 COAL AND COLD LAKE ASB  
EFFECT OF COAL CONCENTRATION

(BENCH RUN SEVERITY)

+ THF Conversion  
 o 975°F+ Conversion  
 x Bench Unit 975°F+ Conversion Data



## SINGLE-STAGE SLURRY CATALYZED CO-PROCESSING

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### INTRODUCTION

UOP Inc. and the Signal Research Center are currently engaged in a Department of Energy (DOE) sponsored program to determine if a slurry catalyzed, single-stage process involving the simultaneous conversion of coal and petroleum resid offers the potential for improved economics.

The program has been structured to accomplish the overall objectives of evaluating the technical feasibility and establishing a process data base on the Co-processing concept. Specific objectives include the establishment of overall criteria for the selection of coal type and petroleum characteristics, evaluation of process performance, and the cost estimation of a conceptual commercial facility.

This paper reviews results from the first phase of the program and early results from the continuous bench-scale unit currently in operation.

### PROPOSED PROCESS CONCEPT

UOP Inc. and the Signal Research Center began development of the resid/coal Co-processing concept in 1970 and were issued a key patent in this area in 1972 (1). The information gained in this work plus the much longer and more extensive experience in petroleum resid upgrading and coal conversion were used to formulate a slurry catalyzed, single-stage process for the simultaneous conversion of coal and petroleum resid. This Co-processing process utilizes an active, well-dispersed catalyst and operates at relatively low temperatures. This allows high coal conversion without cracking of resid and coal to light gases, and minimizes thermal degradation reactions.

### FEEDSTOCK SELECTION

Six vacuum resids, three bituminous coals and one subbituminous coal were selected for study.

The vacuum resids were selected based on their commercial importance (availability) and to provide a wide range of chemical and physical properties. These resids were vacuum fractionated to 510°C at the 5 vol-% point so that all would have similar boiling ranges, thus eliminating any process variations due to different amounts of vacuum gas oil (VGO) in the feedstock.

The chemical and physical properties are shown in Table 1. Figure 1 shows the relationship of API gravity with respect to hydrogen, C<sub>7</sub> insolubles and carbon residue content. The contaminants (C<sub>7</sub> insolubles and carbon residue) increase and hydrogen content decreases with decreasing API gravity.

The coal samples were selected primarily because of their use as references in other studies. The properties are shown in Table 2. The Wyodak Coal as received (C4.1) has a moisture content of 14.7 wt-%. It was dried in the laboratory to a moisture content of 1.78 wt-% (C4.2).

## CATALYST COMPARISON STUDY

The premise of this work involves the concept that an active slurry catalyst will efficiently promote and effect the necessary dissolution and upgrading reactions as compared with a less active catalyst or a non-catalytic process, and thus maximize coal conversion and upgrading of the petroleum resid to produce a high quality syncrude.

Disposable, iron-based slurry catalysts, whose activities have been reported as being much lower than that of other metal slurry catalysts (2), have been shown to provide beneficial catalytic effects in the upgrading of coal and coal/resid mixtures (3,4). An iron-based slurry catalyst was tested to establish a comparison with the active UOP slurry catalyst. The iron-based disposable catalyst selected was a porous iron oxide ( $Fe_2O_3$ ) from Kerr-McGee (5). A run was also made without catalyst.

Lloydminster vacuum resid (R4) and Illinois No. 6 coal (C1) were used as feedstocks. The tests were conducted in an 1800 cc rocker autoclave. The equipment and procedure have been described in previous work (6). The operating conditions are shown below:

Resid/Coal Ratio	2
Pressure, psig	3000
Temperature, °C	Base
Residence Time, hrs	2

The iron-based catalyst was tested at twice the catalyst concentration of the UOP slurry catalyst to compensate for its lower anticipated activity with respect to the active UOP slurry catalyst.

The results of this catalyst comparison study are summarized in Table 3. The addition of either catalyst resulted in dramatic increases in coal conversion and heptane insoluble conversion but had little effect on the non-distillable conversion. The coal conversion and heptane insoluble conversion without the addition of catalyst was 66.6 wt-% and 21.3 wt-%, respectively. The coal conversion and heptane insoluble conversion increased to 80.5 wt-% and 63.9 wt-% with the iron catalyst and increased further with the UOP catalyst to 92.2 wt-% and 81.3 wt-%, respectively. The non-distillable conversion ( $510^{\circ}C+$ ) ranged from 69.3 to 73.6 wt-% for these three tests.

Although the iron oxide catalyst demonstrated some beneficial effects, its overall performance was inferior to the UOP slurry catalyst. The differences between these two catalysts becomes even more apparent when hydrogen consumption and product quality are also included as part of the evaluation. The product properties of the total liquid product for each catalyst system tested are summarized in Table 4.

The UOP slurry catalyst has the best hydrogenation capabilities of the three systems tested. The hydrogen consumption with the UOP slurry catalyst was 2.66 wt-%, compared to 1.84 wt-% and 1.68 wt-% using no catalyst and the iron catalyst, respectively. This higher hydrogen consumption yields a liquid product with the highest API gravity, highest hydrogen content and the lowest heptane insoluble content. The higher API gravity product is important because although the product has the same boiling range as products derived from no catalyst and iron catalyst, it is less aromatic and more like petroleum fractions. Also, the lower heptane insoluble content means that the material would have a lower tendency to poison or foul conventional refinery upgrading catalysts, thus making it more economically attractive to upgrade.

## COAL/RESID REACTIVITY EVALUATION

The reactivities of different coal/resid combinations were evaluated. All the vacuum resids were tested with one coal (Illinois No. 6, C1) and all the coals were tested with one resid (Lloydminster, R4). The subbituminous coal (Wyodak) was tested as received (14.7 wt-% moisture content, C4.1) and also dried (1.78 wt-% moisture content, C4.2). The tests were made at the operating conditions stated above with the UOP slurry catalyst.

Resid reactivity screening results are summarized in Figure 2. Coal conversions ranged from 87.9 to 92.5 wt-%. Hydrogen consumption generally decreased with increasing API gravity. The heptane insoluble and non-distillable conversions followed a similar trend.

Coal reactivity screening results are summarized in Figures 3 and 4. The three bituminous and the dried subbituminous (1.78 wt-% moisture content) coals showed no particular trends. MAF coal conversion and heptane insoluble conversion for each coal were similar. The subbituminous coal as received (14.7 wt-% moisture content), gave lower coal conversion (78.3 vs 90.3 wt-% for dried Wyodak) and lower heptane insoluble conversion (64.5 vs 78.8 wt-% for dried Wyodak).

## CONTINUOUS BENCH-SCALE OPERATIONS

The objectives of the continuous bench-scale operations are to: 1) prove the process concept, 2) direct its development toward the goals of achieving maximum coal concentration in the resid/coal feed and producing the greatest distillate yield, and 3) establish a firm experimental basis on which to evaluate a conceptual commercial facility. The early work reported here has been directed at the first and third objectives.

A simplified block diagram of the pilot plant is shown in Figure 5. The slurry feed (finely ground coal, petroleum resid and catalyst) is combined with hydrogen-rich recycle gas and is then preheated before it enters the bottom of the upflow reactor. The products from the reactor are then separated into a gas and oil stream at the high pressure separator. The gas stream from the high pressure separator is combined with make-up hydrogen before being recycled back to the incoming fresh feed. The oil stream from the high pressure separator is sent to a stripper where the lighter hydrocarbons are separated from the heavier fraction. The lighter hydrocarbon stream is separated further in the debutanizer into C<sub>4</sub> minus and C<sub>4</sub> plus products. The heavier hydrocarbon stream from the stripper is sent to a vacuum fractionator to obtain appropriate fractions.

A temperature and space velocity survey was conducted processing Illinois No. 6 coal (C1.2) and a commercially fractionated Lloydminster resid (R8) with the UOP slurry catalyst. The commercially fractionated Lloydminster resid is lighter than the Lloydminster (R4) used in the autoclave studies, containing 15 vol-% more 510°C minus material. The tests were made at the operating conditions stated below. Three temperatures and three space velocities were run.

### Operating Conditions

Resid	R8, Lloydminster Vacuum Bottoms
Coal	C1.2, Illinois No. 6
Resid/Coal Ratio	2
Pressure, psig	3000
Temperature, °C	Varied
WHSV, G/Hr/cc	Varied

The effects of temperature on product distribution and conversions are shown in Table 5. The product distributions give the expected trends, an increase of lighter

fractions and a decrease of heavier fractions with increasing temperature. Coal conversion and heptane insoluble conversion exhibited an interesting trend in the higher temperature range. At the lowest temperature, 83.0 wt-% of the MAF coal was converted. Coal conversion increased to 91.8 wt-% at the mid-temperature, and then decreased slightly to 90.7 wt-% at the highest temperature. Heptane insoluble conversion behaved similarly, increasing from 72.8 wt-% at the lowest temperature to 82.2 wt-% at the mid-temperature, then decreasing to 72.5 wt-% at the highest temperature. The fact that both coal conversion and heptane insoluble conversion decreased at the highest temperature suggests that the highest temperature is too severe, resulting in thermal degradation reactions. At lower temperatures, catalytic effects predominate over thermal effects.

The effects of residence time on product distribution and conversion are shown in Table 6. The product distributions show an increase of lighter fractions and a decrease of heavier fractions with longer residence time. However, coal conversion and heptane insoluble conversion show adverse responses to the longest residence time. At 1.01 WHSV (g/hr/cc reactor volume), 86.8 wt-% of the MAF coal was converted. Coal conversion increased to 91.8 wt-% at 0.78 WHSV, and then decreased slightly to 90.5 wt-% at the 0.62 WHSV. Heptane insoluble conversion behaved similarly, increasing from 75.7 wt-% at 1.01 WHSV to 82.2 wt-% at 0.78 WHSV, then decreasing significantly to 69.9 wt-% at 0.62 WHSV. Analogous to the high temperature experiment, both decreased coal conversion and decreased heptane insoluble conversion at the lowest space velocity suggest that too severe an operating condition, in this case residence time, is resulting in thermal degradation reactions.

#### CONCLUSIONS

The single-stage, slurry-catalyzed Co-processing concept was successfully demonstrated in laboratory batch experiments. The active UOP catalyst gave high coal conversion and high conversion to liquid product at relatively low temperature and, as a result, thermal degradation reactions and cracking of resid- and coal-derived liquid to light gases were minimized. The liquid hydrocarbon product is of high quality and can be efficiently utilized as a feedstock in existing refineries.

The continuous bench-scale operation gave similar performance to the laboratory batch experiments, satisfying the proof-of-concept objective. In addition, data generated to date initiate a firm experimental basis on which to evaluate a conceptual commercial facility. These data show that the Co-processing process is sensitive to high severity conditions (temperature, residence time). High coal conversion and high conversion to high quality liquid product can be achieved by operating at relatively mild conditions where thermal degradation reactions are minimized.

#### ACKNOWLEDGMENT

The author expresses his thanks to Beckay J. Nelson, John G. Sikonia and Carl Lea of the Signal Research Center and Michael J. Humbach and Charles P. Luebke of UOP Inc. for their contributions to this study; and to Burtron H. Davis of the Kentucky Center for Energy Research Laboratory for the acquisition and preparation of the coal samples. This work is supported by DOE Contract DE-AC22-84PC70002, "Coal Liquefaction Co-Processing".

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4. "Status of Synfuels Development in Japan," NEDO, Synfuels, 3rd Worldwide Symposium, Washington, DC, November 1-3, 1983.
5. A. S. Paranjape and D. E. Rhodes, "Use of Iron Oxide and Hydrogen Sulfide to Improve Integrated Two-Stage Liquefaction," Proceedings of DOE Direct Coal Liquefaction Contractors' Review Meeting, October 17-18, 1984.
6. J. G. Gatsis et al., "Coal Liquefaction Co-Processing," Proceedings of DOE Direct Coal Liquefaction Contractors' Review Meeting, November 19-21, 1985.

TABLE 1

Resid Name	U.S. Mid- Continent (R1)	Kuwait (R2)	Alaskan North Slope (R3)	Lloydminster (R4)	Hondo (R5)	Maya (R6)	Lloydminster (R8)
Total Sample							
API Gravity	12.70	7.90	8.90	3.60	3.70	2.80	6.50
Specific Gravity	0.9813	1.0151	1.0078	1.0474	1.0466	1.0536	1.0254
D-1160, °C							
IBP, vol-%	473.0	472.0	422.0	406.0	478.0	452.0	369.0
5	510.0	505.0	494.0	509.0	512.0	515.0	432.0
10	525.0	517.0	515.0	-	524.0	532.0	463.0
20	546.0	542.0	541.0	-	-	-	505.0
30	568.0	-	-	-	-	-	-
EP	568.0	556.0	550.0	509.0	524.0	532.0	523.0
Overhead, vol-%	30.0	26.0	24.0	6.0	10.0	10.0	26.5
Analysis, wt-%							
Carbon	87.30	84.15	84.10	82.70	81.20	83.90	83.70
Hydrogen	10.25	10.55	10.85	10.15	10.10	9.15	10.00
Oxygen	0.30	0.35	0.27	0.29	0.36	0.48	-
Sulfur	1.0	4.9	2.3	5.6	6.6	4.9	5.1
Nitrogen	0.45	0.35	0.55	0.62	1.10	0.71	0.48
Carbon Residue	16.50	18.00	17.30	22.20	19.90	26.10	17.30
Petroleum Ash	0.030	0.020	0.020	0.090	0.110	0.126	0.051
C <sub>7</sub> Insolubles	8.29	5.95	4.80	18.10	17.80	22.40	13.91
Nickel, ppm	35.0	28.0	38.0	122.0	157.0	116.0	83.0
Vanadium, ppm	113.0	100.0	79.0	278.0	435.0	595.0	165.0
Iron, ppm	62.0	4.5	2.0	82.0	42.0	29.0	3.6
Molecular Weight	839.0	1054.0	810.0	1444.0	1125.0	1015.0	255.0
Furoil Visc., sec (121°C)	755.0	1016.0	1295.0	1921.0	1126.0	2217.0	266.1
Pour Point, °C	38.00	38.00	32.00	91.00	79.00	91.00	120.0
Salt, lb/1000 bbls	2.90	3.50	1.20	3.30	4.00	20.70	5.2

TABLE 2

Coal Analyses

<u>Coal Name</u>	<u>Illinois No. 6 (C1)</u>	<u>Kentucky No. 9 (C2)</u>	<u>Indiana No. V (C3)</u>	<u>Wyodak (As-Received) (C4.1)</u>	<u>Wyodak (Dried) (C4.2)</u>	<u>Illinois No. 6 (C1.2)</u>
<u>Ultimate Analysis, wt-%</u>						
Ash	9.65	8.68	8.12	10.30	12.00	10.56
Carbon	68.60	71.95	69.70	54.70	63.01	68.77
Hydrogen	4.51	4.78	5.40	3.83	4.50	4.84
Nitrogen	1.39	1.54	1.42	0.69	0.90	1.37
Sulfur	3.04	2.97	4.28	0.99	1.08	3.34
Oxygen*	9.66	8.53	9.37	14.79	16.73	7.03
<u>Proximate Analysis, wt-%</u>						
Moisture	3.15	1.55	1.71	14.70	1.78	4.09
Ash	9.65	8.68	8.12	10.30	12.00	10.56
Volatile Matter	39.95	42.35	48.25	37.00	42.60	39.90
Fixed Carbon	47.25	47.42	41.92	38.00	43.62	45.45

\*Difference

TABLE 3

Catalyst Comparison Study

<u>Operating Conditions</u>			
<u>Catalyst Type</u>	None	Fe <sub>2</sub> O <sub>3</sub>	UOP Catalyst
<u>Concentration</u>	0	2 % Base	Base
<u>Performance</u>			
<u>Conversions, wt-%</u>			
Coal	66.6	80.5	92.2
Heptane Insolubles	21.3	63.9	81.3
Non-distillables (510°C+)	69.3	73.6	72.1
<u>Hydrogen Consumption, wt-%</u>	1.84	1.68	2.66

TABLE 4

Catalyst Comparison Study  
Total Liquid Product Properties

Catalyst Type	None	Fe <sub>2</sub> O <sub>3</sub>	UOP Catalyst
API Gravity at 15.6°C	9.3	8.5	13.3
Specific Gravity	1.0050	1.0107	0.9772
Carbon, wt-%	85.15	84.40	85.50
Hydrogen, wt-%	10.05	9.6*	10.30
Oxygen, wt-%	1.00	-	1.23
Sulfur, wt-%	2.75	2.30	2.10
Nitrogen, wt-%	0.60	0.90	0.73
Ash, wt-%	0.005	<0.001	0.003
Heptane Insolubles, wt-%	37.03	14.52	7.37
Carbon Residue, wt-%	14.6	16.5	15.1
Vanadium and Nickel, wt-ppm	19	9	23

\*Estimated

TABLE 5

Continuous Bench-Scale Operations

Effect of Temperature

Temperature, °C	Base - 7	Base + 6	Base + 11
WHSV, G/hr/cc	0.81	0.78	0.79
<u>Product Distribution</u>			
Hetero Gases + H <sub>2</sub> O, wt-%	7.3	8.9	6.7
Hc <sub>pn</sub> . Gas C <sub>4</sub> -, wt-%	1.9	2.5	3.7
C <sub>5</sub> <sup>+</sup> - 371°C, wt-%	26.1	38.0	42.6
371 - 510°C, wt-%	47.1	40.1	39.2
510°C +	13.7	10.1	7.0
MAF Coal	6.1	3.0	3.2
Total, wt-%	<u>102.2</u>	<u>102.6</u>	<u>102.4</u>
<u>Conversions</u>			
Coal, wt-% MAF Coal	83.0	91.8	90.7
C <sub>7</sub> Insolubles, wt-%	72.8	82.2	72.5
510°C+, wt-%	49.2	64.2	65.7
371°C+, wt-%	25.9	40.1	42.0
H <sub>2</sub> Consumption, wt-%	2.16	2.58	2.45

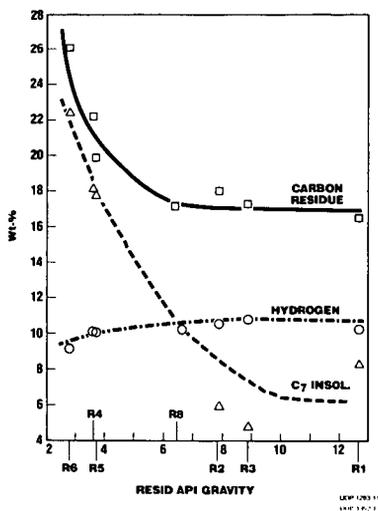
TABLE 6

Continuous Bench-Scale Operations

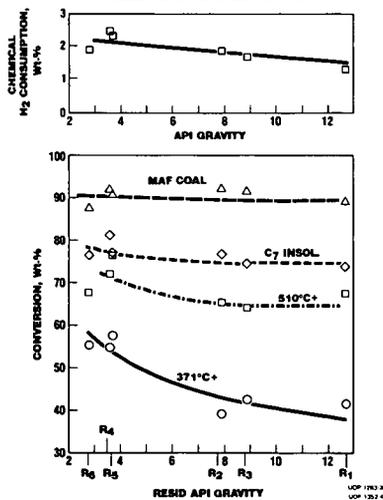
## Effect of Residence Time

Temperature WHSV, G/hr/cc	Base + 4 0.62	Base + 6 0.78	Base +5 1.01
<u>Product Distribution</u>			
Hetero Gases + H <sub>2</sub> O, wt-%	6.3	8.9	8.4
Hcbn. Gas C <sub>4</sub> -, wt-%	3.1	2.5	2.3
C <sub>5</sub> - 371°C, wt-%	42.0	38.0	31.1
371 - 510°C, wt-%	43.4	40.1	41.9
510°C +	4.1	10.1	13.9
MAF Coal	3.3	3.0	4.7
Total, wt-%	<u>102.2</u>	<u>102.6</u>	<u>102.3</u>
<u>Conversion</u>			
Coal, wt-% MAF Coal	90.5	91.8	86.8
C <sub>7</sub> Insolubles, wt-%	69.9	82.2	75.7
510°C+, wt-%	67.7	64.2	56.8
371°C+, wt-%	38.7	40.1	33.2
H <sub>2</sub> Consumption, wt-%	2.19	2.58	2.29

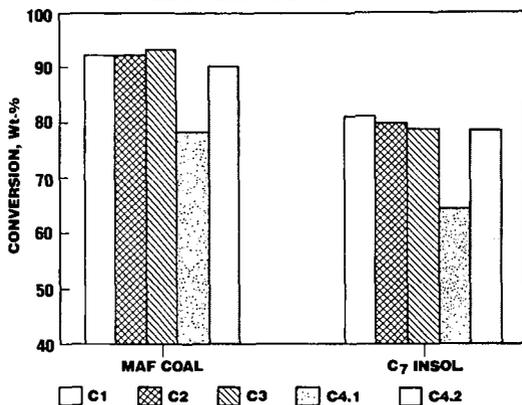
**FIGURE 1**  
**VACUUM RESID FEEDSTOCKS**  
**COMPOSITION**



**FIGURE 2**  
**RESID REACTIVITY SCREENING**  
**(ILLINOIS COAL NO. 6)**

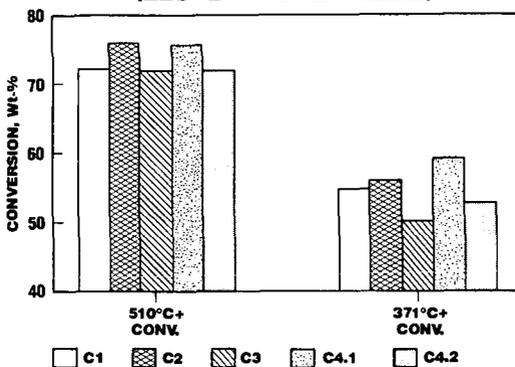


**FIGURE 3**  
**COAL REACTIVITY SCREENING**  
**(LLOYDMINSTER RESID)**



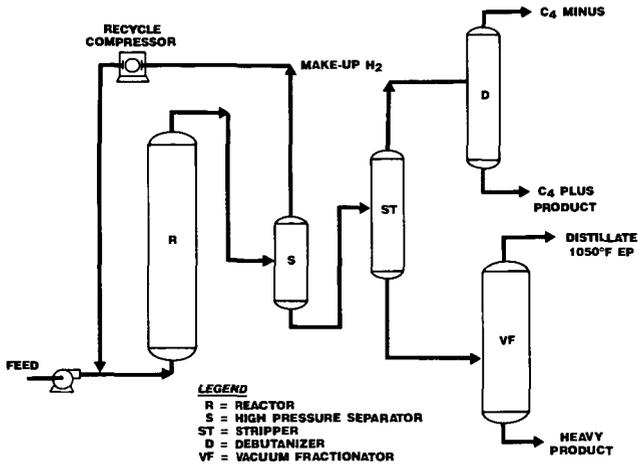
UOP 1283-27  
 UOP 1352-5

**FIGURE 4**  
**COAL REACTIVITY SCREENING**  
**(LLOYDMINSTER RESID)**



UOP 1283-31  
 UOP 1352-6

**FIGURE 5  
PILOT PLANT FLOW SCHEME**



UGP 1327

## COPROCESSING USING H<sub>2</sub>S AS A PROMOTER

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### INTRODUCTION

Coprocessing heavy oils, bitumens or petroleum residues with coal can be considered as a bridge between coal liquefaction and hydrocracking. The existing technologies of liquefaction and hydrocracking can be applied with modification to coprocessing. In terms of operation, coprocessing is less complicated than liquefaction because recycle solvent is eliminated. Since the coprocessing solvent is upgraded simultaneously with coal the reactor volume is utilized more effectively. If residuum conversion levels during coprocessing are as high as those in hydrocracking then coprocessing also offers a significant saving in feedstock costs by substituting a significant portion of the heavy oil with less expensive coal.

CANMET coprocessing involves the simultaneous upgrading of coal and heavy oil or bitumen in a once-through mode of operation using a disposable iron catalyst. The CANMET additive (pulverized coal impregnated with iron sulphate), hereinafter referred to as FeSO<sub>4</sub>, has been identified as both an hydrogenation and coke-reducing catalyst. Process feasibility has been investigated using a variety of coals and heavy oils/bitumens(1). Also, it has been demonstrated that in terms of product yields for subbituminous coals, CANMET coprocessing is superior to liquefaction and is comparable to hydrocracking (2-3).

The effect of H<sub>2</sub>S in hydrocracking of model compounds and in liquefaction is well documented (4-11). The ability of H<sub>2</sub>S to reduce coke formation and increase liquid yield in coal liquefaction has been patented by Exxon Research and Engineering Company (12). It has also been shown that H<sub>2</sub>S has beneficial effects in non-catalytic crude oil hydrorefining processes (13).

In a previous batch autoclave study the use of H<sub>2</sub>S in coprocessing subbituminous coal and bitumen resulted in high coal conversion and distillate yield (14). The increase in product yields in the presence of H<sub>2</sub>S was attributed to its ability to donate its hydrogen to radicals derived from coal and bitumen (15).

The objective of the present study was to verify the positive effects of H<sub>2</sub>S under coprocessing conditions using a continuous-flow bench scale pilot plant and to compare the activity of H<sub>2</sub>S with FeSO<sub>4</sub> under similar operating conditions.

## EXPERIMENTAL

### Process Unit

Coprocessing experiments were carried out in a 1-L continuous-flow stirred tank reactor with a nominal capacity of 1 kg/h of slurry feed while product samples were collected over 1-h periods at steady state. For all the experimental runs reported in this paper, the material balances were within  $\pm 5$  wt %. For comparison purposes, all the data were normalized to 100% material balance by proportioning the losses over each of the product fractions. Other details of the experimental unit are available elsewhere (2).

### Feedstocks

The analysis of Forestburg subbituminous C coal and Cold Lake vacuum bottoms (CLVB) is shown in Table 1. Additives or promoters were  $\text{FeSO}_4$  or  $\text{H}_2\text{S}$  or both. The  $\text{H}_2\text{S}$  was obtained from Matheson and used as received. In experiments where  $\text{H}_2\text{S}$  was used it was pumped as a liquid using a Waters LC pump model 6000A.

## RESULTS AND DISCUSSION

### Product Yields

Previous batch autoclave experiments indicated that  $\text{H}_2\text{S}$  is most effective at low to moderate severities in terms of improving product yields when compared to coprocessing without any additive. At moderate-high severity, using the feedstocks reported in this paper, relatively high coke formation was observed even in the presence of  $\text{H}_2\text{S}$ . For this reason, the CSIR experiments which involved  $\text{H}_2\text{S}$  only were performed at low to moderate severities. For moderate-high severity experiments, iron sulphate was used to assure smooth process operation and to prevent coke formation. Attempts to perform coprocessing experiments in the CSIR unit using CLVB and Forestburg coal without any catalyst even at low severity resulted in coke formation and plant shutdown. Thus, it is not possible to compare the results of experimental runs using  $\text{H}_2\text{S}$  only with those using no additive or promoter as was done in the batch autoclave studies (15). The fact that coprocessing experiments could be performed in the CSIR with  $\text{H}_2\text{S}$  and no other catalyst at low and moderate severities is significant and verifies earlier batch results which indicated that  $\text{H}_2\text{S}$  prevents coke formation under the conditions employed (14-15).

Table 2 compares coprocessing results obtained in the presence of  $\text{H}_2\text{S}$  and iron sulphate at two levels of severities. At both levels replacement of  $\text{FeSO}_4$  with  $\text{H}_2\text{S}$  resulted in higher distillate yield, pitch and coal conversions. The results of batch studies indicated

that product yields depend on H<sub>2</sub>S concentration. At moderate temperature maximum coal conversion and distillate yield were obtained at about 3.5 wt % H<sub>2</sub>S based on maf slurry feed (15). However, the results reported in this work are based on only one experimental run and are at approximately 8 wt % H<sub>2</sub>S based on maf slurry feed. No optimization of H<sub>2</sub>S concentration on product yields was carried out in this CSTR study.

The increase in conversions and distillate yield in the presence of H<sub>2</sub>S can be rationalized by its hydrogen-donor ability. Hydrogen sulphide can donate its hydrogen directly to coal and bitumen-derived radicals or the available hydrogens in H<sub>2</sub>S can be transferred to radicals via coal-derived liquids. The evidence for direct hydrogen donation by H<sub>2</sub>S comes from batch autoclave hydrocracking studies using CLVB (14). At low severity, the presence of H<sub>2</sub>S resulted in a substantial improvement and at moderate severity a slight increase in distillate yield. The considerable increase in distillate yield in the presence of H<sub>2</sub>S suggests that at least in part, hydrogen from H<sub>2</sub>S is transferred to bitumen-derived radicals. The previous study (14) also showed that while the conversion of Forestburg coal in anthracene oil increased with H<sub>2</sub>S, distillate yield did not. However, in coprocessing (batch and CSTR) both coal conversion and distillate yield improved substantially when H<sub>2</sub>S was used. These results may indicate that H<sub>2</sub>S promotes upgrading of bitumen during coprocessing. An apparent synergism between coal and H<sub>2</sub>S is also suggested by less coke formation during coprocessing in the presence of H<sub>2</sub>S relative to the hydrocracking of bitumen only using H<sub>2</sub>S as a promoter (15). Table 2 indicates that at least at low and moderate severities the performance of H<sub>2</sub>S under coprocessing conditions in a CSTR is as good as or better than FeSO<sub>4</sub>.

Table 3 compares the activities of iron sulphate with and without H<sub>2</sub>S. At very low and low severities addition of H<sub>2</sub>S to FeSO<sub>4</sub> resulted in an increase in coal conversions whereas distillate yields and pitch conversions did not change. However, at moderate severity, H<sub>2</sub>S had a significant effect on distillate yield, coal and pitch conversions. The presence of H<sub>2</sub>S at moderate-high severity had small effect on distillate yield and pitch conversion but no effect on coal conversion. It appears that at higher severities the positive effect of H<sub>2</sub>S is masked by the presence of FeSO<sub>4</sub>. A comparison of Tables 2 and 3 reveals that at low severity a higher distillate yield was obtained with the H<sub>2</sub>S only run. However, at moderate severity, no improvement was observed using H<sub>2</sub>S+FeSO<sub>4</sub> compared to H<sub>2</sub>S only. Also, the comparison clearly shows that at moderate severity coal conversion in the presence of H<sub>2</sub>S only (80.4 wt %) approaches that at moderate-high severity using FeSO<sub>4</sub> only (86.3 wt %).

## Product Characteristics

### a) Distillates

Table 4 shows the characteristics of distillate products at four different severities and compares product qualities obtained in the presence of  $H_2S$  with those obtained using  $FeSO_4$  or  $H_2S + FeSO_4$ . At very low severity it appears that the distillate products obtained using  $H_2S + FeSO_4$  are relatively heavier than those obtained in the presence of  $FeSO_4$  only. The sulphur content of the distillate did not change when  $H_2S$  was added to  $FeSO_4$ , however, the aromaticity increased from 26 to 31. This increase parallels that of increased coal conversion upon  $H_2S$  addition (see Table 3) and may imply that some coal-derived liquid contributed to the distillate. Again at low severity, higher coal conversion in the presence of  $H_2S$  only compared to  $FeSO_4$  or  $H_2S + FeSO_4$  resulted in a relatively heavier distillate. The sulphur content of the distillate decreased slightly in the  $H_2S$  only run. At moderate severity, the use of  $H_2S$  alone resulted in a heavier liquid product, lower H/C ratio and higher molecular weight than the distillate obtained using either  $FeSO_4$  or  $H_2S + FeSO_4$ .

From the results shown in Table 4 it appears that the effect of  $FeSO_4$  as a hydrogenation catalyst is more pronounced at relatively higher severities. At moderate severity, although similar coal conversions and distillate yields were obtained with both  $H_2S$  and  $H_2S + FeSO_4$ , a better distillate quality was obtained with  $H_2S + FeSO_4$ . Again the higher molecular weight in the  $H_2S$  only run may suggest that more coal-derived liquid contributes to the distillate but the product is not upgraded to the same degree as when  $FeSO_4$  is used. The oxygen content of the distillate decreased when  $H_2S$  was used instead of  $FeSO_4$ . Addition of  $H_2S$  to  $FeSO_4$  further reduced the oxygen content which indicates that  $H_2S$  reacts with the oxygen functionalities in coal. However, sulphur content of the distillate increased slightly in the presence of  $H_2S$  only. At moderate-high severity, the product quality improved slightly in the presence of  $H_2S$  in terms of higher H/C ratio, lower oxygen content, aromaticity and molecular weight.

### b) Residues

The compositions of residues obtained under different process severities are shown in Fig. 1. At very low severity, the addition of  $H_2S$  to  $FeSO_4$  resulted in slightly higher yields of asphaltenes, preasphaltenes and lower THF insolubles. At low severity, the lowest yield of THF insolubles was obtained with  $H_2S$  which reflects a higher coal conversion than the  $FeSO_4$  and  $H_2S+FeSO_4$  runs. Under these conditions, the relative yields of oils, asphaltenes, and preasphaltenes remained unchanged. At moderate severity, the residue in the  $FeSO_4$  run contained more residual oil than the  $H_2S$  run. However, as shown in Table 2 the total distillate yield as well as the pitch conversion in the  $H_2S$  run are higher. This suggests that the upgrading of heavy material in coprocessing is more efficient using  $H_2S$  than  $FeSO_4$  at least at moderate severities. Little or no change

occurs in the yields of asphaltenes and preasphaltenes at moderate severity using the different additives. At moderate-high severity, adding H<sub>2</sub>S to FeSO<sub>4</sub> resulted in slightly higher pitch conversion and consequently lower residue yield (Table 3). The drop in residue yield is reflected mainly in lower preasphaltenes and asphaltenes yields.

The toluene insolubles of some of the coprocessing residues were also examined using optical microscopy. This technique, supplemented by semi-quantitative elemental analysis by scanning electron microscopy has shown that it is possible to distinguish the originality of coal-derived and bitumen-derived solids in coprocessing residues (16). At moderate severity, the toluene insolubles of the coprocessing residue obtained using H<sub>2</sub>S contains 22.5 vol % coal-derived solids (altered coal or unreacted coal) whereas the residue from the FeSO<sub>4</sub> run contains 52.1 vol % coal-derived materials. These results are consistent with the higher coal conversion in the H<sub>2</sub>S run relative to the FeSO<sub>4</sub> run. Also a small amount, (0.9 vol %) of anisotropic solids in both the H<sub>2</sub>S and FeSO<sub>4</sub> runs was detected whereas none was detected in the H<sub>2</sub>S + FeSO<sub>4</sub> run.

#### CONCLUSIONS

Hydrogen sulphide has been shown to be an effective promoter in achieving high coal conversions and distillate yields when coprocessing subbituminous coal with bitumen vacuum bottoms in a continuous-flow bench scale operation. Results indicate that, at least, at low and moderate severities of operation H<sub>2</sub>S performs as good as or better than FeSO<sub>4</sub> in terms of product yields as well as qualities. However, at higher severities, FeSO<sub>4</sub> is superior to H<sub>2</sub>S.

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**Table 1**  
**Analysis of Feedstocks**

<b>Forestburg Coal</b>		<b>Cold-Lake vacuum bottoms</b>	
<u>Proximate analysis</u> (wt %, as received)		Specific gravity, 15/15°C 1.038	
Moisture	19.7	Pentane insolubles, wt %	23.8
Volatile	37.2	Pitch content, wt %	83.2
Fixed carbon	36.1	Conradson Carbon, wt %	17.1
Ash	7.0	Elemental composition, wt %	
		C	83.34
		H	9.69
		N	0.45
		S	5.84
		O	0.68
<u>Ultimate analysis</u> (wt % DAF)		Metals, ppm	
C	74.34	V	235
H	4.81	Ni	93
N	1.78	Fe	18
O	18.58		
S	0.49		

**Table 2**  
**Comparison of the Effects of H<sub>2</sub>S with FeSO<sub>4</sub>**

<u>Severity</u>	<u>Low</u>		<u>Moderate</u>	
H <sub>2</sub> S (1)	no	yes	no	yes
FeSO <sub>4</sub>	yes	no	yes	no
Distillate yield (2)	22.9	27.3	36.3	43.2
Coal conversion (3)	53.7	67.9	70.4	80.4
Pitch conversion (4)	15.8	20.3	34.1	42.5

(1) 8 wt %, based on maf slurry feed (2) wt %, based on maf slurry feed  
(3) wt %, based on maf coal, (4) maf (+525 °C) in - maf (+525 °C) out  
defined as THF solubility maf (+525 °C) in

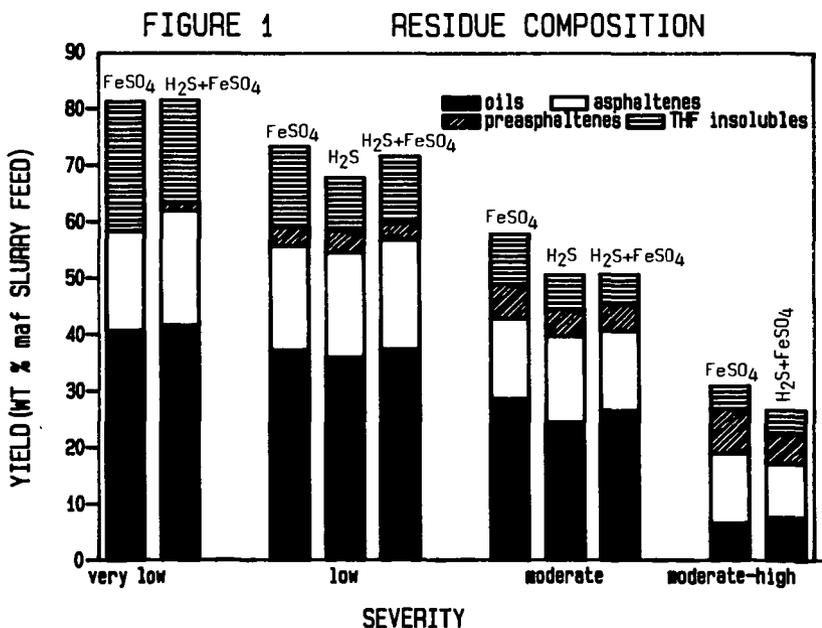
**Table 3**  
**Comparison of The Effects of FeSO<sub>4</sub> and H<sub>2</sub>S + FeSO<sub>4</sub>**

<u>Severity</u>	<u>Very low</u>		<u>Low</u>		<u>Moderate</u>		<u>Moderate-high</u>	
H <sub>2</sub> S (1)	no	yes	no	yes	no	yes	no	yes
FeSO <sub>4</sub>	yes	yes	yes	yes	yes	yes	yes	yes
Distillate yield (2)	15.8	16.5	22.9	22.9	36.3	42.1	60.9	63.1
Coal conversion (3)	27.4	41.1	53.7	61.3	70.4	83.7	86.3	85.9
Pitch conversion (4)	8.1	7.5	15.8	18.6	34.1	42.4	64.8	69.7

(1) 8 wt %, based on maf slurry feed (2) wt %, based on maf slurry feed  
(3) wt %, based on maf coal, (4) maf (+525 °C) in - maf (+525 °C) out  
defined as THF solubility maf (+525 °C) in

**Table 4**  
Distillate Characteristics

Severity	Very low		Low			Moderate			Moderate-high	
H <sub>2</sub> S	no	yes	no	yes	yes	no	yes	yes	no	yes
FeSO <sub>4</sub>	yes	yes	yes	no	yes	yes	no	yes	yes	yes
API <sup>d</sup>	15.2	13.3	17.0	15.9	15.8	22.4	19.8	22.9	25.4	25.9
H/C	1.59	1.53	1.56	1.57	1.54	1.62	1.58	1.63	1.58	1.62
N, wt %	0.26	0.37	0.39	0.41	0.41	0.44	0.47	0.43	0.50	0.50
S, wt %	3.15	3.11	2.98	2.83	2.98	2.30	2.44	2.27	1.64	1.69
O, wt %	0.89	1.30	1.28	1.23	1.31	1.40	1.28	1.02	1.46	0.85
fa	26	31	29	28	30	25	29	24	30	25
Mn, g/mole	-	-	307	320	322	272	305	279	293	278



## TWO-STAGE COPROCESSING OF SUBBITUMINOUS COALS AND BITUMEN OR HEAVY OIL\*

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### ABSTRACT

Pretreatment of subbituminous coal with an appropriately formulated mix of carbon monoxide and water, in presence of bitumen or heavy oil, results in very fast reactions characterized by a high degree of coal solubilization and deoxygenation. The reaction is catalysed by a mixture of alkali metal carbonates and proceeds readily at 380-400°C. The first-stage reaction product appears to be susceptible to further catalytic hydrogenation at 420-460°C with gaseous hydrogen yielding 65-70% (on daf feed) of hydrogen-rich distillable oil, composed mainly of naphtha and middle oil.

The process flowsheet is presented and the comparative economics of two-stage carbon monoxide/steam-hydrogen and hydrogen-hydrogen coprocessing schemes are discussed.

### INTRODUCTION

Alberta is endowed with immense reserves of subbituminous coals (1), bitumen and heavy oil (2). The concept of coprocessing coal and petroleum derived solvents is not a new one (3,4) and there is a consensus that this approach is more attractive economically than conventional coal liquefaction (5). The most attractive feature of the coprocessing concept is its potential for elimination of oil recycle which may increase the output of the installation by up to three times.

It has to be emphasized that under Alberta conditions the economics of a coprocessing plant have to be compared to a heavy oil and/or bitumen hydrocracking plant. The major advantage of coprocessing as opposed to bitumen or heavy oil hydrocracking is the low cost of coal. This has to be weighed against the increased hydrogen consumption, increased plant complexity (conversion of coal to distillate oil requires more severe conditions compared to bitumen) and the element of risk associated with implementation of the new coprocessing technology.

A factor which may have a substantial effect on the economics of coprocessing as compared to bitumen or heavy oil hydrocracking is that of purely chemical nature. It has not been firmly established whether the interaction among coal- and bitumen-derived radical intermediates leads to an increase or a reduction in oil yield or its quality.

On the other hand, it has been demonstrated that hydrocracking of bitumen in a one-stage process in the presence of small (1-3% by weight) quantities of subbituminous coal results in significant improvement in oil yield (6). Similar results can be obtained by employing chars generated from brown coals (4,7) and this furnishes a strong evidence that catalytic effects and not the chemistry of the components of the substrate play a dominant role in a one-stage bitumen

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hydrocracking process with low coal concentrations. However, the objective of coprocessing is to maximize the coal concentration in the feedstock without sacrificing the distillable product yield and quality.

The two-stage process developed at Alberta Research Council is based on solubilization of high oxygen subbituminous coal in bitumen (heavy oil) using a mixture of carbon monoxide/steam at 380-400°C in presence of alkali metal catalyst, followed by catalytic hydrocracking at temperatures of 420-460°C and pressures up to 18.0 MPa.

## EXPERIMENTAL

The experiments were carried out in standard batch autoclave system and in a hot charge/discharge unit (a system developed for studying two-stage liquefaction processes).

### Batch Autoclave Simulated Two-Stage Studies

The batch autoclave experiments were carried out in 1 litre magnedrive autoclaves (manufactured by Autoclave Engineers Ltd.) with internal cooling coils.

The coal/bitumen slurry was charged into an autoclave at room temperature followed by pressurizing the system with carbon monoxide (5.2 MPa) or hydrogen (8.3 MPa). The autoclave was heated up to 390°C, maintained at this temperature for 30 min, and depressurized at elevated temperatures. Gas samples were analysed using a CARLE gas chromatograph. The second stage (hydrogenation) catalyst and sulfur additive were then introduced to the cold reactor which was subsequently repressurized to 8.3 MPa with hydrogen. The reactor was heated to 440°C and held at this temperature for 60 min. Subsequently, the reactor was depressurized as before, cooled to room temperature and discharged. The product work-up procedure was the same as described before (8).

### Hot Charge/Discharge Unit (HCDU)

The HCDU consists of two magnetically stirred reactors of one and two litre capacity and a high pressure vessel to collect the product slurry. The first reactor operates in batch mode and the second one in a semi-continuous mode. Details regarding construction and operation of the system were given elsewhere (8). The product work-up procedure and product analyses were the same as for batch autoclave tests.

## DISCUSSION

Sufficient evidence has been accumulated to show that two-stage coal liquefaction process yields better results compared to conventional single-stage processes (9).

The importance of the first (solubilization) stage in the overall liquefaction process had been ignored until it became evident that depending on the results of the solubilization, the second (hydrogenation) stage proceeds more or less efficiently. Though no results of systematic research on the solubilization-hydrogenation relationship are available, one can speculate that the mechanism of the initial disintegration of coal and the character and properties of the intermediate soluble product may have a major influence on the effectiveness of the hydrogenation step.

The influence of solubilization of low rank coals on their hydrogenation may be particularly important due to their high oxygen content and high reactivity of a major fraction of this oxygen at temperatures significantly below the hydrogenation temperature. Presence of highly reactive oxygen in the coal may

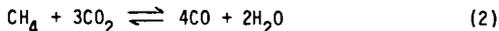
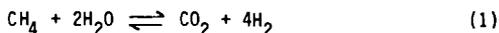
result in retrogressive reactions taking place during solubilization at higher temperatures. Therefore, for Alberta subbituminous coals a mixture of carbon monoxide/steam or hydrogen was tested in low temperature solubilization studies. The work carried out at Alberta Research Council on solubilization of indigenous subbituminous coals in CO/steam in bitumen and/or heavy oil showed that these coals are readily solubilized at a low temperature of 380-400°C with conversion 85-96% (10,11). Although the conversion was accompanied by low hydrocarbon gas generation and advanced deoxygenation for both gases tested (see Table 1), CO/steam appeared to be superior compared with hydrogen in terms of reaction kinetics measured as coal conversions at 390°C (see Table 2).

The susceptibility of the coal solubilized under mild conditions with either hydrogen or carbon monoxide/steam to further hydrogenation in presence of potassium molybdate is presented in Table 3.

Analysis of the results obtained in simulated two-stage autoclave experiments and presented in Table 3 indicates, that in terms of distillable oil yield the solubilization of coal in bitumen in presence of CO/H<sub>2</sub>O-K<sub>2</sub>CO<sub>3</sub> followed by catalytic hydrogenation yields slightly better results compared to solubilization in hydrogen and followed by catalytic hydrogenation. Furthermore, two-stage co-processing where solubilization was accomplished by action of either CO/H<sub>2</sub>O or CO/H<sub>2</sub>O-K<sub>2</sub>CO<sub>3</sub> seems to result in somewhat lower generation of gaseous hydrocarbons compared to solubilization with hydrogen (Table 3). The coal conversion values are by far the highest (98%) for the sample solubilized using CO/H<sub>2</sub>O-K<sub>2</sub>CO<sub>3</sub>.

In conclusion, on the basis of autoclave studies the two-stage CO/H<sub>2</sub>O-K<sub>2</sub>CO<sub>3</sub> - H<sub>2</sub> route appears to be marginally more appealing than the H<sub>2</sub>-H<sub>2</sub> route in terms of product yields and conversion.

The Alberta Research Council route requires that CO be used as reducing gas in the first stage of the liquefaction process. It is noteworthy that the reforming technology for conversion of natural gas (CH<sub>4</sub>) to either H<sub>2</sub> or CO is well known and in both cases is equally efficient in terms of the quantities of the reducing gas produced.



The conversion of methane to CO instead of H<sub>2</sub> is more attractive in view of the elimination of the demand for water and the potential for recycling the CO<sub>2</sub> produced in the first stage of the coprocessing. The disadvantage of reforming with CO<sub>2</sub> lies in endothermic nature of this reaction and in a need for separation of gases (namely CO, CO<sub>2</sub> and H<sub>2</sub>).

The block diagram of the coprocessing plant based on the concept of CO/H<sub>2</sub>O-K<sub>2</sub>CO<sub>3</sub> - H<sub>2</sub> reaction is presented in Figure 1.

The process is composed of three trains: 1) distillation of bitumen and agglomeration of coal; 2) generation and separation of reaction gases; and 3) solubilization, hydrogenation, distillation and refining of volatile products.

Earlier work showed that bitumen based bridging liquid was very effective in removal of a major portion of mineral matter (particularly silica and clays) from subbituminous coals during their agglomeration (12). It is expected that deashing of coal may have a beneficial influence on liquefaction catalyst performance and resolve the problems associated with erosion of pressure let-down valves (13).

The overall mass balance of the optimized two-stage CO/H<sub>2</sub>O-K<sub>2</sub>CO<sub>3</sub> - H<sub>2</sub> coal/bitumen process is presented in Table 4. The soluble extract (#525°C) accounts for 12.3% of the feedstock (coal + bitumen) as compared with about 19% (see Table 3) obtained from simulated two-stage autoclave tests. The reduction in generation of extractable matter was achieved through more advanced hydrogenation compared to autoclave tests. As a result the distillable oil yield after optimization was increased to 70.1% (see Table 5) compared to 66.2% obtained in an autoclave (Table 3). Equally important, the process generates mainly light (-375°C) oil, which accounts for about 90% of total oil produced. It is expected that in a continuous operation higher yields of distillable oils can be obtained. Progress in development of an active, inexpensive and disposable catalyst should have a major impact on further improvement of the ARC process concept.

Recently completed economic feasibility studies on two-stage coal/bitumen coprocessing (14) indicate that the Alberta Research Council concept to carry out the solubilization stage in CO/steam atmosphere adds about \$100 million to the cost of the coprocessing plant and this accounts for approximately 8% of total plant cost. However, when the feasibility studies were completed (early 1985) the data indicating that the CO/steam-K<sub>2</sub>CO<sub>3</sub> solubilization results in higher yield of distillable oils compared to hydrogen solubilization (see Table 3) were not available. It is noteworthy that 4% higher oil yield in plant production could readily offset the additional cost associated with CO/steam solubilization. Furthermore, there are other factors (like reaction kinetics) which seem to favor CO/steam solubilization and which do not seem to be fully accounted for in the feasibility studies.

Under the circumstances it is concluded that there is a need for further verification of the effectiveness of the CO/steam-K<sub>2</sub>CO<sub>3</sub> versus H<sub>2</sub> solubilization. It is essential to carry out continuous two-stage coal/bitumen tests in both (CO/steam-K<sub>2</sub>CO<sub>3</sub> - H<sub>2</sub> versus H<sub>2</sub>-H<sub>2</sub>) modes in order to obtain more reliable yield data and conversion values for economic analysis.

#### ACKNOWLEDGEMENT

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Table 1

DEOXYGENATION OF THE FEEDSTOCK (COAL AND BITUMEN) AND  
HYDROCARBON GAS YIELDS ON SOLUBILIZATION OF HIGHVALE COAL  
IN BITUMEN USING CO/STEAM OR H<sub>2</sub> AT 390°C

	CO/Steam	H <sub>2</sub>
Hydrocarbon Gas Yield (C <sub>1</sub> -C <sub>4</sub> ) <sup>a</sup> (%)	1.0	0.9
Deoxygenation <sup>b</sup> (%)	86	94

a) on daf feedstock

b) defined as:

$$1 - \frac{O \text{ in (distillable + extractable) products}}{O \text{ in (coal + bitumen) feedstock}} \times 100\%$$

Table 2

THE EFFECT OF RESIDENCE TIME ON  
CONVERSION FOR THE SOLUBILIZATION OF  
HIGHVALE COAL IN BITUMEN WITH  
CO/STEAM OR H<sub>2</sub> AT 390°C

Time (min)	Coal Conversion (on daf coal)	
	CO/Steam	H <sub>2</sub>
0	58	10
15	65	34
30	85	65
60	86	68

Table 3

PRODUCT YIELDS AND COAL CONVERSIONS FROM THE  
TWO-STAGE CO-PROCESSING OF BITUMEN AND HIGHVALE COAL

2nd Stage Catalyst	K <sub>2</sub> MoO <sub>4</sub> - CH <sub>3</sub> SSCH <sub>3</sub>		
1st Stage Reducing Gas	H <sub>2</sub>	CO/H <sub>2</sub> O	CO/H <sub>2</sub> O-K <sub>2</sub> CO <sub>3</sub>
Yield <sup>a</sup>			
Hydrocarbon Gas (C <sub>1</sub> -C <sub>5</sub> )	7.2(+0.8) <sup>b</sup>	5.2(+0.2)	5.3 <sup>c</sup>
Distillable Oil (IBP-525°C)	62.3(+0.9)	57.7(+0.8)	66.2(+0.7)
Soluble Extract	18.0(+0.2)	19.3(+0.9)	18.7(+0.3)
Material Balance	94.1(+3.1)	90.4(+0.2)	96.1 <sup>c</sup>
Coal Conversion (% daf coal)	90(+1)	91(+1)	98(+0)

a) Yields are presented as % daf organic feed (bitumen + coal).

b) All data are quoted as the average values of two duplicate experiments. Figures in brackets show the spreads for the two experiments.

c) Single data point.

Table 4

OVERALL MASS BALANCE FOR THE OPTIMIZED ARC TWO-STAGE  
 $\text{CO}/\text{H}_2\text{O}-\text{K}_2\text{CO}_3 - \text{H}_2$  COAL/BITUMEN PROCESS

Bitumen Coal - 2.5/1  
 Basis 100 kg - feed (daf)

Component	Input	Output
$\text{C}_5$ -200°C	3.1	11.0
200-375°C	15.0	40.1
375-525°C	16.1	19.0(2)
+ 525°C	37.2	12.3
Coal	28.6	
Ash	1.5(1)	
Unconverted Coal		2.7
Residue		1.84
Water	10.26	
$\text{H}_2$	0.6	
CO	26.1	
$\text{CO}_2$		44.7
$\text{H}_2\text{S}$		1.5
$\text{NH}_4$		0.46
$\text{C}_1$ - $\text{C}_4$		5.2
Catalyst	0.34	
	<u>138.8</u>	<u>138.8</u>

- (1) Ash reduced to 5% by deashing.  
 (2) Estimate of yield after optimization.



## COAL LIQUEFACTION/RESID HYDROCRACKING VIA TWO-STAGE INTEGRATED CO-PROCESSING

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### BACKGROUND

Lummus Crest Inc. (LCI), a subsidiary of Combustion Engineering Inc., has been developing technology for the simultaneous processing of coal and heavy petroleum liquids under a joint development contract with the U. S. Department of Energy. The LCI co-processing route is an outgrowth of its Integrated Two-Stage Liquefaction (ITSL) technology developed over the past decade by LCI for coal liquefaction. A 33-month R&D contract was initiated in October 1984 with the objective of determining the technical and economic feasibility of coal liquefaction via the LCI co-processing route.

The project was formulated into five major program tasks as follows:

- Task 1: Project Management Plan
- Task 2: Feedstock Analysis
- Task 3: Co-Processing Reactivity Screening
- Task 4: Continuous Bench-Scale Operations
- Task 5: Cost Estimate of Conceptual Commercial Facility

The first three tasks have been completed and the continuous Bench-Scale Operations task has recently been initiated. The balance of this paper will describe experimental methods, the LCI co-processing approach and the results of recent bench-scale unit operations.

### SOME JUSTIFICATIONS FOR CO-PROCESSING

Since co-processing inherently requires two separate feedstocks, namely coal and petroleum resid, it is possible to assess any potential process advantages from two viewpoints. From the refiner's viewpoint, the aromatic-rich, coal-derived extracts, being well known hydrogen donor solvents, can improve the hydroprocessing conversion of heavy, low grade petroleum feedstocks. On a constant energy cost basis, the syncrude cost contribution from a coal feedstock may be less than that from a petroleum feedstock.

For example, if one assumes a typical net syncrude yield of  $0.0005 \text{ M}^3/\text{Kg}$  (3.0 bbl/ton) for a run-of-mine bituminous coal priced at  $\$0.033/\text{kg}$  ( $\$30/\text{ton}$ ), then the coal feedstock cost of the coal syncrude is about  $\$62/\text{M}^3$  ( $\$10.00/\text{bbl}$ ). This compares to petroleum crude prices, even under the current suppressed spot market, in excess of  $\$74\text{-}100/\text{M}^3$  ( $\$12\text{-}16/\text{bbl}$ ). The situation is even more pronounced in the case of a typical subbituminous coal. Although the net yield of liquids from subbituminous coal is lower than that from bituminous coal ( $0.0003 \text{ M}^3/\text{kg}$  vs.  $0.0005 \text{ M}^3/\text{kg}$  for bituminous), the corresponding subbituminous R.O.M. coal cost is not proportionately lower but rather about 73 percent lower than that of the bituminous coal ( $\$0.0088/\text{kg}$  vs.  $\$0.033/\text{kg}$ ). This translates to a subbituminous coal feedstock cost of the coal liquids of about  $\$32.6/\text{M}^3$  ( $\$5.20/\text{bbl}$ ). In both cases, it is envisioned that a relatively low level of coal-derived liquids would be blended with petroleum resid feedstock so as not to greatly alter the downstream refinery processability of the petroleum-coal liquid mixtures.

From a coal liquefaction plant owner's viewpoint, the introduction of petroleum resid allows for a reduction in the large and costly solvent recycle systems. Additional advantages include:

- o Reduces net hydrogen consumption and correspondingly reduced hydrogen production costs;
- o Avoids the need for a costly deashing step;
- o Provides for a more rapid introduction of coal into the domestic energy networks; and
- o Allows the consideration of smaller-scale, less capital intensive plant sizes in an over-the-fence concept rather than in a grass-roots, mega-project concept.

#### LCI CO-PROCESSING APPROACH

Of the three key co-processing routes - thermal, thermocatalytic, biochemical - the LCI approach represents a hybrid of the first two in that it consists of a two-stage method. The first-stage is a thermal reaction system paralleling the Short Contact Time (SCT) reaction system developed for LCI's ITSL Process. The second-stage consists of a catalytic reaction system based on LCI's proprietary expanded-bed technology known as LC-Fining<sup>SM</sup>. The SCT reactor is close-coupled to the LC-Fining<sup>SM</sup> reactor to allow for rapid stabilization of coal extracts by the LC-Fining<sup>SM</sup> catalyst thereby minimizing undesirable free radical condensation reactions.

Figures 1 and 2 show two alternative flowschemes depending upon the source and type of the petroleum resid. The scheme shown in Figure 1 is predicated on the use of a heavy refinery stream such as the unconverted resid from a catalytic hydrocracker. In this scheme, the petroleum feedstock is blended with the coal and a recycle gas oil stream prior to the first-stage, SCT thermal reactor.

The scheme shown in Figure 2 is predicated on the use of a virgin vacuum residua which is fed directly into the LC-Finer<sup>SM</sup> along with the SCT coal extract. The first-stage reactor of the LC-Finer<sup>SM</sup> can be operated to simultaneously optimize the production of a) a donor solvent-rich gas oil recycle stream; b) an unconverted but hydrotreated recycle resid stream having improved solvency for coal; and c) hydrocracked C<sub>5</sub>-524°C (C<sub>5</sub>-975°F) distillates.

#### EXPERIMENTAL APPROACH

The experimental approach to obtaining key process data required for the preliminary design and estimate of a conceptual commercial facility has been accomplished in a variety of test units. Initial work for screening candidate coal and petroleum feedstocks was carried out in microautoclave reaction systems shown schematically in Figure 3. This was followed by testing in a continuous, close-coupled test unit under once-through conditions utilizing solvents characteristic in composition to what is expected at steady-state, but synthetically generated. The test unit, shown schematically in Figure 4, consists of an SCT reaction system comprised of a 6.2 mm i.d. by 343 cm long horizontal coil heater followed by a vertical SCT reactor having a volume of 118 cc. The SCT

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(sm) LC-Fining is a service mark of Lummus Crest Inc. for engineering, marketing and technical services related to hydrocracking and hydrodesulfurization processes for reduced crude and residual oils.

system, which could be operated with either SCT reactors described above, was close-coupled to a stirred autoclave catalytic hydrocracker. The continuous bench-scale unit being operated in Task 4 consists of the above SCT reactor systems close-coupled to a small diameter, expanded-bed LC-Fining<sup>SM</sup> reactor system. This unit can operate in a recycle mode which consists of batch collection of hydrotreated liquids from the LC-Finer<sup>SM</sup> followed by batch slurring of the coal and the thus collected recycle liquids. Both SCT and LC-Finer<sup>SM</sup> reactors are operated continuously.

### RESULTS OF BENCH-SCALE TESTING

Process variables studies, carried out in the continuous close-coupled test units, have recently been completed. The bulk of the test scans concentrated on scouting of both SCT and LC-Fining<sup>SM</sup> reaction conditions close to that of the anticipated region of preferred commercial operations. Tests were made with two coal-petroleum combinations that were selected from the analysis of the microautoclave test data. These combinations consisted of a bituminous coal - Pittsburgh seam with Athabasca vacuum resid - and a subbituminous coal - Wyodak with Arab Heavy vacuum resid. During the scans, two sets of data were obtained indicating the effect of LC-Fining<sup>SM</sup> reactor temperature and solvent/coal ratio on co-processing performance.

### EFFECT OF TEMPERATURE

The impact of LC-Fining<sup>SM</sup> temperature at constant SCT reaction conditions is shown in Table 1. From these data, we have calculated pseudo-kinetic rate constants for each of the performance criteria based on simplified kinetic models. These values are indicated below:

<u>Co-Processing (SCT &amp; LC-F) Performance Parameter</u>	<u>Pseudo-Rate Constant, hr<sup>-1</sup></u>		
	<u>404C</u>	<u>416C</u>	<u>432C</u>
Desulfurization	0.75	1.09	1.67
Demetallization	0.55	0.90	1.12
524C+ Conversion	0.54	0.72	1.11
Denitrogenation	0.29	0.43	0.90

The feedstock in all tests consisted of 25 percent coal/37.5 percent hydrotreated petroleum resid/37.5 percent coal-derived gas oil. The order of reactivity as measured by the specific co-processing performance parameters in descending order is:

Desulfurization > Demetallization > Conversion > Denitrogenation

It is also interesting to note that in all three tests, the preasphaltene content in the product of the single-stage LC-Finer<sup>SM</sup> has been reduced to less than 2 percent.

### EFFECT OF SOLVENT QUALITY AND SOLVENT/COAL RATIO

The impact of solvent/coal ratio and solvent quality at constant SCT and LC-Fining<sup>SM</sup> reaction conditions is shown in Table 2. The following interesting observations have been made based on the data shown:

- o At constant coal slurry concentration, reducing the ratio of the solvent (524°C - boiling range) to coal from 1.5/1 to 1.0/1 had a minimal effect on observed coal conversions.

- o However, the reduction in the said solvent/coal ratio did adversely affect syncrude characteristics and net distillate yields.

It should be kept in mind that the high LC-Fining<sup>SM</sup> severity used in this particular test campaign was aimed at assessing per pass performance (e.g., conversion, desulfurization, etc.) limits during co-processing. In the conceptual commercial concept depicted in Figures 1 and 2, it is anticipated that the first-stage LC-Finer<sup>SM</sup> located immediately downstream of the SCT reactor will be operated under optimal conditions for generating recycle gas oil solvents having high hydrogen donor capacity. At these severities, it is anticipated that the 524°C+ conversions would be lower than the values shown in Table 4. The additional required feed conversions, i.e., overall conversions in excess of 80 percent, could be achieved in a second-stage LC-Finer<sup>SM</sup> operated at higher, more conventional petroleum hydrocracking severities.

In test BSCL-20, a 524°C- recycle solvent during co-processing was simulated by blending a neat coal-derived hydrogenated solvent with a neat petroleum-derived hydrogenated solvent in the same ratio as that of the coal and petroleum resid fed in that run. By comparing these results to those of test BSCL-9 made only with coal-derived 524°C- solvent, it is possible to estimate the relative solvent quality index (SQI) of the petroleum-derived gas oil solvent in comparison to that of the coal-derived gas oil solvent. The SQI of the particular petroleum gas oil utilized in this test has been estimated to be about 60 percent of that of the coal-derived solvent based on relative solvent performance as measured by observed net distillate yields. Optimization of the petroleum resid hydrocracking step in which the simulated gas oil solvent was generated has the potential to increase the latter's SQI value closer to that of the coal-based solvent.

#### FUTURE WORK

The continuous bench-scale unit will be operated in the recycle mode to demonstrate the effect of solvent maintenance on co-processing performance as a function of feedstock types (Pittsburgh seam and Wyodak coals; Arab Heavy and Athabasca residua); coal/resid ratios; solvent/coal ratio and catalyst age. These data will serve as the basis for formulating a conceptual commercial plant design. Towards the end of the Task 4 experimental program, a catalyst life test at preferred co-processing conditions will be made to demonstrate the technical feasibility of the base case design.

#### ACKNOWLEDGEMENTS

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**TABLE 1**  
**EFFECT OF LC-FINING<sup>SM</sup> TEMPERATURE ON CLOSE-COUPLED CO-PROCESSING PERFORMANCE**  
**SUMMARY OF TEST CONDITIONS AND RESULTS**

<u>Run No.</u> (BSCL-)	<u>9</u>	<u>10</u>	<u>11</u>
<b>I. Test Conditions</b>			
SCT Temperature, °C (°F)	449(840)	449(840)	449(840)
LC-Fining <sup>SM</sup> Temperature, °C (°F)	432(810)	416(780)	404(760)
Coal Space Velocity to SCT, Kg/Hr/M <sup>3</sup>	3400	3400	3400
Solvent/Coal Wt. Ratio	1.5	1.5	1.5
Resid/Coal Wt. Ratio	1.5	1.5	1.5
<b>II. Test Results</b>			
Coal Conversion, Wt.% MAF	96.0	93.8	93.7
524°C+ (975F+) Conversion, Wt.%	75.8	67.3	58.4
Net Distillate Yield, Kg 524°C-/100 Kg 524°C+	58.1	55.9	48.3
Desulfurization, %	82.5	75.7	66.0
Denitrogenation, %	71.7	55.0	43.0
Resid Demetallization, %	76.0	72.0	59.0
Preasphaltenes Concentration, %	1.7	1.5	1.9

- 
- (1) Feedstocks: Pittsburgh seam coal; Prehydrotreated 524°C+ Athabasca resid
  - (2) Solvent: 524°C- gas oil characteristic of a coal-derived recycle solvent produced in LCI's ITSL PDU during Wyodak coal operations
  - (3) SCT Condition: 137 atm; 360 M<sup>3</sup> H<sub>2</sub>/M<sup>3</sup> feed
  - (4) LC-Fining<sup>SM</sup> Conditions: Shell 324M catalyst; 137 atm; 0.4R hr<sup>-1</sup>; 530 M<sup>3</sup> H<sub>2</sub>/M<sup>3</sup> feed

**TABLE 2**  
**EFFECT OF SOLVENT QUALITY AND SOLVENT/COAL RATIO ON CLOSE-COUPLED**  
**CO-PROCESSING PERFORMANCE**

**SUMMARY OF TEST CONDITIONS AND RESULTS**

Run No. (BSCL-)	<u>9</u>	<u>21</u>	<u>20</u>
<b>I. <u>Test Conditions</u></b>			
Solvent/Coal Wt. Ratio	1.5	1.0	1.5
Coal/Resid Wt. Ratio	0.67	0.50	0.67
Coal Slurry Concentration, Wt. %	25.0	25.0	25.0
<b><u>524°C- Solvent Composition, Wt. %</u></b>			
ITSL*	100	100	40
Petroleum Gas Oil**	0	0	60
SCT Temperature, °C (°F)	449(840)	449(840)	449(840)
LC-Fining <sup>Sm</sup> Temperature, °C (°F)	432(810)	432(810)	432(810)
Coal Space Velocity to SCT, Kg/Hr/M <sup>3</sup>	3400	3400	3400
<b>II. <u>Test Results</u></b>			
Coal Conversion, Wt. % MAF	96.0	93.4	94.2
524°C+ (975F+) Conversion, Wt. %	75.8	66.2	64.2
Net Distillate Yield, Kg 524°C-/100 Kg 524°C+	58.1	51.0	46.0
Desulfurization, %	82.5	75.0	77.2
Denitrogenation, %	71.7	65.0	67.1
Resid Demetallization, %	76.0	69.0	71.0
Preasphaltenes Concentration, %	1.7	2.2	2.0

\* 524°C- gas oil characteristic of a coal-derived recycle solvent produced in LCI's ITSL PDU during Wyodak coal operations.

\*\* 524°C- gas oil characteristic of a petroleum-derived recycle solvent produced during LC-Fining<sup>Sm</sup> of virgin Athabasca bitumen.

1. Feedstocks: Pittsburgh seam coal; prehydrotreated 524°C+ Athabasca resid
2. SCT Conditions: 137 atm; 360 M<sup>3</sup> H<sub>2</sub>/M<sup>3</sup> feed
3. LC-Fining<sup>Sm</sup> Conditions: Shell 324M catalyst; 137 atm; 0.4R Hr<sup>-1</sup>; 530 M<sup>3</sup> H<sub>2</sub>/M<sup>3</sup> feed

Figure 1. SCHEMATIC OF LCI CO-PROCESSING CONCEPT WITH HYDROCRACKED PETROLEUM RESIDUA

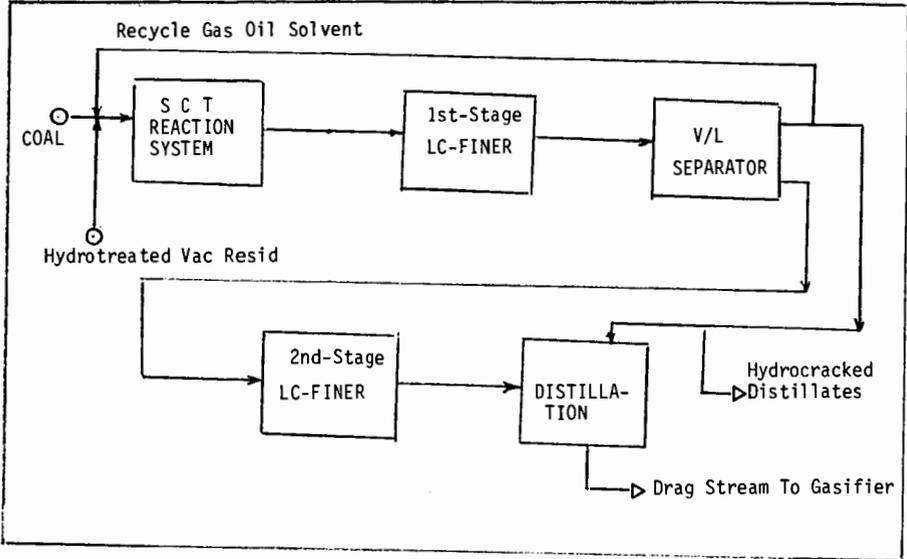
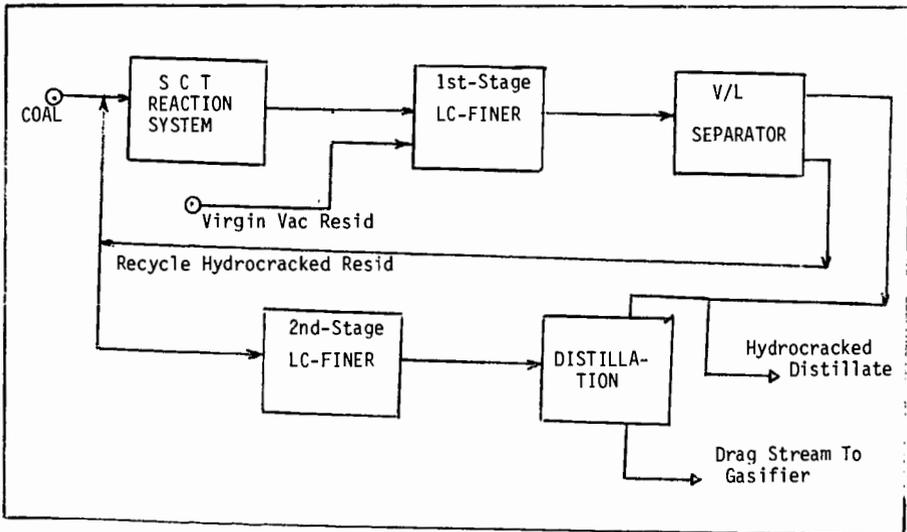
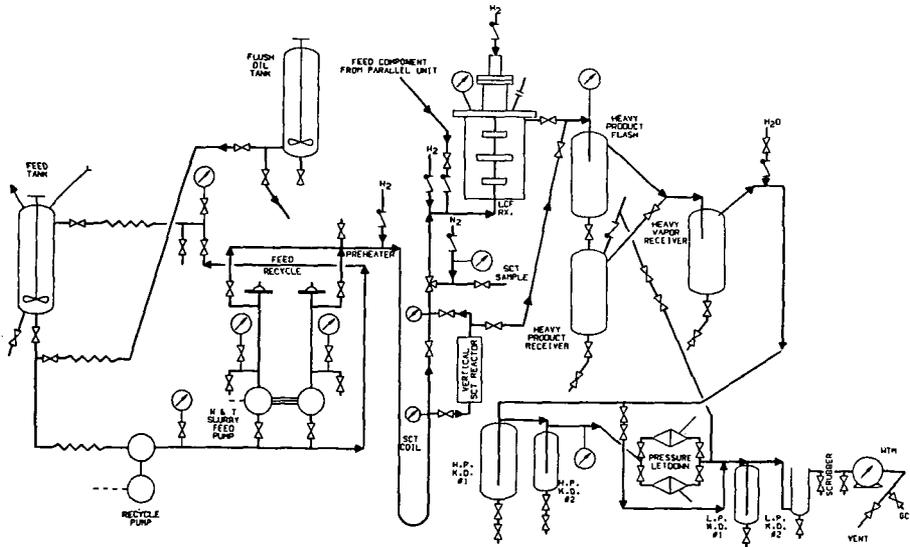
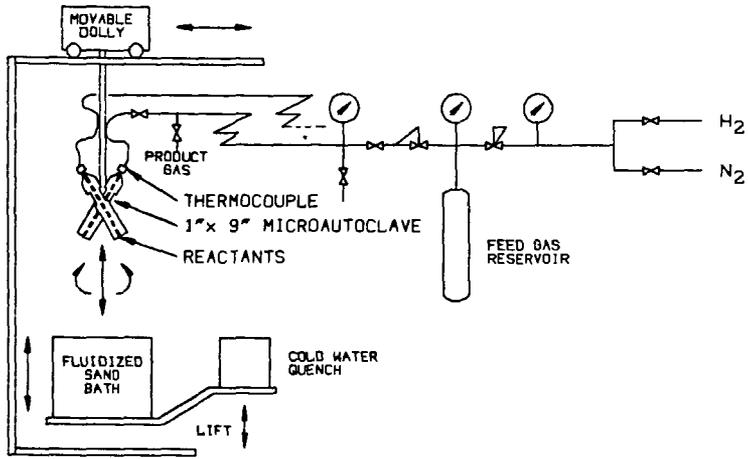


Figure 2. SCHEMATIC OF LCI CO-PROCESSING CONCEPT WITH VIRGIN PETROLEUM RESIDUA



**FIGURE 3**  
**SCHEMATIC OF MICROAUTOCLAVE TEST UNIT**



**FIGURE 4** SCHEMATIC OF LCI'S CONTINUOUS CO-PROCESSING TEST UNIT

## SIMULATION OF A COAL/PETROLEUM RESID COPROCESSING PILOT PLANT SCHEME

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### ABSTRACT

Coproprocessing involves the conversion of coal and heavy oil in the presence of hydrogen to products that can be further upgraded into commercial fuels; the upgrading can be carried out in an existing refining operation. This relatively new concept eliminates or significantly reduces the need for expensive solvent recycle, and thus has the potential for improved economic performance over current direct coal liquefaction processes.

A simulation of a single-stage coprocessing pilot plant involving the simultaneous conversion of resid and coal has been carried out using the ASPEN PLUS simulator. Limited experimental data were available for only one run, and results should be considered preliminary. The Assay Data Analysis and Pseudocomponent Correlation System of ASPEN PLUS has been used to develop a set of pseudocomponents for coal/resid liquids and to estimate corresponding physical and thermodynamic properties. Correlations based on coal liquids and petroleum liquids have been utilized. For some process equipment, petroleum liquids correlations are better than coal liquids correlations. Testing for the presence of a free water phase and the treatment of heavy resid as a single high-boiling pseudocomponent has improved simulator performance.

### INTRODUCTION

Serious research efforts are under way to develop alternative energy sources in order to prevent petroleum supply disruptions from having adverse impact upon the economy of those countries dependent on external supplies of petroleum. During the last twenty years, considerable work has been done in attempts to understand the scientific and technological applications of coal conversion schemes for production of liquid fuels to supplement dwindling petroleum reserves. A relatively new concept addressing this issue involves coprocessing heavy oil with relatively low-cost coals to produce liquid distillates. A review of coal-oil coprocessing technology has been given by Cugini [1]. This review addresses the state of the technology, and several important research efforts required to advance the technology beyond the current level of knowledge. One important area of research required to improve understanding of coprocessing technology is the characterization of the heavy nondistillable feedstock and product oils. Estimations of physical and thermodynamic properties of feedstock and product oils are required to design the commercial reactor and the product separation train and to estimate material flows and compositions for internal and external streams of the coprocessing plant.

There are several sources of information related to coprocessing of coal and heavy oil in bench-scale and pilot-plant operations [2-4]. However, insufficient information is given in these reports to properly characterize the thermodynamic and physical properties of the liquid products as a function of operating conditions. Coal and heavy oil coprocessing in a continuous bench-scale plant has recently been initiated at UOP, Inc. and the Signal Research Center, Inc. [5]. The work related to this study has been described in sufficient detail to allow characterization of the products. The present effort describes the results of a simulation of the single-stage coprocessing bench-scale unit at Signal Research Center, Inc., using the ASPEN PLUS simulator to determine physical and thermodynamic properties

of the liquid products. This bench-scale work forms a preliminary basis to conduct process modeling studies for a range of operating conditions used with this concept.

#### EXPERIMENTAL

The simulation studies were based on one catalytic coprocessing run at the UOP pilot plant (Figure 1). Two parts of Lloydminster resid to one part of Illinois No. 6 coal constituted the feed. The Lloydminster resid was fractionated so that 95% of the resid consisted of 950°F+ material. Total feed rate to the reactor was 3.75 lb in 12 hours. Coal conversion defined as toluene insolubles was 86%. Operating conditions for the separators include the following: high-pressure separator--temperature = 302°F, pressure = 3114.7 psia; three-phase separator--temperature = 86°F, pressure = 3014.7 psia; low-pressure separator--temperature = 284°F, pressure = 19.7 psia; debutanizer--temperature = 43°F, pressure = 17.7 psia; vacuum fractionator--temperature = 608°F, pressure = 0.94 psia. The effluent from the low-pressure separator and gases from the vacuum pump are sent to the debutanizer, where C<sub>6</sub>+ material is condensed and off-gases are sampled. The vacuum fractionator is a packed column that operates with an overhead reflux. Dimensions of the debutanizer and vacuum fractionator towers and of their packing were not available. For lack of better information on the number of equivalent theoretical plates in the debutanizer and vacuum fractionator, simulations for both units were performed as simple flash calculations.

Experimental values were available for the three-phase separator vapor stream, the debutanizer vapor stream, the vacuum fractionator bottoms, and a combined composition for the vacuum fractionator overhead and debutanizer bottoms. Gas phase components were analyzed by gas chromatography. Boiling point distributions were obtained by gas chromatographic simulated distillation.

#### FLOWSHEET SIMULATION METHODOLOGY

The ASPEN PLUS simulator [6] has been used for the flowsheet analysis of the separator system downstream from the reactor in the UOP coprocessing pilot plant (Figure 1). ASPEN PLUS was originally designed for the analysis of fossil fuel conversion processes, although it has proven useful for many process industries. It has been used to develop a reference data base system of thermophysical properties of coal liquids needed for vapor-liquid equilibrium and for heat and material balance calculations [2], and to simulate the preliminary separator system downstream from the reactor in the SRC-II coal liquefaction process [7].

A preliminary step in the simulation process is the development of an ASPEN flowsheet. Figure 2 represents the ASPEN flowsheet for the separator system following the reactor in the coprocessing pilot-plant flow diagram in Figure 1. The outlet stream from the reactor is the process feed stream for the simulation. The five separators include a high-pressure separator, a three-phase separator, a low-pressure separator, a debutanizer, and a vacuum fractionator. All are modeled as flash units where vapor-liquid equilibrium calculations are performed to produce vapor and liquid outlet streams. Mixer units are used to combine material streams into one stream. Names associated with the streams, and unit operation models for ASPEN identification purposes are designated in Figure 2.

Thermophysical properties used for the simulations were based on three ASPEN PLUS option sets. The option set used for lighter components up to C<sub>6</sub> is based primarily on the Redlich-Kwong-Soave thermophysical model. Heavier components were analyzed using the ASPEN PLUS Assay Data Analysis and Pseudocomponent Correlation System for petroleum liquids and coal liquids. Standard API procedures were used for the petroleum liquids thermophysical models, and correlations developed primarily at Aspen Technology, Inc., were used for the coal liquids thermophysical models. From assay analyses of the vacuum fractionator process streams, a set of

20 pseudocomponents was developed to represent the heavier components; each pseudocomponent represents about a 50°F cut of liquid distillate. Since the process feed stream included both coal and petroleum liquids, separate simulation runs were made where thermophysical properties for each pseudocomponent were analyzed using the correlation option set for coal liquids and the set for petroleum liquids. Comparisons have been made for the performance of each option set.

### RESULTS AND DISCUSSION

The composition for the process feed stream to the high-pressure separator is estimated from experimental product slates for the vacuum fractionator, the debutanizer, and the three-phase separator (see Table 1). Gases and identified compounds range from H<sub>2</sub> to pentane. Liquid distillates are represented as pseudocomponents and range from an average boiling point of 111°F to 1091°F (pseudocomponents are prefaced by PC and followed by the average boiling point of the approximately 50°F cut). The initial boiling point (IBP) of the liquid distillate is 69.8°F. For conciseness in the presentation of results, the pseudocomponents have been expressed as four distillate fractions (see Table 2).

TABLE 1. Process Feed Stream Composition for High Pressure Separator

Components*	Flows (lb/hr)	Components*	Flows (lb/hr)
H <sub>2</sub>	0.0593	PC428	0.0075
CO	0.0051	PC477	0.0168
H <sub>2</sub> S	0.0552	PC525	0.0163
CH <sub>4</sub>	0.0637	PC575	0.0163
C <sub>2</sub> H <sub>6</sub>	0.0364	PC625	0.0167
C <sub>3</sub> H <sub>8</sub>	0.0255	PC675	0.0174
C <sub>4</sub> H <sub>10</sub>	0.0105	PC725	0.0158
I-C <sub>4</sub> H <sub>10</sub>	0.0028	PC774	0.0139
C <sub>5</sub> H <sub>12</sub>	0.0034	PC825	0.0128
I-C <sub>5</sub> H <sub>12</sub>	0.0034	PC876	0.0113
H <sub>2</sub> O	0.0108	PC924	0.0113
PC111	0.0052	PC973	0.0048
PC176	0.0017	PC1022	0.0034
PC226	0.0020	PC1091	0.0503
PC276	0.0025	Ash	0.0108
PC327	0.0041	Unconverted Coal	0.0135
PC376	0.0053	Nondistillate Solids	0.0456

\*Pseudocomponents are 50°F cuts and are represented by PC followed by the average boiling point.

TABLE 2. Process Feed Stream Distillate Fractions Expressed as Pseudocomponents.

Distillate Fraction	Pseudocomponent Range	Flows (lb/hr)
IBP-350°F	PC111-PC327	0.0155
350°-450°F	PC376-PC428	0.0128
450°-950°F	PC477-PC924	0.149
950°F+	PC973-PC1091	0.0585

### Three-Phase Separator

For the three-phase separator overheads, the effect of the correlation option is given in Table 3. There is some improvement using the petroleum-liquids option set. Use of the coal-liquids option set results in an overall error for total mass flow of overhead of 1.86%, and the petroleum-liquids option set results in an error of 0.73%.

TABLE 3. Comparison of Calculated and Experimental Overhead Flows (lb/hr) for the Three-Phase Separator as a Function of Physical Properties Calculations Method

Components	Correlation Option Set		
	Coal Liquids	Petroleum Liquids	Experimental
H <sub>2</sub>	0.0591	0.0589	0.0587
CO	0.0051	0.0051	0.00513
H <sub>2</sub> S	0.0516	0.0511	0.0498
CH <sub>4</sub>	0.0629	0.0626	0.0621
C <sub>2</sub> H <sub>6</sub>	0.0349	0.0346	0.0340
C <sub>3</sub> H <sub>8</sub>	0.0233	0.0229	0.0225
C <sub>4</sub> H <sub>10</sub>	0.0086	0.0084	0.00849
I-C <sub>4</sub> H <sub>10</sub>	0.0024	0.0023	0.00212
C <sub>5</sub> H <sub>12</sub>	0.0023	0.0022	0.00263
I-C <sub>5</sub> H <sub>12</sub>	0.0025	0.0023	0.00263

### Debutanizer

For the debutanizer overheads, the effect of the correlation option is given in Table 4. There is improvement using the petroleum-liquids option set. Use of the coal-liquids option set results in an overall error for total mass flow of overhead of 16.4%, and the petroleum-liquids option set results in an error of only 1.37%.

TABLE 4. Comparison of Calculated and Experimental Overhead Flows (lb/hr) for the Debutanizer as a Function of Physical Properties Calculations Method

Components	Correlations Options Set		
	Coal Liquids	Petroleum Liquids	Experimental
H <sub>2</sub>	2.31 x 10 <sup>-4</sup>	3.91 x 10 <sup>-4</sup>	6.09 x 10 <sup>-4</sup>
CO	2.79 x 10 <sup>-5</sup>	4.59 x 10 <sup>-5</sup>	--
H <sub>2</sub> S	3.5 x 10 <sup>-3</sup>	3.9 x 10 <sup>-3</sup>	--
CH <sub>4</sub>	7.84 x 10 <sup>-4</sup>	1.1 x 10 <sup>-3</sup>	1.60 x 10 <sup>-3</sup>
C <sub>2</sub> H <sub>6</sub>	1.4 x 10 <sup>-3</sup>	1.8 x 10 <sup>-3</sup>	2.35 x 10 <sup>-3</sup>
C <sub>3</sub> H <sub>8</sub>	2.1 x 10 <sup>-3</sup>	2.5 x 10 <sup>-3</sup>	2.96 x 10 <sup>-3</sup>
C <sub>4</sub> H <sub>10</sub>	1.5 x 10 <sup>-3</sup>	1.8 x 10 <sup>-3</sup>	1.95 x 10 <sup>-3</sup>
I-C <sub>4</sub> H <sub>10</sub>	3.34 x 10 <sup>-4</sup>	4.02 x 10 <sup>-4</sup>	6.51 x 10 <sup>-4</sup>
C <sub>5</sub> H <sub>12</sub>	6.15 x 10 <sup>-4</sup>	7.41 x 10 <sup>-4</sup>	8.08 x 10 <sup>-4</sup>
I-C <sub>5</sub> H <sub>12</sub>	6.10 x 10 <sup>-4</sup>	7.31 x 10 <sup>-4</sup>	8.08 x 10 <sup>-4</sup>
C <sub>6</sub> <sup>+</sup>	1.05 x 10 <sup>-3</sup>	1.35 x 10 <sup>-3</sup>	2.88 x 10 <sup>-3</sup>

### Vacuum Fractionator

As a measure of simulation adequacy, total vapor and liquid flows computed by simulation were compared with experimental data. Total mass flow of overhead and

bottoms is less sensitive to the number of theoretical stages than are the individual distillate fraction flows. The effect of the correlation option set (coal-liquids vs. petroleum-liquids) on the vacuum fractionator simulation performance was determined. Since simulated distillate flows were in considerable disagreement with experimental values for the reported operating pressure of 0.94 psia, additional simulation runs were made to observe the effect of assumed column pressures. For the petroleum-liquids option set, a value of 4.5 psia gave the best match of calculated total overhead and bottom flows to experimental flows. Correspondingly, a value of 6.0 psia was found for the coal-liquids option set. Given that the reported column pressure, 0.94 psia, is closer to 4.5 psia than to 6.0 psia, this result gives an indirect indication that the petroleum-based option set better describes the experimental system. The actual operating pressure for the vacuum fractionator was known to increase above 0.94 psia during the experimental run, but no information is available as to the extent of increase. The results for the flows of the distillate fractions are presented in Tables 5-7. Table 5 represents results for vacuum bottoms flows, and Table 6, for vacuum overhead flows (calculated vacuum overhead flows also include values for debutanizer bottoms flows in order to agree with experimental measurements). Table 7 gives a comparison of the pressure and correlation option set in terms of an overall percentage error for both bottoms and overhead at the operating pressure of 0.94 psia. Use of the petroleum-liquids option set gives better agreement, although the percentage of error relative to experimental error is still considerable.

TABLE 5. Comparison of Calculated and Experimental Vacuum Bottoms Flows (lb/hr) as a Function of Physical Properties Calculation Method and System Pressure

Correlation Option Set	Boiling Point Range, °F	Calculated	Experimental
<u>Coal Liquids</u>			
P = 0.94 psia	IBP-350	$1.52 \times 10^{-6}$	--
	350-450	$8.46 \times 10^{-5}$	--
	450-950	$5.60 \times 10^{-3}$	$5.16 \times 10^{-2}$
	<u>950+</u>	<u><math>3.24 \times 10^{-2}</math></u>	<u><math>5.92 \times 10^{-2}</math></u>
	Total	$3.80 \times 10^{-2}$	$1.11 \times 10^{-1}$
P = 6.0 psia	IBP-350	$5.38 \times 10^{-5}$	--
	350-450	$2.94 \times 10^{-4}$	--
	450-950	$5.47 \times 10^{-2}$	$5.16 \times 10^{-2}$
	<u>950+</u>	<u><math>5.67 \times 10^{-2}</math></u>	<u><math>5.92 \times 10^{-2}</math></u>
	Total	$1.12 \times 10^{-1}$	$1.11 \times 10^{-1}$
<u>Petroleum Liquids</u>			
P = 0.94 psia	IBP-350	$4.92 \times 10^{-6}$	--
	350-450	$2.47 \times 10^{-5}$	--
	450-950	$1.40 \times 10^{-2}$	$5.16 \times 10^{-2}$
	<u>950+</u>	<u><math>5.38 \times 10^{-2}</math></u>	<u><math>5.92 \times 10^{-2}</math></u>
	Total	$6.78 \times 10^{-2}$	$1.11 \times 10^{-1}$
P = 4.5 psia	IBP-350	$5.59 \times 10^{-5}$	--
	350-450	$2.75 \times 10^{-4}$	--
	450-950	$5.21 \times 10^{-2}$	$5.16 \times 10^{-2}$
	<u>950+</u>	<u><math>5.79 \times 10^{-2}</math></u>	<u><math>5.92 \times 10^{-2}</math></u>
	Total	$1.10 \times 10^{-1}$	$1.11 \times 10^{-1}$

**TABLE 6. Comparison of Calculated and Experimental Vacuum Overhead Flows (lb/hr) as a Function of Physical Properties Calculation Method and System Pressure**

Correlation Option Set	Boiling Point Range, °F	Calculated	Experimental
<u>Coal Liquids</u>			
P = 0.94 psia	IBP-350	$1.07 \times 10^{-2}$	$1.34 \times 10^{-2}$
	350-450	$1.28 \times 10^{-2}$	$1.90 \times 10^{-2}$
	450-950	$1.43 \times 10^{-1}$	$8.97 \times 10^{-2}$
	950+	$2.60 \times 10^{-2}$	$8.17 \times 10^{-5}$
	Total	$1.93 \times 10^{-1}$	$1.22 \times 10^{-1}$
P = 6.0 psia	IBP-350	$1.07 \times 10^{-2}$	$1.34 \times 10^{-2}$
	350-450	$1.25 \times 10^{-2}$	$1.90 \times 10^{-2}$
	450-950	$9.38 \times 10^{-2}$	$8.97 \times 10^{-2}$
	950+	$1.70 \times 10^{-3}$	$8.17 \times 10^{-5}$
	Total	$1.19 \times 10^{-1}$	$1.22 \times 10^{-1}$
<u>Petroleum Liquids</u>			
P = 0.94 psia	IBP-350	$1.05 \times 10^{-2}$	$1.34 \times 10^{-2}$
	350-450	$1.28 \times 10^{-2}$	$1.90 \times 10^{-2}$
	450-950	$1.34 \times 10^{-1}$	$8.97 \times 10^{-2}$
	950+	$4.60 \times 10^{-3}$	$8.17 \times 10^{-5}$
	Total	$1.62 \times 10^{-1}$	$1.22 \times 10^{-1}$
P = 4.5 psia	IBP-350	$1.05 \times 10^{-2}$	$1.34 \times 10^{-2}$
	350-450	$1.25 \times 10^{-2}$	$1.90 \times 10^{-2}$
	450-950	$9.64 \times 10^{-2}$	$8.97 \times 10^{-2}$
	950+	$5.08 \times 10^{-3}$	$8.17 \times 10^{-5}$
	Total	$1.24 \times 10^{-1}$	$1.22 \times 10^{-1}$

**TABLE 7. Comparison of Physical Properties Calculation Method on Vacuum Fractionator Effluent Stream Mass Flow Rates**

Correlation Option Set	% Error*	
	Vacuum Bottoms	Vacuum Overhead
<u>Coal Liquids</u>		
P = 0.94 psia	65.8	58.2
<u>Petroleum Liquids</u>		
P = 0.94	38.9	32.8

\*Absolute value of (Calculated - Experimental)/Experimental.

Effects of pressure and correlation option set on pseudocomponent composition for the vacuum fractionator are reflected in Figures 3-6. Figures 3 and 4 represent the effect on the vacuum bottoms stream, and Figures 5 and 6, the effect on the overhead stream. These figures indicate that the petroleum-liquids option set gives better values than the coal-liquids option set and that the effect of pressure is considerable.

Low Pressure Separator

A temperature of 284°F was used for the operating condition of the low-pressure separator in the simulator. Since, experimentally, a temperature range of 248°F-284°F was given, it was decided to make a simulation run at the lower temperature to determine any effects of the assumed temperature on the effluent flow rates. Results for the lower temperature indicate only a small increase in bottoms flows of 1.3% and an decrease in overhead flows of 11.8%.

Effect of Free Water Phase on the Debutanizer

Simulations were carried out on the debutanizer to determine the impact of the presence of a free water phase (Table 8). Without the invocation of the option to test for the presence of free water, no distillate and only a small amount of lighter gases are predicted by the simulator to be present in the debutanizer bottoms. With the test for the presence of water invoked, the presence of a free water phase is confirmed, and results indicate a substantial increase in bottoms flow and a decrease in overhead. Both of these predictions agree with experiment, as shown in Table 8. All simulations have tested for the presence of a free water phase.

**TABLE 8. Effect of Treatment of Water on the Debutanizer Effluent Product Flows (lb/hr)**

Products	Assumed Absence of Free Water Phase		Assumed Presence of Free Water Phase		Experimental Overhead
	Overhead	Bottoms	Overhead	Bottoms	
Gases-C <sub>5</sub>	6.93 x 10 <sup>-3</sup>	3.90 x 10 <sup>-6</sup>	1.11 x 10 <sup>-2</sup>	1.16 x 10 <sup>-3</sup>	1.18 x 10 <sup>-2</sup> 2.88 x 10 <sup>-3</sup>
IBP-350°F	3.79 x 10 <sup>-3</sup>	0	1.05 x 10 <sup>-3</sup>	4.86 x 10 <sup>-3</sup>	
350°-450°F	1.53 x 10 <sup>-3</sup>	0	1.08 x 10 <sup>-7</sup>	1.16 x 10 <sup>-3</sup>	
450°-950°F	1.31 x 10 <sup>-3</sup>	0	4.69 x 10 <sup>-8</sup>	8.46 x 10 <sup>-4</sup>	
950°F+	1.02 x 10 <sup>-7</sup>	0	0	6.52 x 10 <sup>-8</sup>	

**TABLE 9. Effect of Treatment of Heavy Resid on Vacuum Bottoms**

Product	Heavy Residue Treated as	
	Solid Material (Flows, lb/hr)	Pseudocomponent (Flows, lb/hr)
Gases-C <sub>5</sub>	0	1.44 x 10 <sup>-8</sup>
IBP-350°F	0	1.52 x 10 <sup>-6</sup>
350°-450°F	0	8.47 x 10 <sup>-6</sup>
450°-950°F	0	5.59 x 10 <sup>-3</sup>
950°F+	0	3.25 x 10 <sup>-2</sup>
Nondistillate Solid	0.0456	0

Effect of Treatment of Heavy Resid on Vacuum Bottoms

The method of treatment of heavy resid has an impact on predicted composition and flow rate of vacuum bottoms as reflected in Table 9. The data are for the simulation of the vacuum fractionator at the pressure of 0.94 psia and using coal-liquids correlations. When the heavy resid is treated as a nondistillate solid, i.e., material with negligible vapor pressure, no distillates are predicted to appear in the vacuum bottoms. When the heavy resid is treated as a 1091°F pseudo-

component, distillate products are predicted in the bottoms. This treatment of the resid fraction corresponds to that of McKeegan and Klunder [8], who also assigned a single normal boiling point to the nondistillate material in their simulation of the separator system in the SRC-II coal liquefaction process (although they used a much higher temperature). The plot in Figure 4 for  $P = 0.94$  psia, as well as for  $P = 6.0$  psia, reflects the presence of heavy resid treated as the 1091°F pseudocomponent. These plots are in line with the experimental observation of the presence of significant amounts of liquid distillate product in the vacuum bottoms stream. All simulation results for the vacuum fractionator presented in Tables 5-7 and Figures 3-6 have treated the heavy resid as a 1091°F pseudocomponent.

#### CONCLUSIONS

The very preliminary results reported here indicate that the use of petroleum-liquids correlations may result in an improvement over coal-liquids correlations in the simulation of the coprocessing of Lloydminster with Illinois No. 6 coal. Agreement between simulation and experiment is improved by using a higher assumed pressure than the experimental pressure for the vacuum fractionator, by treating the presence of water as a free water phase, and by treating the heavy resid as 1091°F distillate rather than an inert solid material. It is necessary to obtain better definition of the separation equipment used and the operating conditions employed, and to acquire a larger data set in order to evaluate the present capability for simulating the separation steps in coprocessing.

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#### 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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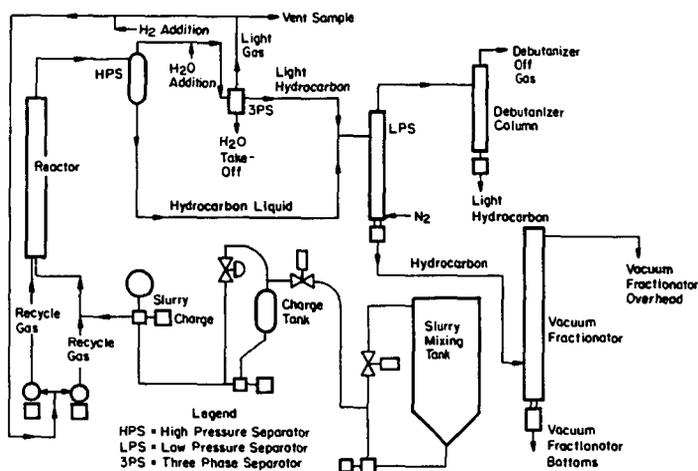


Figure 1 - UOP Coprocessing Pilot-plant Flow Diagram.

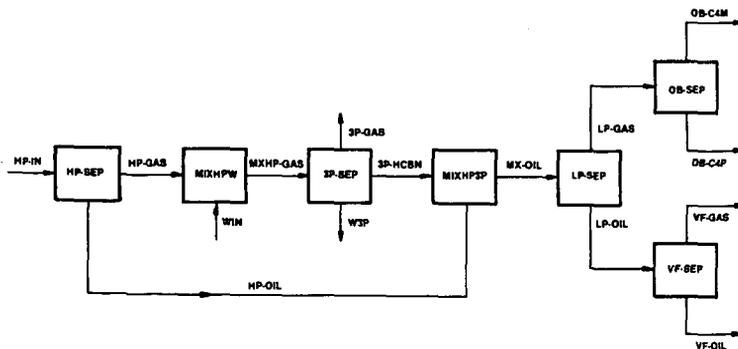


FIGURE 2. ASPEN FLOWSHEET OF SEPARATOR SYSTEM FOR UOP COPROCESSING PILOT-PLANT FLOW SCHEME.

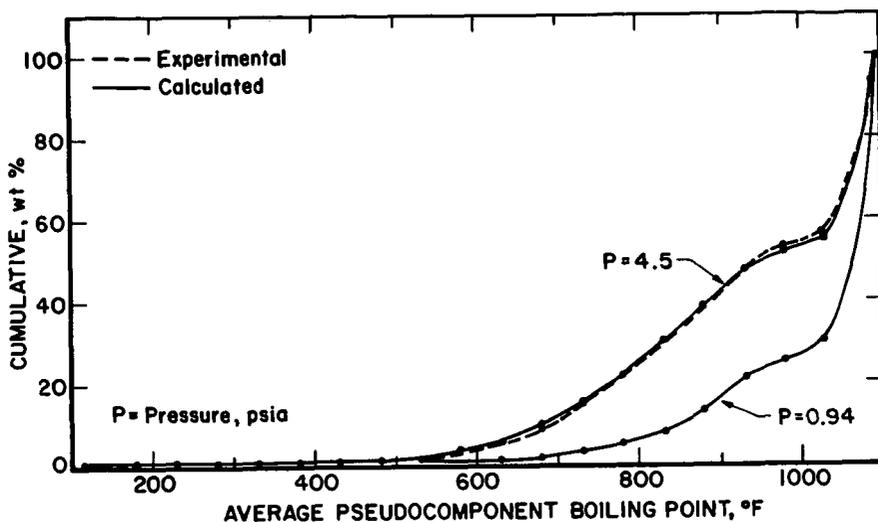


Figure 3 - Composition of Vacuum Bottoms Pseudocomponents Using Petroleum Liquids Correlations.

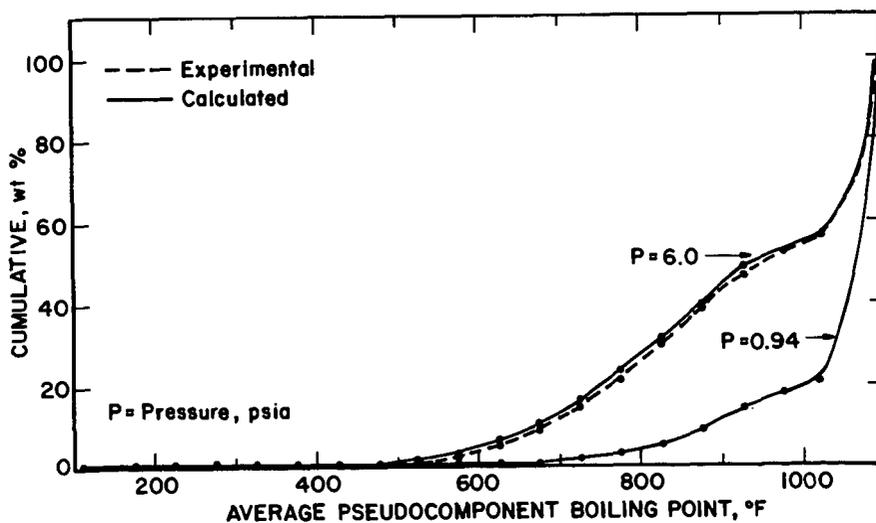


Figure 4 - Composition of Vacuum Bottoms Pseudocomponents Using Coal Liquids Correlations.

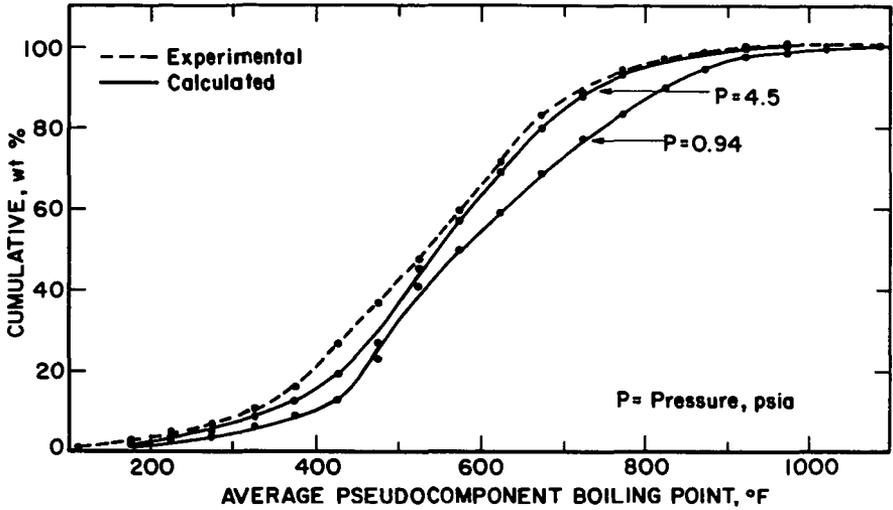


Figure 5 - Composition of Vacuum Overhead Using Petroleum Liquids Correlations.

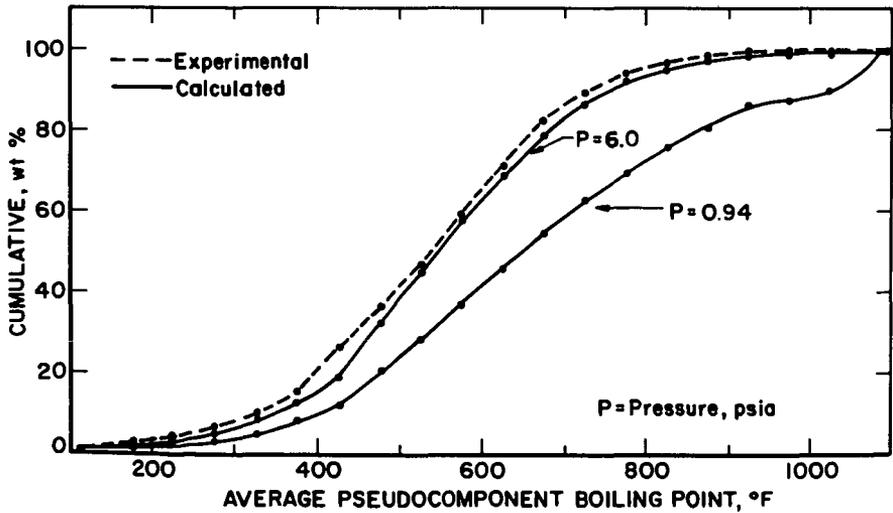


Figure 6 - Composition of Vacuum Overhead Using Coal Liquids Correlations.

## AN ASSESSMENT OF THE POTENTIAL FOR COAL/RESIDUAL OIL COPROCESSING

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### Abstract

Among the promising new techniques to produce liquid hydrocarbon fuels from coal is coal/petroleum coprocessing based upon the use of heavy oil, tar sand bitumen and petroleum residua as "solvents" for the conversion of coal. Coprocessing is the simultaneous hydrogenation of coal and heavy oil fractions in specially designed reactors with coal contents by weight ranging from as low as 1% to potentially as high as 50-60% depending upon the technology employed. The results of a study on the potential for coal/residual oil coprocessing in the United States are addressed in this paper.

### Introduction

Economics, the desire for less dependence upon the importation of foreign oil, and the depletion of lighter crudes in the United States has led the refining industry to process heavier crudes and bitumens. Upgrading and converting these heavy oils to distillate liquids using conventional petroleum thermal cracking, catalytic cracking and/or hydrocracking technologies has required the installation of costly equipment to handle the heavier oils. There exists in the literature sufficient evidence to suggest that heavy oil converts more readily in the presence of coal and that significant demetallization, desulfurization, denitrification and conversion of asphaltenes to oils also occurs. Thus the simultaneous conversion of coal and petroleum heavy oil fractions to produce distillate liquid products while upgrading the remaining heavy oil merits further investigation. This type of process, termed, coal/oil coprocessing has the potential for being an effective method for converting coal to liquids and for introducing coal liquids into the market place in a cost effective evolutionary manner while greatly reducing the capital investment associated with the historical approach for establishing a liquefaction industry. Among the additional potential benefits for the implementation and utilization of the coprocessing concept are:

- a) Provision of a link or bridge between present day refining technology and a total coal based synfuels industry.
- b) Improved economics compared to direct coal liquefaction due to smaller plant sizes, due to lower hydrogen requirements and the elimination of the use of process derived solvent recycle.
- c) Residuum demetallization, improved product yields and mix.
- d) Minimization of the production of gases and undesirable by-products; such as high sulfur coke.
- e) Continued use of the U.S. hydrocarbon fuel infrastructure.
- f) A means of extending petroleum reserves by reducing crude utilization requirements.

### Coprocessing Schemes

The coprocessing schemes under consideration are generally an extension of two-stage coal liquefaction and application of residuum hydrocracking technology. It has been recognized that a possible synergism exists between coal derived liquids and petroleum derived residua. Coprocessing improves the quality of synthetic liquid fuel products from coal by diluting them directly with petroleum-derived liquids. Coal liquids contain a much higher proportion of aromatics compared to conventional petroleum-derived liquids, and the non-aromatic portion tends to be naphthenic rather than paraffinic. Coal liquids contain significant amounts of highly-polar compounds, and asphaltenes, but a relatively low amount of sulfur containing compounds.

Further, petroleum-derived naphtha, is low in nitrogen and oxygen. Coal-derived naphtha, on the other hand, has higher nitrogen and oxygen contents, is easier to reform, and has a higher octane number. Thus, combining coal-derived liquids with petroleum-derived liquid can provide some positive impacts on the overall product quality.

Broadly speaking, the coprocessing processes can be divided into four categories:

- o Hydro-catalytic processes
- o Extractive processes
- o Thermal processes (non-catalytic)
- o Hydro-thermal processes

The first category includes HRI, Lummus, CANMET, UOP, Chevron and Kerr-McKee processes. The second category includes processing variations incorporated for solids removal and deasphalting by Kerr-McGee, UOP and Lummus. The Cherry-P-process falls into the thermal process category. The process conditions are somewhat between those visbreaking and delayed coking. The Pyrosol process falls into the last category above and utilizes a mild hydrogenation of coal and heavy oil in the first stage. The second stage processes residuum under hydrogen pressure to produce more oil.

### Refinery Integration Considerations

Since the late 1970's intensive capital investments in residuum upgrading and hydrotreating capacity have been made by the refinery industry for the conversion of heavier crude oil fractions to gasoline and distillate fuels. At the same time, the number of operating refineries in the United States has decreased from 319 to 191. As shown in Figure 1, this decrease has been accomplished primarily by the deactivation of a number of low capacity refineries operating in the hydroskimming or topping mode. The major driving force for this realignment in refining capacity has been largely due to a growing imbalance between the residuum content of available crude oil and a decrease in demand for residual fuel oil. Residual fuels such as No. 6 Fuel Oil, Bunker C, etc., are by-products of refining. As such, their production and availability are based on the demand for transportation and distillate fuels. Based upon data in the Oil and Gas Journal, residuum processing (thermal and hydrocracking) capacity as a percent of overall refining capacity has essentially increased 20% since 1980 to provide supply elasticity for the changing residual fuel demand, representing about 19% of the today's U.S. crude processing capacity. The future outlook is for this trend to continue as fuel oil is replaced by other energy forms such as coal, nuclear and natural gas. It is important to note that this processing of the heavy ends to yield prime products represents a reduction in the amount of crude oil required to meet gasoline and distillate fuel demand. Table 1 presents a profile of the Refining Industry in the U.S. While coal liquefaction research and development has demonstrated significant progress in recent years, it has not addressed the fundamental causes for the high

cost of coal liquefaction, the high recycle oil requirements. In all direct liquefaction processes coal is slurried with a process derived recycle oil at a typical ratio of 2:1 recycle oil to coal feed. Coprocessing of residuum and coal reduces the high cost associated with recycle oil by eliminating or reducing the requirements for recycle oil.

Coprocessing hydrocracking technology was originally developed for processing heavy crude with coal additives as a means of inhibiting the formation of coke. The CANMET hydrocracking process is based upon this concept. This emerging technology shows promise of high demetallization, residuum hydrocracking, and high conversion of the pitch (975°F) fraction. Coal additives include 1.0 - 2.0 wt.% of fine coal and ferrous sulfate.

Integration of the CANMET type process initially to an existing refinery and/or idle units is a first step toward utilization of coal and heavy oils (pitch and asphaltenes). A once through process arrangement without the use of a recycle stream may also be possible at lower coal concentrations.

Coprocessing technologies to be included in a staged approach are HRI, Lummus, and the Cherry-P processes which can process up to 50 wt.% of coal in heavy oil fraction.

Implementation of coprocessing will likely require additional refinery hydrogen generation. This will probably be based upon steam reforming of hydrocarbon gases and light naphtha. Steam reforming is a well established and adopted method of generating hydrogen. The expansion of reforming units can be accomplished more easily than integrating gasification units into refineries.

Hydrostabilization of product distillates are incorporated into a refinery to provide hydrotreatment and product stabilization prior to distribution outside the refinery complex. Further pretreatments for heteroatom removal may be required in a refinery utilizing coprocessing derived liquids.

The introduction of coal/residuum coprocessing will tend to reduce crude requirements. The extent of reduction will be dictated by market demands as well as product yields and qualities of the coprocessing distillate liquids. Other positive factors are 1) the use of existing refinery and infrastructure, 2) better economics than direct liquefaction, 3) compatibility with the use of heavier crudes, and 4) the capability of installing a coprocessing unit independently from existing refinery operations.

#### Potential Coal Requirements

An estimate of the potential coal requirements for coal/oil coprocessing for the general refinery types in the United States is presented in Table 2. These capacities represent an upper limit for the application of coal/residua coprocessing as fuel oil production was assumed to be zero. It was also assumed that coprocessing is more economic than vacuum distillation (both cases are highly unlikely). Based upon a 1985 production capacity of 890 million tons of coal in the U.S.; coal producing capacity would have to increase by one-third if the upper limits of coal/residua coprocessing were achieved.

The most likely near term application for coal/oil coprocessing appears to be for residuum conversion capacity additions to low conversion refineries to improve profitability and to high conversion refineries to provide the capability for handling future feedstocks with increasingly higher residuum content. This premise is based on the assumption that present trends toward a heavier crude feedstocks and lighter reduced fuel oil requirements will continue. In terms of refinery capacity, average size Hydroskimming or Topping and High Conversion Refineries

processing 25,000 and 150,000 bbl/day of heavy crude (25<sup>0</sup> API), respectively, will require approximately 850 and 4,000 tons/day of coal, respectively, when coprocessing at slurry concentrations of 50%. These coal capacities are well within existing transportation and handling experience for coal fired industrial/utility boiler applications.

#### Process Economics

While the detailed engineering required to develop definitive coprocessing economics was beyond the scope of the effort, this paper would not be complete without presenting some guidelines. For this purpose, the installation of a coprocessing plant with a residuum throughput of 10,000 bbl/day (600-700 tons/day of coal) to a refinery (Figure 2) is estimated to cost of the order of \$170MM. This cost includes coal handling and preparation, coal/residuum conversion and allowances for hydrocarbon steam reforming for hydrogen generation (~ 40% of the cost). Land and owner costs are not included in the estimate. In addition, it must be stressed that actual costs are refinery specific and will vary greatly, depending upon the adequacy and availability of refinery utility systems and the degree of integration capability.

#### Development Program Requirements

A potentially broad variety of coals and petroleum residua are candidates for coprocessing. The properties of these feedstocks will have to be investigated in bench scale experiments to define product quality. In addition, better characterization of hydrogen requirements are required to improve economies. These data are required to facilitate the design and integration of coprocessing units into existing refineries.

#### Conclusions

Although continued Research and Development are required to define product quality and yields, coprocessing of coal and residual oil shows promise. It is anticipated that initial application of coprocessing will involve the utilization of small amounts of coal (1-2 wt.%) in existing refineries. This will be followed by demonstration units (10,000-15,000 bbl/day) utilizing a staged approach, processing 30-40 wt.% coal. Commercial units should be able to process up to 50-60 wt.% coal and will be integrated into high and low conversion refineries using vacuum residua as feedstocks and that there is a potential for the installation of upwards of 100 units of 10-15,000 bbl/day capacity.

TABLE 1

OIL REFINING PROFILE (CONTINENTAL USA)

	<u>Hydroskimming</u>	<u>Low Conversion</u>	<u>High Conversion</u>	<u>Specialty Plants</u>
Number of Refineries	24	59	61	41
Capacity, K BBL/day	560	4,685	9,215	475
% Capacity	4	31	62	3
Major's Operate, %	30	25	90	Low

Source - Oil and Gas Journal

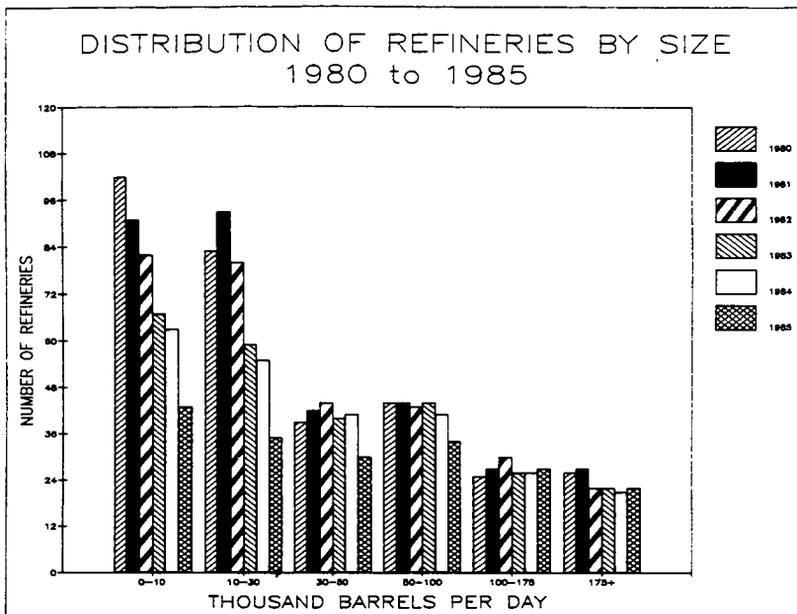
TABLE 2

IMPACT OF CONVERSION OF EXISTING REFINERY CAPACITY TO ADVANCED COPROCESSING OF FUTURE HEAVY CRUDES

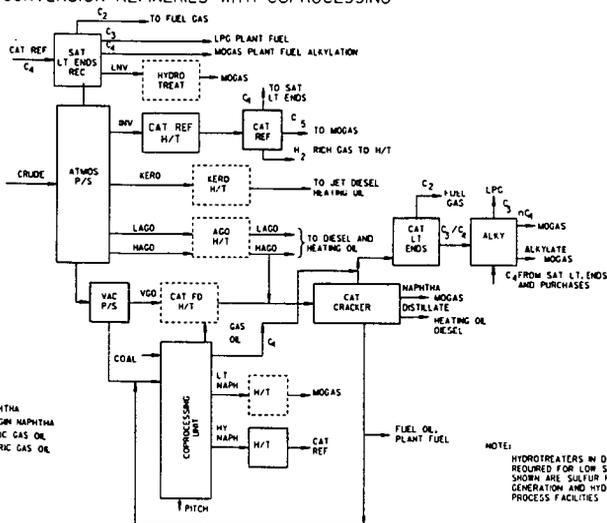
<u>Existing Refinery Type</u>	<u>Coal Consumption, MMTY</u>	
	<u>Atmospheric Residuum</u>	<u>Residuum</u>
Hydroskimming	9 - 11	3 - 6
Low Conversion	74 - 94*	30 - 50
High Conversion	146 - 185*	58 - 99*
	229 - 290	91 - 155

\* Requires Shutdown of Existing Units  
 -- Prime Application for Coprocessing

FIGURE 1



### FIGURE 2 FLOW DIAGRAM HIGH CONVERSION REFINERIES WITH COPROCESSING



## CHEMICAL AND TOXICOLOGIC CHARACTERIZATION OF CO-PROCESSING AND TWO-STAGE DIRECT COAL LIQUEFACTION MATERIALS

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### INTRODUCTION

Research and development of advanced coal liquefaction technology is being supported by the U.S. Department of Energy (DOE) as a means of utilizing domestic supplies of coal to produce petroleum-substitute fuels. As a component of this effort, the U.S. DOE has supported the chemical analyses and toxicological evaluations of coal conversion products and internal process materials to assess the potential health effects and industrial hygiene concerns associated with coal liquefaction technology.

Recent advances in coal liquefaction have included two-stage direct coal liquefaction processes and petroleum resid/coal co-processing technology. Two-stage coal liquefaction processes are generally comprised of a first-stage thermal or liquefaction reactor followed by a second-stage hydrogenation step. Petroleum resids and coal are simultaneously converted to liquefaction products in co-processing technology. The purpose of this paper is to report the preliminary results of the chemical analysis and toxicological testing of a coal liquefaction co-processing sample set, and to compare these results to those obtained from two-stage coal liquefaction materials.

### SAMPLES

Samples for comparative chemical analysis and toxicological evaluation were provided from the proprietary UOP, Inc. co-processing technology (Des Plaines, Illinois) and the integrated, non-integrated, reconfigured integrated, and close-coupled reconfigured integrated two-stage coal liquefaction processes (ITSL, NTSL, RITSLS, and CCRITSL respectively) from the Wilsonville Advanced Coal Liquefaction Research and Development Facility (Wilsonville, Alabama) operated by Catalytic, Inc. A summary is contained in Table 1 of the co-processing samples received from UOP, Inc. and the two-stage coal liquefaction materials analyzed for comparative purposes. Since the samples provided were from pilot plant or bench-scale advanced coal liquefaction origins, they may not necessarily be representative of materials produced on a commercial basis.

A description of the proprietary UOP, Inc. catalyzed, slurry, single-stage coal liquefaction co-processing technology has been given by Gatsis, *et al.* (1). ITSL and NTSL processes have been described by Later (2). For a brief overview of the RITSLS and CCRITSL, see Gough *et al.* (3).

### EXPERIMENTAL

Samples were chemically characterized by chemical class fractionation, gas chromatography, gas chromatography-mass spectrometry, and low-voltage probe-inlet mass spectrometry. Toxicological activity was measured using the standard histidine reversion microbial mutagenicity test and an initiation/promotion assay for mouse skin tumorigenesis. A brief description of these methods follow.

#### Chemical Class Fractionation

Samples were fractionated according to the method described by Later *et al.* (4) and Later and Lee (5) by sequential elution of standardized alumina (1.5% water, Later *et al.*, 6) with 20 ml hexane, 50 ml

Table 1. Samples Analyzed

PNL Number	Process	Description
51396-005	UOP	Lloydminster Petroleum Resid. Nominal boiling point (bp) >840°F, including non-distillables, no solids.
51396-004	UOP	Illinois No. 6 Coal and Lloydminster Petroleum Resid Slurry Feed. Nominal bp >840°F, including solids and non-distillables.
51396-001	UOP	Liquid Process Solvent (LPS). Nominal bp >212°F, including solids and non-distillables.
51396-003	UOP	Vacuum Fractionator Overhead Product. Nominal bp ~212-910°F.
51396-002	UOP	Vacuum Fractionator Bottoms Product. Nominal bp >910°F, including solids and non-distillables.
5226-059	ITSL	Hydrotreater (HTR) Distillation Column Bottoms. Nominal bp ~450-850°F. Run #242.
5226-022	NTSL	HTR Distillation Column Bottoms. Nominal bp ~450-850°F. Run #241.
50378-100	RITSL	HTR Heavy Distillate Product. Nominal bp >500°F, including resids and ash. Run #247.
50378-101	RITSL	HTR Heavy Distillate Product. Nominal bp >500°F, less resids and ash. Run #247.
50378-139	CCRITSL	HTR Heavy Distillate Product. Nominal bp >500°F. Run #249.

benzene, 70 ml chloroform:ethanol (99:1), and 50 ml methanol to produce aliphatic hydrocarbon (AH), polycyclic aromatic hydrocarbon (PAH), nitrogen-containing polycyclic aromatic compound (NPAC), and hydroxy-substituted PAH (hydroxy-PAH) fractions, respectively. The weight percent contribution of each fraction was determined gravimetrically after solvent removal by rotoevaporation at 40°C and drying under a stream of nitrogen.

#### Gas Chromatography

Selected fractions were analyzed by gas chromatography using a Hewlett-Packard (HP) 5880A gas chromatograph equipped with a 30-m x 0.25-mm-ID fused silica capillary column coated with 0.25- $\mu$ m film thickness DB-5 (J & W Scientific). The oven was temperature-programmed to 280°C at 4°C/min after 2 minutes isothermal at 50°C with a 5 minute isothermal period at the upper temperature limit. Splitless injection was used with hydrogen as carrier gas at 100 cm/sec linear velocity. The injection port and flame ionization detector were operated at 275 and 300°C, respectively. Fractions were analyzed at 5.0 mg/ml dilutions with 2-chloroanthracene added as an internal standard at a final concentration of 25 ng/ $\mu$ l.

#### Gas Chromatography/Mass Spectrometry (GC/MS)

GC/MS analyses were performed on an HP-5982A quadrupole mass spectrometer interfaced to an HP-5710 gas chromatograph equipped with a 15-m x 0.25-mm-ID DB-5 fused silica capillary column (J & W Scientific). Gas chromatographic conditions were similar to those described above, except the oven was temperature-programmed at 8°C/min. The MS was operated in the electron impact mode at 70 eV, and scan rates were typically 100 atomic mass units (amu)/sec.

#### Low-Voltage Probe-Inlet Mass Spectrometry (LVMS)

A VG ZAB 2-F double-focusing MS operated in the electron impact mode using ionizing electron energies of 10-12 eV was used for the LVMS analyses. Each sample (10 to 20  $\mu$ g) was loaded into a glass capillary tube, which was then inserted into the source affixed to the end of a direct insertion probe. The probe was heated in a linear fashion from ambient to 250-280°C while the MS scanned repeatedly throughout the desorption period. The MS was operated with an accelerating voltage of 6000 or 7000 V, a magnet scan rate of 2 to 3 sec/mass decade, a source temperature of 250°C, and a dynamic resolving power (as determined by the VG 2035 data system) of 1:2000. The intensities of each mass across the entire profile were summed, generating an average spectrum that was representative of the entire sample.

### Microbial Mutagenicity

Standard agar-plate mutagenicity assays were performed as described by Ames *et al.* (7) using *Salmonella typhimurium*, TA98 microbial tester strain with S9 metabolic activation. Revertant colonies per petri plate were counted using a Biotran II automated colony counter. The specific mutagenic activities of samples are expressed as revertant colonies of *S. typhimurium*, TA98 per  $\mu\text{g}$  of test material as estimated by linear regression analysis of dose-response data. The following criteria were used for selecting the best dose range for estimating a linear dose response: at least a four-point dose range; approximate doubling of response for doubled dose concentration; a correlation coefficient of 0.8 or greater; and an intercept on the response (ordinate) axis within 20% of the negative control for the day.

### Initiation/Promotion (I/P) Assay for Mouse Skin Tumorigenicity

The I/P mouse skin tumorigenicity assays were performed on selected samples as described by Mahlum (8) using female CD-1 mice (Charles River Laboratories, Portage, MI), approximately 6 to 8 weeks of age with 30 animals per test group. Each test material was diluted 1:1 with acetone or methylene chloride, and 50  $\mu\text{l}$  of the diluted material was applied to the shaved backs of the mice (approximately 25 mg dose per mouse). Two weeks after initiation, 5- $\mu\text{g}$  doses of phorbol myristate acetate (0.1 mg/ml acetone) were applied to the initiated area, twice weekly for 24 weeks. The mice were shaved as necessary throughout the study, usually weekly. Animals were observed regularly for tumor growth, and the number of tumors per animal was counted biweekly. The data are expressed as the total number of tumors per mouse normalized to groups of 30 mice.

## RESULTS AND DISCUSSION

The results of the chemical class fractionation by alumina column chromatography are given in Table 2 for the advanced coal liquefaction products and internal process materials studied. The Lloydminster petroleum resid and the slurry feed from the UOP co-processing technology had low levels of AH compared to the other materials fractionated using these methods. The UOP slurry feed also gave a lower total recovery of material from the neutral alumina than did the other materials, indicating there was a high concentration of insoluble or intractable components in the slurry feed presumably due to the presence of

Table 2. Chemical Class Fractionation Data

Sample <sup>b</sup>	Process	Fraction Weight Percent <sup>a</sup>				
		AH	PAH	NPAC	Hydroxy-PAH	Total
51396-005	UOP	12	50	36	3	101
51396-004	UOP	8	26	22	2	58
51396-001	UOP	26	26	23	10	85
51396-003	UOP	53	27	8	6	94
51396-002	UOP	19	27	30	11	87
5226-059	ITSL	63	26	5	9	103
5226-022	NTSL	45	34	7	15	101
50378-100	RITSL	58	36	4	2	100
50378-101	RITSL	57	39	4	2	102
50378-139	CCRITSL	60	43	5	4	112

<sup>a</sup>Average of two determinations

<sup>b</sup>For description, see Table 1

the coal itself. The chemical composition of the UOP vacuum fractionator overhead product (51396-003) was comparable to an average composition of the two-stage coal liquefaction products, as determined by this chemical class fractionation. The UOP bottoms product had a decreased AH composition and an increased NPAC and hydroxy-PAH content compared to the lower boiling UOP overhead product. Similar results have been noted for both single- and two-stage coal liquefaction materials, namely, that higher boiling fractions have had decreased AH content and increased heteroatom content compared to their lower boiling counterparts (9).

The PAH fractions isolated from the samples were analyzed in greater detail since this chemical fraction has historically been the most tumorigenic fraction isolated from coal liquefaction products and internal process materials when analyzed using these methods. High-resolution gas chromatograms of the PAH fractions isolated from the UOP, ITSL, and NTSL distilled products are shown in Figure 1. Many of the major components in each of these fractions are labelled with their identifications from retention time and GC/MS data. The major components identified in the UOP vacuum fractionator overheads were similar to the major components identified in both the ITSL and NTSL hydrotreater distillation column bottoms; PAH compounds were present ranging from two to four aromatic rings in size. Alkyl-substituted PAH and some hydroaromatics (particularly of  $m/z$  168 and 182, the parent and methyl-substituted dihydrofluorenes or dihydrophenalenes) were also detected in all three products. The components identified in the RITSL and CCRITSLPAH fractions were similar to those detected in the UOP, ITSL, and NTSL PAH fractions of Figure 1, except they were of a higher molecular weight range; the methylchrysene isomer was the component of highest concentration in both the RITSL and CCRITSL distilled products.

The LVMS spectra from the analyses of the PAH fractions isolated from the UOP, ITSL, and NTSL distilled products are shown in Figure 2. The UOP product PAH fraction was more complex than either of the two-stage coal liquefaction PAH fractions shown. For example, there were signals for a greater number of masses representing 40% or more of the total ion current (TIC) in the UOP product PAH fractions than there were for the ITSL and NTSL PAH fractions. There was also relatively more materials that gave rise to the series including masses 232, 246, 260, and 274 amu in the UOP distilled product PAH fractions as compared to the ITSL and NTSL distilled product PAH fractions, showing some differences in the composition of the co-processing and two-stage coal liquefaction samples.

Table 3 contains the results of microbial mutagenicity testing of the crudes and chemical class fractions isolated from some of the advanced coal liquefaction samples studied. No mutagenic activity was detected in any of the AH or PAH fractions isolated from the UOP petroleum resid/coal co-processing materials, as was also the case for the distilled two-stage coal liquefaction products. Regardless of process, the majority of the microbial mutagenicity was expressed by the isolated NPAC fractions, with

Table 3. Microbial Mutagenicity Data

Sample <sup>a</sup>	Process	Response (rev/ $\mu$ g); Chemical Class Fraction				
		Crude	AH	PAH	NPAC	Hydroxy-PAH
51396-004	UOP	0	0	0	0	<1
51396-001	UOP	6	0	0	10	4
51396-003	UOP	4	0	0	48	2
51396-002	UOP	3	0	0	6	6
5226-059	ITSL	0	0	0	3	0
5226-022	NTSL	6	0	0	65	<1
50378-100	RITSL	0	0	0	22	3
50378-101	RITSL	4	0	0	32	0

<sup>a</sup>For description, see Table 1

some mutagenic response also expressed by the hydroxy-PAH fractions (particularly in the UOP vacuum fractionator bottoms product, 51396-002). The microbial mutagenic response of the UOP vacuum fractionator overhead product more closely resembled the response of the NTSL and RITSL distilled products, showing increased mutagenic activity as compared to the ITSL distilled product.

Initiation/promotion results, given as total number of tumors per mouse  $\pm$  standard error, for the ITSL and NTSL hydrotreater distillation column bottoms were  $1.3 \pm 1.2$  and  $1.1 \pm 1.4$ , respectively.

#### ACKNOWLEDGMENTS

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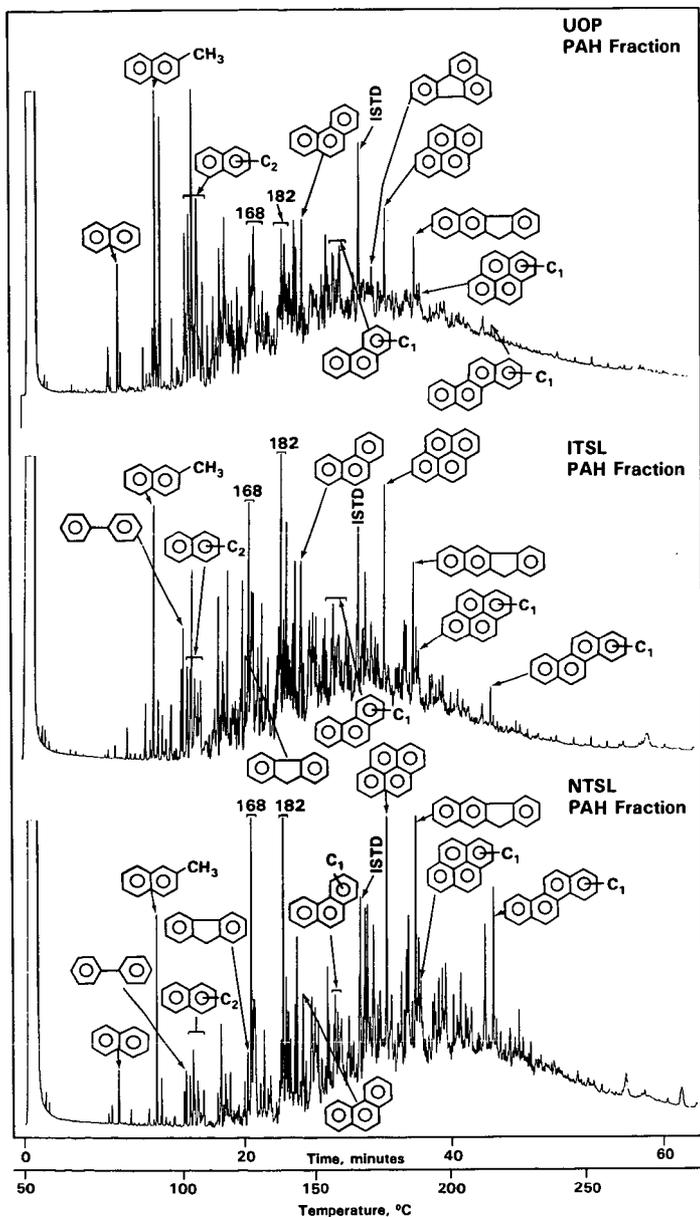


Figure 1. High Resolution Gas Chromatograms of the PAH Fractions Isolated from the UOP Vacuum Fractionator Overhead Product (top), ITSL (middle) and NTSL (bottom) Hydrotreater Distillation Column Bottoms. See Text for Conditions.

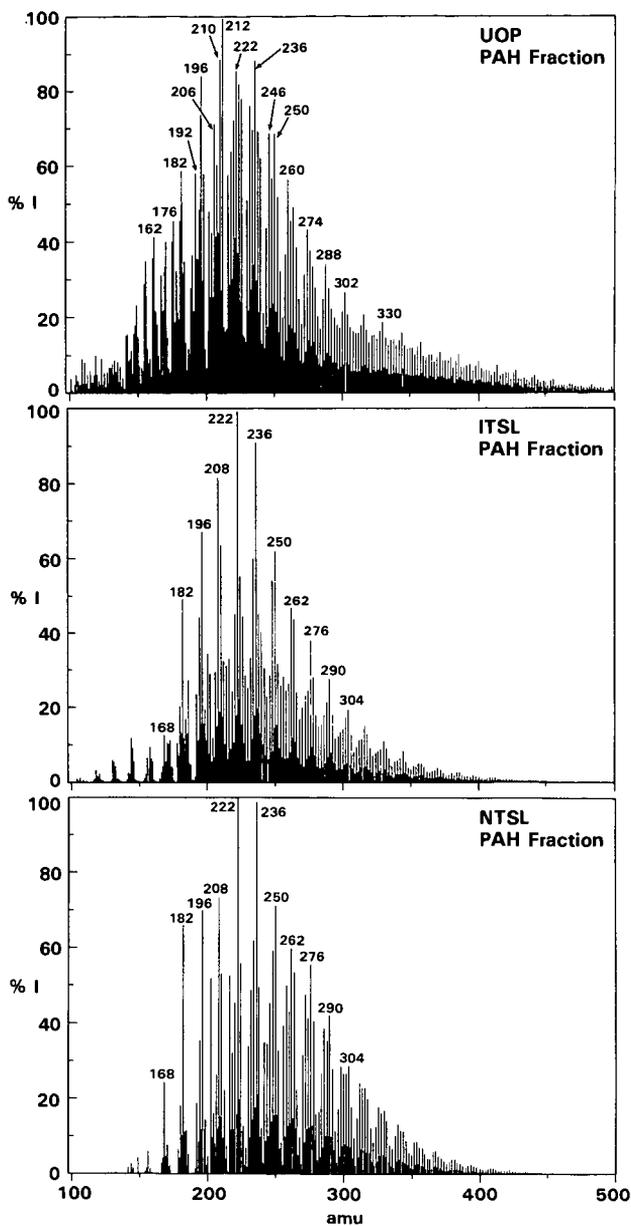


Figure 2. LVMS Spectra. See Figure 1 for Sample Descriptions. See Text for Conditions.

PROCESS DEVELOPMENT STUDIES OF  
TWO-STAGE LIQUEFACTION AT WILSONVILLE

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INTRODUCTION

The Advanced Coal Liquefaction R&D Facility at Wilsonville, Alabama, has been in operation for over 12 years. It is the largest direct coal liquefaction pilot plant still in operation in the United States. Process investigations have evolved from the original study of the Solvent Refined Coal Process for making a clean solid fuel to the recent investigation of two-stage liquefaction processes for making clean distillate fuels. This paper presents results from the current study of various processing schemes designed to reduce the cost of fuels produced by two-stage liquefaction plants.

Most important among these configurations is direct coupling of the thermal and catalytic reactors. Such close-coupled operation should lower the cost of two-stage fuels by increasing overall thermal efficiency and improving product quality. Results from Wilsonville runs are characterized by discussion of representative product yield and product quality data. Also, a comparison of performance and stability of Shell 324 and Amocat 1C catalysts is presented.

Other pertinent tests in the close-coupled mode are discussed with particular emphasis on the effect of higher system space velocity and on the impact of solids recycle.

PROCESS CONFIGURATION COMPARISON

The integrated TSL (ITSL) mode and the close-coupled (CC-ITSL) mode are shown in Figures 1 and 2, respectively. In both modes, the reaction stages are integrated by the recycle of hydrotreated resid with the goal of producing "all-distillate" yield slates. The CC-ITSL configuration differs from ITSL in that for the CC-ITSL mode, products from the thermal reactor are fed directly to the catalytic reactor without pressure letdown or significant cooling. Accordingly, vacuum-flashed product from CC-ITSL is deashed downstream of the catalytic reactor rather than upstream as in the ITSL mode. Close-coupled operation thus eliminates thermal inefficiency of the cool down/reheat cycle associated with deashing between reaction stages.

PROCESS PERFORMANCE

A wide range of thermal and catalytic stage operating conditions were investigated in the CC-ITSL mode to determine their effects on product yield structure and quality. For comparison purposes, Table 1 lists five sets of CC-ITSL conditions and yields relative to one typical set of ITSL conditions and yields. Illinois No. 6 coal from Burning Star Mine was used in all the runs.

An initial baseline run (250B) was conducted using aged Shell 324 catalyst to quantify the impact of coupling the reactors. No interstage vapor separation was utilized in Run 250B, although a high pressure separator was installed and operated during the remainder of the run. The major effect of close-coupled operation was an increase in hydrogen consumption with a corresponding improvement in distillate product quality (Table 2). Hydrogen and sulfur values were significantly better for CC-ITSL (250B) when compared to ITSL (244). This improvement resulted from the fact that all the TSL product was derived from the

catalytic stage in Run 250B, whereas in Run 244 approximately 45 wt % was produced by the catalytic hydrotreater (Table 3). Higher quality products are made by the catalytic stage.

Subsequent operation in CC-ITSL was devoted to study of performance of a new catalyst, Amocat 1C. As noted previously, interstage vapor separation was employed throughout this period. A comparison of "all-distillate" operation at the same coal feed rate for Shell 324 and Amocat 1C revealed that distillate and hydrocarbon gas yields were similar (Run 250B versus Run 250C). An alternate deashing solvent was used in Run 250C in order to maintain stable performance while processing the highly soluble feed generated by the fresh Amocat catalyst. This resulted in greater rejection of resid to ash concentrate with concomitantly less TSL resid produced. A lower hydrogen consumption was observed for Run 250C. This phenomenon could be attributed to the effect of interstage separation (i.e., not hydrotreating all distillate products) and/or to relatively lower hydrogenation activity of the Amocat catalyst.

Higher system space velocities were explored by increasing coal feed rates. The goal was to demonstrate the production of high quality (CC-ITSL) distillates at reduced cost. Yield data are reported for Run 250 Periods C, D, and E in Table 1. Product quality data and unit contributions to distillate production for Period D are given in Tables 2 and 3, respectively. The data clearly indicate that "all-distillate" yield slates were produced at increased throughputs by compensatory increases in reactor temperatures. Product quality did not change significantly at the higher rates. It should also be noted that products from higher space velocity CC-ITSL were substantially better than those from lower space velocity ITSL.

Near the conclusion of Run 250, a test of solids (unconverted coal and ash-cresol insolubles) recycle was performed (Figure 3). The objective was to decrease size of the critical solvent deashing unit by deashing a higher solids content vacuum bottoms stream. Deashed resid was recycled as a component of the liquefaction solvent. Lower organic rejection to the ash concentrate was demonstrated with the concentrated feed. Based on this result, the concept of solids recycle may be investigated in a future close-coupled run using catalyst in both reactors.

Batch deactivation trends for resid conversion in the catalytic reactor were developed for the ITSL (deashed bituminous)- Shell 324 and CC-ITSL (close-coupled bituminous)-Amocat 1C modes, using a first order resid conversion model (1). The trends are plotted in Figure 4 together with batch deactivation data from Wilsonville Run 247 ("simulated" close-coupled). The trends showed initial periods of rapid deactivation, followed by slower deactivation rates. Higher resid conversion rate constants were observed for close-coupled operation using the Amocat 1C catalyst. The close-coupled resid/Amocat combination was more reactive than the other feed/catalyst (Shell 324) combinations. Figure 5 further illustrates this point in an Arrhenius plot.

#### RELATIVE ECONOMICS

Results from an economic screening study performed by Lummus Crest Inc. indicated a reduction in the required product selling price for CC-ITSL products compared to ITSL products (Table 4). The study was based on a conceptual commercial 10,000 TPD plant using Illinois No. 6 coal. The relatively lower price was due to higher distillate production and improved distillate quality for the close-coupled case (2).

#### SUMMARY

- The major effect of close-coupled operation was an increase in hydrogen consumption with a corresponding improvement in distillate product quality.
- At the same coal feed rate, C<sub>4</sub>+ distillate and hydrocarbon gas yields were similar for close-coupled operation with Shell 324 and Amocat 1C catalysts. A lower hydrogen consumption was observed in the Amocat operation. This phenomenon could be attributed to the effect of interstage separation and/or to the relatively lower hydrogenation activity of the Amocat catalyst.
- "All-distillate" yield slates were produced at higher system space velocities by compensatory increases in reactor temperatures.
- Product quality was not significantly affected at higher system space velocities.
- Operating with solids recycle in the close-coupled mode, lower organic rejection to ash concentrate was demonstrated at a relative reduction in feed rate to the critical solvent deashing unit.
- A comparison of resid conversion rate constants indicated that the close-coupled resid/Amocat 1C combination was more reactive than other feed/catalyst (Shell 324) combinations.
- Results from an economic screening study for a conceptual commercial 10,000 TPD plant indicated a reduction in the required product selling price for CC-ITSL plant products compared to ITSL plant products.

#### ACKNOWLEDGMENTS

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Table 1

## PROCESS CONDITIONS AND YIELDS

Configuration Run No.	ITSL		CC-ITSL(1)		CC-ITSL(2)		CC-ITSL(2)		CC-ITSL(2)	
	244	250B	250C	250D	250E	250F	250G	250H	250I	250J
Catalyst Type	Shell 324	Shell 324	Amocat 1C	Amocat 1C						
<b>Thermal Stage</b>										
Reactor temperature (°F)	810	810	810	825	830	835				
Coal space velocity [lb/hr-ft <sup>3</sup> (>700°F)]	28	25	25	37	45	37				
Inlet H <sub>2</sub> partial pressure (psi)	2040	2800	2380	2380	2380	2380				
Solvent-to-coal ratio	1.8	1.8	1.8	1.8	1.8	1.9(5)				
<b>Catalytic Stage</b>										
Reactor temperature (°F)	730	730	700	740	750	760				
Space velocity (lb feed/hr-lb cat)	1.0	1.0	1.3	2.1	2.6	2.2				
Catalyst age (lb resid/lb cat)	1070	1450(3)	350(3)	750(3)	1100(3)	550(3)				
<b>TSL Yield(4) (% MAF Coal)</b>										
C <sub>1</sub> -C <sub>3</sub> Gas	6	6	5	7	6	8				
C <sub>4</sub> + Distillate	57	61	61	64	58	62				
Resid	7	6	2	-2	7	7				
Ash concentrate (ash-free)	20	18	22	18	19	15				
Hydrogen Consumption	-5.4	-6.5	-5.6	-6.1	-5.7	-6.5				

(1) Without interstage vapor separation.

(2) With interstage vapor separation.

(3) Catalyst age is (lb resid + ash + unconverted coal)/lb catalyst.

(4) Elementally balanced yield structure.

(5) Recycle solvent contains unconverted coal and ash (cresol insolubles-CI).

Table 2

## PROPERTIES OF DISTILLATE PRODUCTS

Distillation Cut	Wt % of Crude	Elemental (Wt %)				S	O (diff)
		C	H	N			
ITSL (Run 244)(1)							
Naphtha (IBP-350°F)	18.6	85.21	12.86	845 ppm	0.36	1.50	
Distillate (350-650°F)	46.1	86.34	10.73	0.23	0.22	2.48	
Gas Oil (650°F+)	35.3	89.07	9.69	0.31	0.16	0.76	
CC-ITSL (Run 2508)(2)							
Naphtha (IBP-350°F)	19.0	85.31	14.51	0.17	0.01	-	
Distillate (350-650°F)	46.8	87.43	12.12	0.21	0.06	0.18	
Gas Oil (650°F+)	34.2	88.41	10.88	0.57	0.04	0.10	
CC-ITSL (Run 2500)(3)							
Naphtha (IBP-350°F)	18.6	85.35	14.25	0.22	0.18	-	
Distillate (350-650°F)	45.0	87.45	11.73	0.32	0.09	0.41	
Gas Oil (650°F+)	36.4	88.77	10.27	0.43	0.07	0.46	

(1) Samples obtained with catalytic stage temperature of 730°F, space velocity of 1.0 lb feed/hr-lb catalyst, and catalyst age of 1400 lb resid/lb catalyst (Shell 324).

(2) Samples obtained with catalytic stage temperature of 730°F, space velocity of 1.0 lb feed/hr-lb catalyst, and catalyst age of 1450 lb (resid + ash + unconverted coal)/lb catalyst (Shell 324).

(3) Samples obtained with catalytic stage temperature of 740°F, space velocity of 2.1 lb feed/hr-lb catalyst, and catalyst age of 750 lb (resid + ash + unconverted coal)/lb catalyst (Amocat 1C).

Table 3

UNIT CONTRIBUTIONS TO DISTILLATE PRODUCTION

Configuration	ITSL	CC-ITSL(1)	CC-ITSL(2)
Run No.	244	250B	250D
Catalyst Type	Shell 324	Shell 324	Amocat 1C
<u>Unit Contributions(3)</u>			
Thermal Stage	55	0	25
Catalytic Stage	45	100	75

(1) Without interstage vapor separation.

(2) With interstage vapor separation.

(3) Wt % of total distillate production.

Table 4

ECONOMIC SCREENING STUDY(1)  
(10,000 TPD PLANT)

	ITSL (BASE)	CC-ITSL
Relative Capital Cost	1.00	1.04
Relative Operating Cost	1.00	1.01
Relative Production Rate(2)	1.00	1.10
Relative Required Product Selling Price(3)	1.00	0.93
Thermal Efficiency (%)	68.1	69.6

(1) Performed by Lummus Crest, Inc. under EPRI RP832-11.

(2) Based on barrels of crude oil equivalent with consideration for quality of distillate products.

(3) First year.

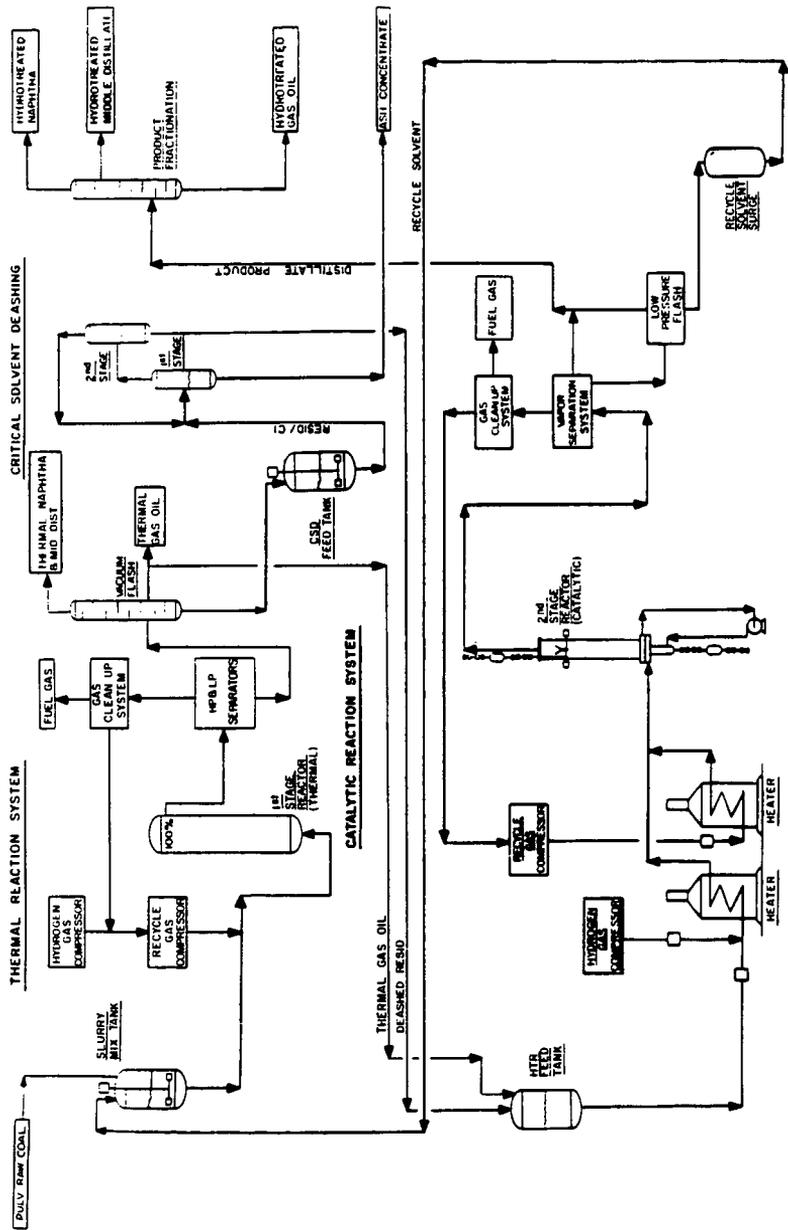


FIGURE 1: INTEGRATED TWO STAGE LIQUEFACTION SYSTEM  
INTER-STAGE DEASHING

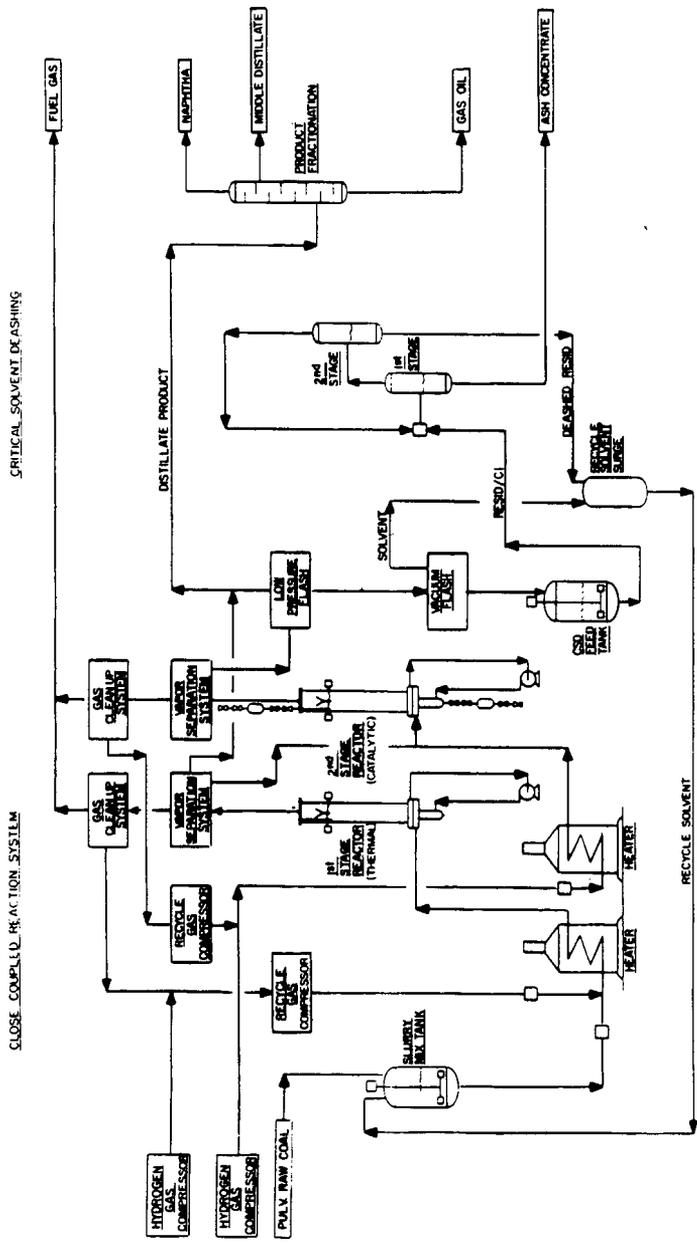


FIGURE 2: CLOSE COUPLED INTEGRATED TWO STAGE LIQUEFACTION SYSTEM THERMAL - CATALYTIC WITH INTER-STAGE VAPOR SEPARATION

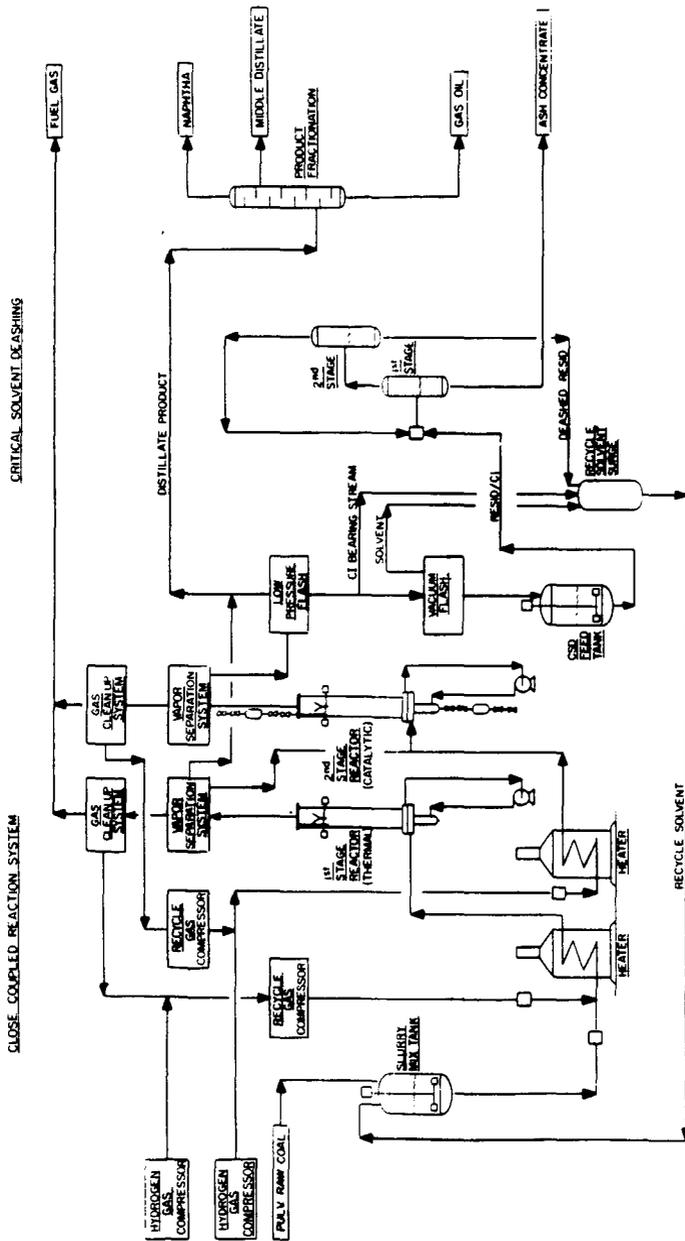


FIGURE 3. CLOSE COUPLED INTEGRATED TWO STAGE LIQUEFACTION SYSTEM  
THERMAL - CATALYTIC WITH CI RECYCLE

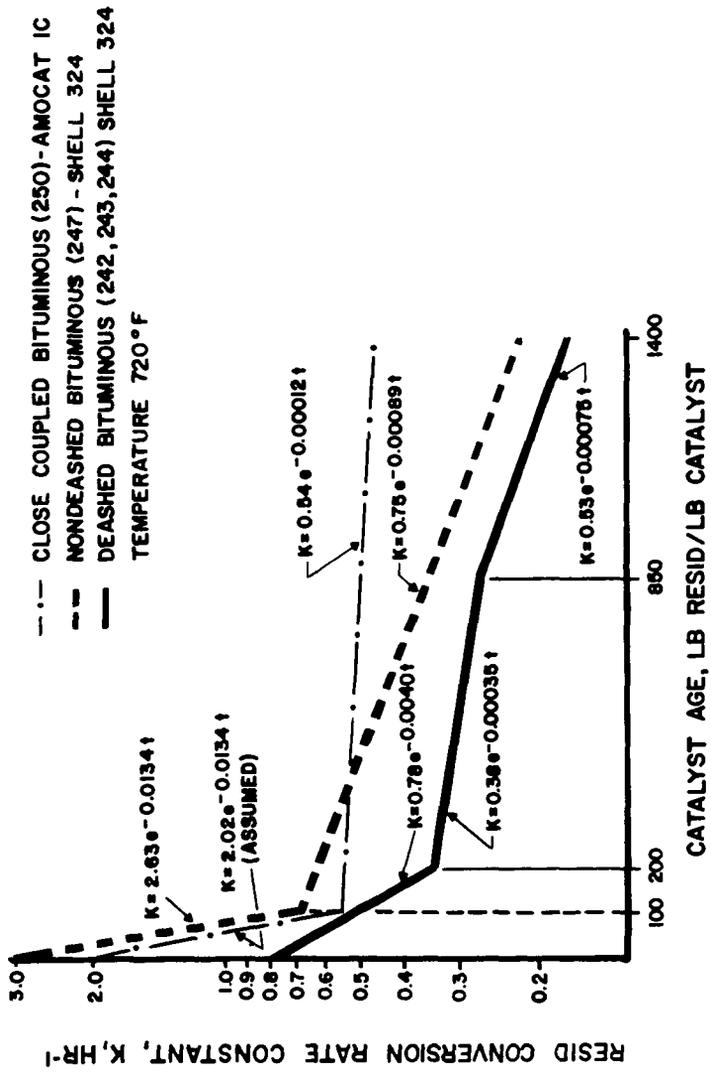


FIGURE 4. CATALYST DEACTIVATION TRENDS

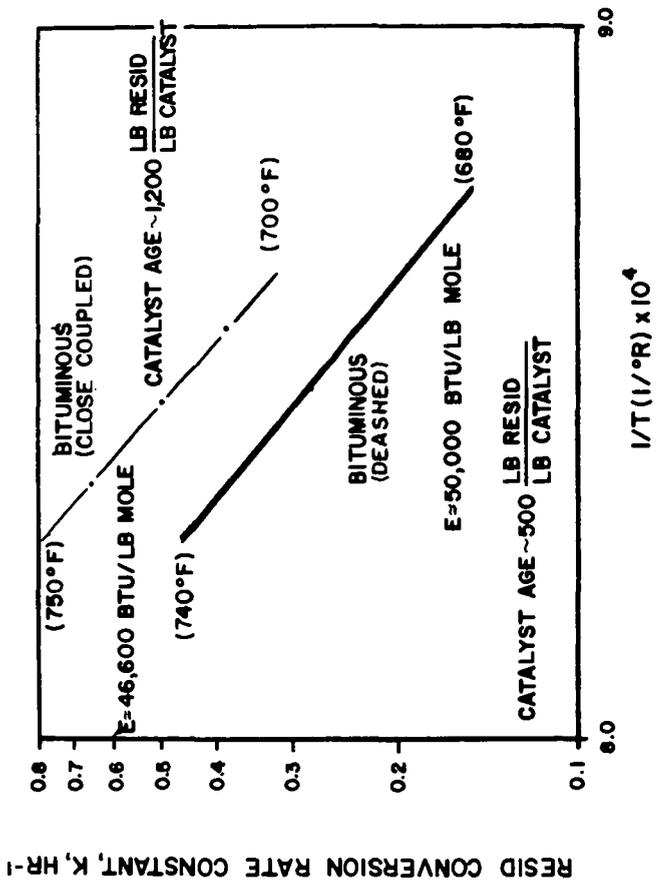


FIGURE 5. COMPARISON OF RESID CONVERSION RATE CONSTANTS

## THE IMPACT OF THE CHEMICAL CONSTITUENTS OF HYDROTREATER FEED ON CATALYST ACTIVITY\*

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### INTRODUCTION

The deposition of carbonaceous material on direct coal liquefaction catalysts is known to cause rapid and significant catalyst deactivation (1,2). Studies of hydrotreater catalyst samples from several different runs at the Wilsonville Advanced Coal Liquefaction R & D Facility have shown that greater than 75% of their hydrogenation activity and 50% of their hydrodesulfurization activity were lost within the first few days of coal processing (3). Hydrotreating light thermal resid from the third stage of the Kerr McGee critical solvent deasher yielded the least deactivation whereas hydrotreating the heavier nondeashed resid yielded the largest buildup of carbonaceous deposits and the greatest deactivation. These trends were due to differences in the compositions of the hydrotreater feeds. Previously reported work (4) has shown that carbonaceous deposits cause homogeneous poisoning of active sites and about a 50% decrease in the catalyst effective diffusivity, which is the diffusion coefficient within the extrudates.

As a result of the work on the Wilsonville catalysts, we have initiated a program to identify the hydrotreater feed components that are most detrimental to catalyst activity. Studies of the effect of hydrotreater feed boiling point cut on catalyst activity (5) have shown that processing a -550F component yields a 23% decrease in extrudate hydrogenation activity whereas hydrotreating an 850F+ component results in an 82% loss. Although hydrodesulfurization activity was not affected by the low boiling fraction, a 70% loss resulted from hydrotreating the highest boiling fraction.

In this paper we report the impacts on catalyst activity of four different chemical classes of compounds found in hydrotreater feeds. These chemical classes included the aliphatic hydrocarbons, neutral polycyclic aromatic compounds (PAC), nitrogen polycyclic aromatic compounds (N-PAC) and hydroxy polycyclic aromatic hydrocarbons (HPAH).

### EXPERIMENTAL PROCEDURES

A hydrotreater process stream obtained from the Wilsonville facility and four classes of chemical compounds separated from this stream were each catalytically hydrogenated in microreactors. The starting feeds and used catalysts from these experiments were then characterized and the catalysts were tested for hydrogenation activity.

\* This work supported by the U. S. Dept. of Energy at Sandia National Laboratories under Contract DE-AC04-76DP00789.

## Materials

The catalyst was Shell 324M with 12.4 wt% Mo and 2.8 wt% Ni on an alumina support in the form of extrudates measuring about 0.8 mm in diameter and 4 mm in length. Prior to use, the catalyst was presulfided with a 10 mol% H<sub>2</sub>S in H<sub>2</sub> mixture at 400C and atmospheric pressure for two hours. The V-178 hydrotreater process stream used in this study was obtained from the Wilsonville facility's run 247, which processed Illinois #6 bituminous coal in the Reconfigured Integrated Two-Stage Liquefaction process configuration(6). The V-178 stream, identified by the number of the storage tank from which it was derived prior to entering the hydrotreater, is the light portion of the hydrotreater feed and comprises about 35 wt% of the total feed. Distillation of the V-178 showed that the initial boiling point was 400F and 96.1 wt% boiled below 850F (5).

The V-178 process stream was separated into four chemical classes by adsorption column chromatography using neutral aluminum oxide (7). A 10 g sample was dissolved in chloroform and adsorbed onto 50 g alumina, which was then dried and placed on top of 100 g alumina in a 22 mm id column. The aliphatic hydrocarbon fraction was eluted first using hexane, then the PAC using benzene, followed by the N-PAC using chloroform and the HPAH using 10% ethanol in tetrahydrofuran. Solvent was removed from each fraction by evaporation under vacuum.

## Hydrotreating Experiments

Each chemical class and the V-178 process stream were hydrotreated with presulfided catalyst in 26 cc batch microreactors at 300C for 2 hours with a 1200 psig H<sub>2</sub> cold charge pressure. The microreactors were charged with 0.5 g feed, 0.17 g presulfided catalyst and 1.5 g hexadecane, which was added to provide adequate mixing in the reactors because of the small amounts of feed available. The aged catalysts were Soxhlet extracted with tetrahydrofuran prior to analysis or activity testing. Elemental analyses of the V-178 stream, the four fractions and the aged catalysts were performed using standard methods.

## Activity Testing

Hydrogenation activities of fresh and aged catalysts were determined by measuring the rate of hydrogenation of pyrene to dihydropyrene (4) in 26 cc microreactors at 300C with 450 psig H cold charge pressure. Experiments with catalyst ground to -200 mesh and whole extrudates enabled determination of the losses of both intrinsic and extrudate activities respectively.

## RESULTS AND DISCUSSION

### Feed and Catalyst Compositions

The compositions of the V-178 stream and the amounts and compositions of the four separated chemical classes, given in Table 1, show that the V-178 contains significant amounts of aliphatic hydrocarbons and the PAC fraction, and only low concentrations of nitrogen and hydroxy compounds. The 95% total recovery for the four chemical classes is good for this type of

separation. The high quality of the separations of the aliphatic hydrocarbons and PAC fraction is indicated by the much higher H/C ratio of the aliphatic fraction (1.70) compared to the PAC fraction (1.16) and the low concentrations of nitrogen and oxygen in these two fractions. In contrast, the N-PAC and HPAH fractions both have significant amounts of oxygen and nitrogen indicating the presence of compounds that contain both heteroatoms or possibly some overlap of the fractions.

Results of analyses of the aged catalysts, given in Table 2, show that catalytic hydrotreating of the aliphatic and PAC fractions yielded lower carbon accumulations on the catalysts than hydrotreating the V-178 or the N-PAC and HPAH fractions. Likewise, the catalysts used to hydrotreat the N-PAC and HPAH fractions have significantly higher accumulations of nitrogen than the catalysts used to hydrotreat the aliphatics and the PAC fractions. The 0.6 and 0.5 wt% accumulations resulting from our two hour experiments are comparable to the levels (0.5 to 0.6 wt%) observed on the first catalysts, with catalyst ages of about 20 lb resid/lb catalyst, withdrawn from Wilsonville runs. These results show that the nitrogen buildup on the catalyst under process conditions must be very rapid.

#### Hydrogenation Activity

The measured intrinsic activity losses ( $\alpha$ ) and the measured remaining extrudate activities (F) are given in Table 3. A quantitative mathematical expression, reported previously (8), relates F to  $\alpha$  and effective diffusivity. Use of this equation enabled us to determine the catalyst effective diffusivities. The catalysts used to hydrotreat the V-178 and the aliphatic hydrocarbon and PAC fractions showed a 20% decrease in effective diffusivity from the fresh catalyst value of  $5 \times 10^{-6}$  cm<sup>2</sup>/sec/cm<sup>3</sup>, whereas those used to hydrotreat the HPAH and N-PAC fractions had greater than a 50% decrease. Recalculating the F values without these changes in effective diffusivity (i.e. with fresh catalyst effective diffusivity) (Table 3) shows that less than 10% of the loss of fresh extrudate activity is due to the changes in effective diffusivity.

The relationship between F (corrected for changes in effective diffusivity) and  $\alpha$  also enabled us to differentiate the two limiting modes of deactivation -- homogeneous and shell-progressive poisoning. A plot of F vs  $\alpha$  for the results from the hydrogenation activity testing of the V-178 and the four chemical classes is shown in Figure 1. Since the  $\alpha$  values increase more rapidly than the F values, the dominant mode of deactivation for these catalysts is homogeneous poisoning of active sites (9). As can be seen in Figure 1, the aliphatic hydrocarbons and the PAC fraction caused less deactivation than the V-178, whereas the N-PAC and HPAH caused more deactivation. This trend in deactivation is inversely correlated with the carbon contents of the aged catalysts given in Table 2. The catalysts used to process the aliphatics and the PAC fraction have lower carbon contents than the catalyst used to hydrotreat the V-178, whereas the catalysts used to hydrotreat the N-PAC and HPAH fractions have higher carbon contents. Hydrotreating the N-PAC fraction yields the greatest deactivation with about an 87% loss of extrudate hydrogenation activity and 98% of the active sites poisoned.

## CONCLUSIONS

Separation of a light hydrotreater process stream into four chemical classes has shown that about half of the stream is composed of aliphatic hydrocarbons. There are also small amounts of N-PAC and HPAH fractions. Hydrotreating each of these four fractions and the whole process stream with catalyst has shown that all four fractions cause deactivation. The greatest deactivation is due to the N-PAC fraction, although the HPAH fraction also yields greater deactivation than the whole process stream. The deactivation is caused primarily by active site poisoning, with a lesser amount due to a decrease in effective diffusivity.

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Table 1. Compositions of the V-178 stream and the four chemical classes in weight percents.

		<u>C</u>	<u>H</u>	<u>N</u>	<u>O</u>	<u>H/C</u>
V-178		87.69	10.05	0.23	1.08	1.38
	<u>Wt % of V-178</u>					
Aliphatic hydrocarbons	46	87.27	12.36	< 0.10	0.10	1.70
Neutral polycyclic aromatic compounds (PAC)	35	90.15	8.70	0.10	0.17	1.16
Nitrogen polycyclic aromatic compounds (N-PAC)	5	83.60	7.93	3.61	2.81	1.14
Hydroxy polycyclic aromatic compounds (HPAH)	9	78.18	8.25	1.13	9.44	1.27

Table 2. Analyses of aged catalysts from microreactor runs (reported as weight percents).

<u>Catalyst</u>	<u>C</u>	<u>N</u>
V-178 run	3.87	0.3
Aliphatic hydrocarbon run	2.36	0.1
PAC run	2.71	0.1
N-PAC run	4.53	0.6
HPAH run	5.02	0.5

Table 3. Results of activity testing experiments  
(for fresh catalyst  $F = 1.00$ ,  $\alpha = 0.0$ )

<u>Reactor Feed</u>	<u>F measured</u>	<u><math>\alpha</math> measured</u>	<u>F*</u>
V-178	0.44	0.72	0.52
Aliphatic hydrocarbons	0.72	0.39	0.78
PAC	0.59	0.58	0.64
N-PAC	0.05	0.98	0.13
HPAH	0.19	0.92	0.26

\* Corrected for changes in effective diffusivity.

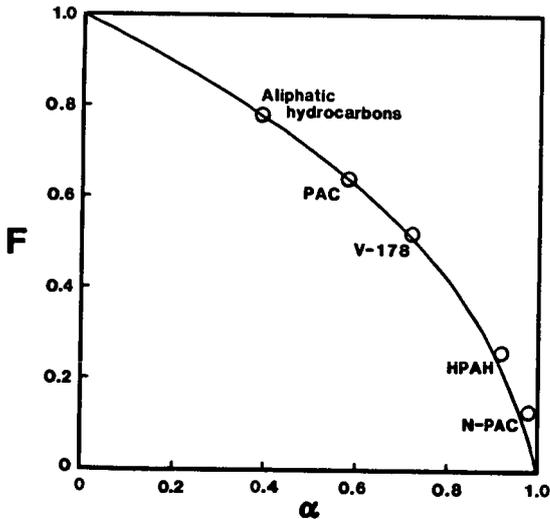


Figure 1.  $F$  vs  $\alpha$  plot for V-178 and the four chemical classes.

## IMPROVEMENT IN COAL LIQUEFACTION SOLVENT QUALITY BY DEWAXING

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### ABSTRACT

Recycle oils from the Integrated Two-Stage Liquefaction (ITSL), H-Coal and Solvent Refined Coal (SRC) processes were dewaxed by variants of commercial dewaxing processes yielding up to 47 wt % "wax". Dewaxing methods used include the ketone and the urea adduction techniques. The clean waxes are reasonably pure paraffins. The dewaxed oils were substantially better coal liquefaction solvents than the original (non-dewaxed) oils in batch liquefaction tests. For example, in one case, dewaxing improved the conversion of a standard coal to tetrahydrofuran solubles at standard reaction conditions from 71% with the original oil to 87% with the dewaxed oil. These data provide a direct indication of the inimical effect of paraffinic components on solvent quality. The impact of solvent quality is particularly relevant to two-stage liquefaction, in which thermal first-stage reactions proceed in a recycle solvent. In addition, these results indicate the technical feasibility of dewaxing coal liquefaction recycle oils by commercially available technology to improve solvent quality and to produce a useful by-product. Dewaxing could be applied to any liquefaction process that uses a deashed (preferably distillate) recycle stream.

### INTRODUCTION

Paraffinic and other saturated hydrocarbons are well known components of coal and coal liquefaction products (1). The presence of substantial quantities of saturated hydrocarbons in coal liquefaction recycle solvents has been reported (2). Increasing concentrations of these compounds (as well as of highly alkylated compounds) have been linked to a decreasing quality of the recycle oil as a donor solvent for coal liquefaction (2). Other work has demonstrated that the effectiveness of coal liquids as coal liquefaction donor solvents shows a negative correlation with the paraffinic nature of the coal liquid (3). In the development of the Consol Synthetic Fuels (CSF) (4) and Exxon Donor Solvent (EDS) (5) processes, it was recognized that the build-up of saturated hydrocarbons in the recycle solvent resulted in deteriorating solvent quality. Paraffinic and other saturated hydrocarbons are known to be non-donors (6) or at least very poor donors (7,8) at coal liquefaction conditions. Their presence in recycle oils reduces solvent quality, at least by diluting the active solvent molecules and at worst by acting as a detrimental antisolvent that leads to reduced solvent effectiveness.

Saturated hydrocarbons in coal liquefaction recycle oils are formed in part by complete hydrogenation of aromatics to form naphthenes. However, the majority of the paraffins (and particularly the n-paraffins) must ultimately arise either unchanged directly from the coal (9) or as products of the cracking of alkyl side-chains or of larger paraffins. If the recycle solvent is higher boiling than the major liquefaction products, saturates must exit the recycle loop by cracking to lighter products. Paraffins, however, tend to crack selectively to gases (5) thus consuming expensive hydrogen while producing undesirable gas.

The quality and paraffin content of the recycle solvent at equilibrium is fixed for each liquefaction process by the plant configuration, feed coal and operating conditions in use at any time. To reduce the paraffin content of the recycle solvent in order to improve its quality, operating conditions must be changed if the

feed coal and plant configuration are held constant. However, by changing operating conditions, product yield slate and/or product quality may be undesirably affected.

This paper presents a novel application of commonly used commercialized technology to improve the quality of coal liquefaction recycle solvents. That technology, in common use in the petroleum refining industry, is dewaxing. When applied to coal liquefaction recycle solvents, dewaxing improves donor solvent quality by removing predominantly the paraffins and other saturated hydrocarbons that are undesirable components. If applied commercially, a high-value by-product wax could be sold. For example, recent price ranges (10) of related products follow: paraffin wax, \$0.16-0.46/lb; petrolatum, \$0.30-0.40/lb; montan wax, \$0.58-0.65/lb; micro-crystalline wax, \$0.36-0.48 lb; and mineral oil, \$2.68-3.10/gal. These prices are considerably greater than commanded by fuels. Removal of paraffins and other saturates from the liquefaction process this way may also reduce gas production and hydrogen consumption and would reduce the occurrence of wax precipitation at low temperature from products with boiling points similar to the dewaxed stream.

Various dewaxing methods are now, or have been, in commercial use in the petroleum industry (11) including pressing and sweating, centrifugation, solvent dewaxing (e.g., the propane and ketone processes) and urea adduction methods. The bulk of the experiments reported here used a laboratory version of the ketone process, though the urea adduction process was also tested, both with promising results. Commercially, methyl ethyl ketone is typically employed in the ketone process (11); acetone was used in our experiments for convenience. These experiments demonstrate on a small scale the technical feasibility of improving coal liquefaction solvent quality by dewaxing using commercially available technology.

The impact of solvent quality is particularly relevant to processes using a thermal reactor in which coal liquefaction proceeds in and depends upon a recycle solvent such as the ITSL, SRC-I, SRC-II and EDS processes. Dewaxing should be directly applicable to processes that recycle at least one distillate-only stream such as ITSL (the reconfigured mode in use at Wilsonville), SRC-I, EDS (without bottoms recycle) and H-Coal. It should also be possible to dewax any intermediate distillate stream if the recycle does not contain a separate distillate component. One experiment demonstrated that a deasphalted residual oil could also be dewaxed.

## EXPERIMENTAL

### Ketone Dewaxing

A weighed amount (about 85 g) of the oil to be dewaxed was mixed with acetone (Fisher HPLC grade) in the desired ratio (1/2 to 1/3.3 by volume) in a beaker equipped with a magnetic stirrer. All oils tested, except the single 850°F<sup>+</sup> resid, dissolved readily at room temperature. The contents were cooled while stirring in a dry ice/acetone bath to the desired temperature to precipitate the waxes. When the desired temperature (-20 or -50°C) was reached, the mixture was immediately filtered, while still cold, in a Buchner funnel equipped with a glass-fiber filter (Reeve Angel #934AH). The filter cake (wax) was washed with additional cold acetone approximately equaling the volume of the original oil/acetone mixture. This filtrate was set aside. The wax cake was washed through the filter with freshly distilled tetrahydrofuran (THF). Each filtrate (acetone and THF) was rotary evaporated at about 60°C to constant weight to remove all traces of solvents, leaving the dewaxed oil and the waxes, respectively, which were then weighed and analyzed. The product waxes were usually a white solid though some of the less pure waxes were discolored.

One sample, a solid deasphalted 850°F<sup>+</sup> resid, was ketone dewaxed using a somewhat different method. The solid (32g) was dissolved in 120g of an 80/20 v/v solution of acetone and freshly distilled toluene, then dewaxed as above at -50°C. These

waxes (12% of oil) were very impure and so were subjected to a second dewaxing procedure similar to the first except that the solvent used was 100 mL of a 70/30 v/v mixture of acetone and toluene. This product was a very hard brown waxy solid.

#### Urea Dewaxing

One oil sample was dewaxed by the urea adduction method. About 50g of the oil was weighed and diluted with an equal weight of  $\text{CH}_2\text{Cl}_2$  (MCB reagent). To this mixture was slowly added about 50 mls of an aqueous solution of urea (Fisher certified) saturated at 80°C which crystallized upon cooling on contact with the oil/ $\text{CH}_2\text{Cl}_2$  solution. The mixture was stirred for one hour, filtered in a Buchner funnel equipped with a glass-fiber filter, then washed with several aliquots of  $\text{CH}_2\text{Cl}_2$ . This filtrate was set aside. The filter-cake was washed with warm water to dissolve the urea leaving the waxes on the filter. The water wash was discarded. The waxes were washed through the filter with freshly distilled THF. The  $\text{CH}_2\text{Cl}_2$  and THF filtrates were stripped of solvent by rotary evaporation to produce the dewaxed oil and the waxes, respectively, which were weighed and analyzed. The product wax was a white solid.

#### Solvent Quality (Microautoclave) Tests

Samples were tested for their effectiveness as coal liquefaction donor solvents using a standard microautoclave test. This test, called the modified equilibrium test, has been described in detail previously (3). Briefly, 6g of a standard coal and 9g of the sample to be tested are heated to 750°F for 30 min without added gas in a 30 mL microautoclave. The contents are cooled and extracted with THF to determine the conversion of coal to solubles. This test is an authentic coal liquefaction experiment. Solvent effects can be tested easily because there is no interfering catalyst or extraneous gas present. The results of this test serve as an empirical measure of donor solvent quality. Coal conversions obtained with several pure model compounds follow: n-tetradecane, 25.4%, 1-methylnaphthalene, 48.2%, tetralin, 85.4%. This test is reproducible to 1.2% absolute (standard deviation).

#### Other Analyses

Samples were analyzed by  $^1\text{H-NMR}$  using a procedure described in detail elsewhere (3) to determine the effectiveness of dewaxing and to determine the purity of the waxes. Briefly, the  $^1\text{H-NMR}$  spectrum is divided in regions roughly corresponding to different proton types. For example, the region between 10.0 and 4.7 ppm is assigned to aromatic protons and the region between 1.4 and 0.5 ppm is assigned to paraffinic protons. Paraffinic protons are protons on internal  $-\text{CH}_2-$  groups or  $-\text{CH}_3$  groups of paraffins and long alkyl chains. Reproducibility is 0.2% absolute (standard deviation).

Gas chromatography (GC) was performed with a Perkin-Elmer Sigma 2000 instrument equipped with dual flame ionization detectors. The column, a 30m x 0.25mm DB-5 column from J&W Scientific, was initially at 50°C for 4 min, then programmed to 280°C at 4°C/min and held for 20 min. Carrier gas was 20 psig  $\text{H}_2$ . Injector and detector temperatures were 300°C. A split injection of 0.2 $\mu\text{L}$  of sample (0.1g/mL in THF) was used. Quantitation was based on peak areas referred to an n-decane internal standard.

Elemental analyses (C, H, N and S) were performed with Leco CHN-600 and SC32 instruments. Though these instruments were designed for the analysis of coals, not oils, reliable N and S determinations can be made. C and H values are less reliable, but are probably accurate to  $\pm 1\%$  absolute.

#### Feed Oils

All samples were authentic coal liquefaction recycle oils.

- #1 ITSL subbituminous distillate - A composite of the 850°F<sup>-</sup> distillate portions of twenty daily samples taken between 5/6 and 8/6/84 of the recycle solvent (V-131B) from Wilsonville Run 246 made with Wyoming (Clovis Point mine) subbituminous coal.
- #2 ITSL subbituminous distillate - The 850°F<sup>-</sup> distillate portion of a sample of hydrotreater flashed bottoms (V-1067) taken 9/14/85 from Wilsonville Run 249 made with Wyoming (Clovis Point mine) subbituminous coal.
- #3 ITSL bituminous distillate - A composite of the 850°F<sup>-</sup> distillate portions of fourteen daily samples taken between 9/12 and 12/9/84 of the recycle solvent (V-131B) from Wilsonville Run 247 made with Illinois 6 (Burning Star mine) bituminous coal.
- #4 H-Coal subbituminous distillate - the 1000°F<sup>-</sup> distillate portion (96.1%) of a composite of seventeen daily samples taken between 9/1 and 9/17/80 of the "clean oil" (a component of the recycle solvent) from H-Coal PDU Run 10 made with Wyoming (Wyodak mine) subbituminous coal.
- #5 SRC-1 bituminous distillate - the 1000°F<sup>-</sup> distillate portion (95.6%) of a sample of recycle solvent taken 10/2/78 from Wilsonville Run 149 made with Kentucky #9 bituminous coal.
- #6 ITSL subbituminous deasphalted resid - the hexane-solubles of a composite of the 850°F<sup>+</sup> resid portions of twenty-one daily samples taken between 5/6 and 8/6/84 of the recycle solvent (V-131B) from Wilsonville Run 246 made with Wyoming (Clovis Point mine) subbituminous coal.

## DISCUSSION

Results from dewaxing experiments using authentic coal liquefaction recycle oils are discussed below. In this report, "wax" refers to the precipitated portion of the oil obtained in the procedure, "dewaxed oil" refers to the non-precipitated portion and "feed oil" refers to the original, untreated oil. It should be recognized that the ketone process as commercially practiced is performed in two stages called dewaxing and de-oiling (11). Except in one case, these experiments were done in a single stage. Therefore, it is expected that these results could be further improved.

Experimental conditions and yields are shown in Table 1. Results of microautoclave liquefaction tests are shown in Table 2. Analyses of the various oils are shown in Table 3. <sup>1</sup>H-NMR spectra and gas chromatograms of the feed oil, dewaxed oil and waxes from experiment 5 are shown in Figures 1 and 2.

### Wax Yields

Wax yields ranged from 3 to 47 wt % (Table 1). Wax purity spanned a range as well. Generally, the greatest yields of wax and the purest waxes were produced from oils derived from subbituminous coal (feed oils #1, 2 and 4). Those oils were very paraffinic, as determined by the paraffinic hydrogen content from <sup>1</sup>H-NMR and by GC (Table 3) and would be expected to produce the most wax. This is consistent with the concept that lower rank coals tend to be more paraffinic. One highly paraffinic oil produced from subbituminous coal (feed oil #2) yielded 47% of a reasonably pure wax (Tables 1 and 3).

The wax yields obtained in these experiments would not be expected to be attained at equilibrium in a liquefaction process employing dewaxing. The liquefaction processes from which these samples were taken all employed recycle and therefore, the total feed to these liquefaction processes included varying amounts of wax components. If dewaxing of all or part of the recycle were used, the wax content of the feed would be reduced thereby reducing the wax content of the product. It may be possible to dewax only that portion of the recycle solvent that is necessary

to keep wax levels below some set point. Dewaxing only a portion of the recycle solvent could reduce both capital and operating costs of the dewaxing unit.

#### Improvement in Donor Solvent Quality

In all cases, donor solvent quality, as measured by microautoclave tests, increased upon dewaxing. In general, the improvement in solvent quality upon dewaxing, as measured by the difference in the microautoclave tests with the feed oil and the corresponding dewaxed oil, increased with increasing wax yield. Thus, only 3% wax was removed in experiment 11 giving an improvement in donor solvent quality from 63 to 66%, whereas 47% wax was removed in experiment 14 giving an improvement in donor solvent quality from 71 to 87%. Clearly, the increase in donor solvent quality results from reducing the concentration of paraffins and other saturates which are non-donors and are generally considered to be poor physical solvents for coal liquids. In fact, paraffins have been found to be inimical to solvent quality in both microautoclave tests (3) and in the development of the CSF (4) and EDS (5) processes.

In direct coal liquefaction processes, the quality of the recycle oil generally is fixed by the feed coal, the operating conditions and the characteristics of the process. Making changes in operating conditions to improve the product slate or to compensate for catalyst deactivation can have the undesirable side effect of reducing solvent quality which, in turn, can affect product yields unexpectedly. Alternately, operating conditions that provide a high quality recycle solvent may not be desirable from a product yield or product quality standpoint. Dewaxing provides a means of improving recycle solvent quality that is independent of liquefaction conditions and may permit simultaneous optimization of product and recycle-solvent qualities.

It is interesting to note that the three dewaxed distillate ITSL recycle solvents all gave similar coal conversions in the microautoclave tests, even though the non-dewaxed feed oils gave significantly different results as shown below.

Run No.	Feed Oil	Coal Conversion, wt % MAF	
		Feed	Dewaxed
5	#1	80.9	88.2
13	#3	79.2	86.2
14	#2	70.8	87.1

This result would indicate that not only can donor solvent quality of recycle oils be improved by dewaxing, but that donor solvent quality can also be made more constant regardless of feed coal.

#### Effect of Temperature on Ketone Dewaxing

Experiments were performed with three feed oils at both -20 and -50°C. In each case, the lower temperature produced about twice as much wax (Table 1). The dewaxed oils produced at -50°C were better coal liquefaction donor solvents as measured by microautoclave tests (Table 2). This is consistent with the lower paraffinic content of those dewaxed oils (Table 3). However, the waxes produced at -50°C were lower purity paraffins than those produced at -20°C as evidenced by the increased aromaticities and carbon contents and decreased hydrogen and paraffinic hydrogen contents and by the GC results (Table 3). Even though the additional material removed at -50°C was largely not paraffinic, its removal further improved donor solvent quality. It is believed that the additional material removed at -50°C largely consists of highly saturated and alkylated compounds. Clearly, ketone dewaxing can be performed to maximize the improvement in solvent quality or to maximize the purity of the product wax depending on operating temperature. It should be possible to optimize both features simultaneously by selecting appropriate

temperature, time and solvent power conditions. These experiments were all operated with no hold time at temperature. Commercial petroleum dewaxing operations tailor solvent power by using solutions of varying ratios of ketone and toluene as the dewaxing solvent (11). Commercial petroleum operations also improve the selectivity of the process by operating in two stages in which the wax is separated and then de-oiled (11).

#### Ketone Dewaxing of Resid

One deasphalted 850°F<sup>+</sup> resid sample was dewaxed (experiment 12) yielding 7.9% of a very hard wax. The results of <sup>1</sup>H-NMR and elemental analyses (Table 3) indicate the wax is reasonably pure paraffin. This wax was too high boiling for complete GC analysis, but the eluted components were predominantly n-paraffins containing 24 to over 40 carbon atoms. This wax was very hard and had a freezing point upon cooling of 54°C by differential scanning calorimetry. This experiment showed that deasphalted resids can be dewaxed and may indicate that full-range coal liquefaction recycle oils can be dewaxed providing that they are solids-free and asphaltene-free. This may have applicability in ITSL and the developing Catalytic Two-Stage Liquefaction process in which the full-range recycle oil is typically solids-free and, when processing subbituminous coal, contains relatively low levels of asphaltenes (12,13).

#### Nature and Quality of Product Waxes

The product waxes were predominantly saturated hydrocarbons. This is evidenced by their very low H-aromaticities (as low as 0.3% aromatic/total hydrogen) and their elemental analyses (Table 3). Specifically, these saturated hydrocarbons were mostly paraffins as shown by the high concentration of paraffinic protons from <sup>1</sup>H-NMR analysis (as high as 91% paraffinic/total hydrogen). Even pure paraffins do not give 100% paraffinic protons in this <sup>1</sup>H-NMR analysis because of spinning side bands. For example, pure n-tetracosane gives 92.1% paraffinic protons in this analysis. n-Paraffins predominate in the gas chromatograms of the waxes (Table 3 and Figure 3), accounting for as much as 60% of the wax. The carbon preference indices (14) of the waxes were near unity, averaging 1.03 with a standard deviation of 0.04 (range = 0.92 to 1.09).

Dewaxing is most efficient for the higher molecular weight n-paraffins as seen by the GC data in Table 3. For all but one experiment, the n-paraffin of greatest concentration has the highest carbon number in the wax and the lowest carbon number in the dewaxed oil.

Enough wax was produced in experiments 13 and 14 to test the effectiveness of the wax as a donor solvent. The waxes from these experiments were also two of the least pure waxes recovered. As shown in Table 2, these waxes performed considerably more poorly than the corresponding feed oils, though not as poorly as pure n-tetracosane which gave 25.4% coal conversion in the same test. It is expected that the purer waxes would behave more similarly to the n-tetracosane.

#### ACKNOWLEDGEMENT

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TABLE 1  
EXPERIMENTAL CONDITIONS AND PRODUCT YIELDS

Experiment No.	Feed Oil I.D.	Conditions		Yields, wt %		
		T, °C	Acetone/Oil, v/v	Wax	Dewaxed Oil	Mass Balance
<u>Urea Adduction Method</u>						
2	#1	Room	(b)	5.0	88.8	93.8
<u>Ketone Method</u>						
4	#1	-20	2.0	9.1	90.7	99.8
5	#1	-50	3.3	20.6	79.3	99.9
14	#2	-50	3.0	47.4	52.0	99.4
7	#3	-20	3.0	14.5	83.2	97.7
13	#3(a)	-50	3.0	32.7	66.5	99.1
9	#4	-20	3.0	5.2	93.9	99.1
10	#4	-50	3.0	9.2	90.0	99.1
11	#5	-50	3.0	3.2	96.3	99.5
12	#6	-50	(c)	7.9	90.7	98.6

- (a) Redistilled to 1000°F immediately before experiment (98.3% distillate).  
 (b) Urea method used, see Experimental section.  
 (c) 850°F residual oil used as feed, see Experimental section.

TABLE 2  
MICROAUTOCLAVE TEST RESULTS

Experiment No.	Coal Conversion, wt % MAF		
	Feed Oil	Dewaxed Oil	Waxes
2	80.9	84.9	-
4	80.9	87.1	-
5	80.9	88.2	-
14	70.8	87.1	55.1
7	80.1	83.7	-
13	79.2	86.2	62.5
9	55.7	55.4/57.2	-
10	55.7	60.5	-
11	63.3	65.6	-

TABLE 3  
ANALYSES OF FEEDS AND PRODUCTS

Experiment No.	Fraction	Hydrogen Types by <sup>1</sup> H-NMR, %		Elemental Analysis, wt % (a)				n-Paraffins by GC		
		Aromatic	Paraffinic	C	H	N	S	Conc., wt %	Range	Max. Conc.
2	Feed	14.6	42.6	89.1	10.0	0.3	<0.1	5.7	15-33	22
	Dewaxed	17.0	34.2	88.4	9.8	0.4	<0.1	3.2	15-32	22
	Wax	2.6	82.5	80.9	13.9	0.9	<0.1	47.7	13-35	25
4	Feed	14.6	42.6	89.1	10.0	0.3	<0.1	5.7	15-33	22
	Dewaxed	19.5	32.5	88.4	9.9	0.4	<0.1	1.7	15-24	17
	Wax	2.2	88.4	84.7	14.6	0.1	<0.1	51.4	15-35	25
5	Feed	14.6	42.6	89.1	10.0	0.3	<0.1	5.7	15-33	22
	Dewaxed	19.3	28.8	89.4	9.1	0.3	<0.1	0.5	15-28	18
	Wax	2.7	71.2	87.0	12.8	0.3	<0.1	29.2	13-35	25
14	Feed	9.3	49.4	87.9	11.0	0.3	<0.1	6.2	15-34	26
	Dewaxed	15.3	33.6	89.4	10.2	0.4	<0.1	1.0	15-23	17
	Wax	4.1	62.0	87.4	12.7	0.2	<0.1	15.9	15-34	26
7	Feed	10.8	40.7	88.5	10.2	0.2	<0.1	2.3	15-31	20
	Dewaxed	12.5	38.4	88.9	10.0	0.2	<0.1	1.2	15-28	19
	Wax	4.6	57.6	87.6	11.9	0.1	<0.1	11.8	15-35	25
13	Feed	10.8	42.5	88.4	10.8	0.2	<0.1	1.9	15-31	20
	Dewaxed	14.1	35.2	89.1	10.2	0.3	<0.1	0.6	15-24	17
	Wax	5.0	55.4	88.0	12.4	0.2	<0.1	5.5	15-32	23
9	Feed	21.3	40.3	88.9	10.3	0.4	<0.1	6.2	16-31	16
	Dewaxed	22.9	35.6	88.6	10.3	0.4	<0.1	3.5	16-23	17
	Wax	0.3	91.3	84.7	15.3	0.1	<0.1	58.9	14-33	19
10	Feed	21.3	40.3	88.9	10.3	0.4	<0.1	6.2	16-31	16
	Dewaxed	24.6	32.5	88.6	9.8	0.5	<0.1	2.3	14-24	15
	Wax	1.9	90.9	84.4	15.4	0.1	<0.1	60.1	14-35	16
11	Feed	25.9	31.4	86.6	9.5	0.8	0.3	2.8	15-30	15
	Dewaxed	26.9	30.1	86.4	9.3	0.8	0.3	0.9	15-24	15
	Wax	0.8	86.7	84.6	14.5	0.1	<0.1	53.1	12-36	17
12	Feed	20.7	33.8	90.0	8.5	0.6	<0.1	-	-	-
	Dewaxed	23.8	26.4	90.2	8.0	0.4	<0.1	-	-	-
	Wax	2.8	76.9	87.0	12.7	0.4	<0.1	-	24->40	-

(a) carbon and hydrogen values probably only accurate to  $\pm 1\%$  absolute.

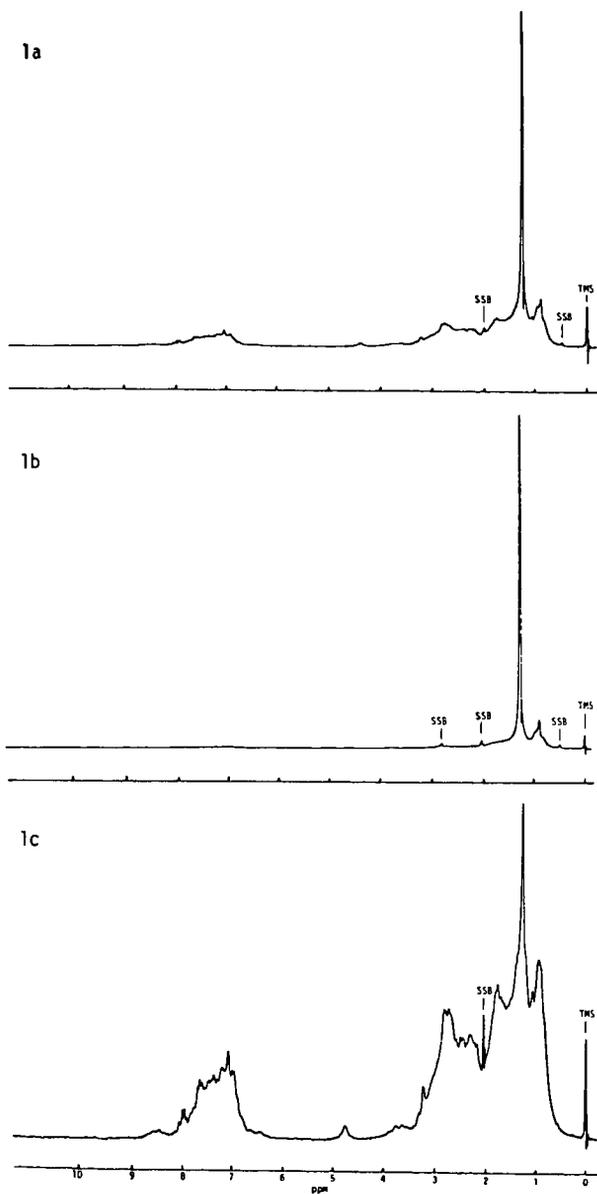


Figure 1.  $^1\text{H-NMR}$  spectra of samples from experiment 5. (a) feed oil, (b) wax, (c) dewaxed oil. TMS - tetramethylsilane internal reference, SSB - spinning side band.

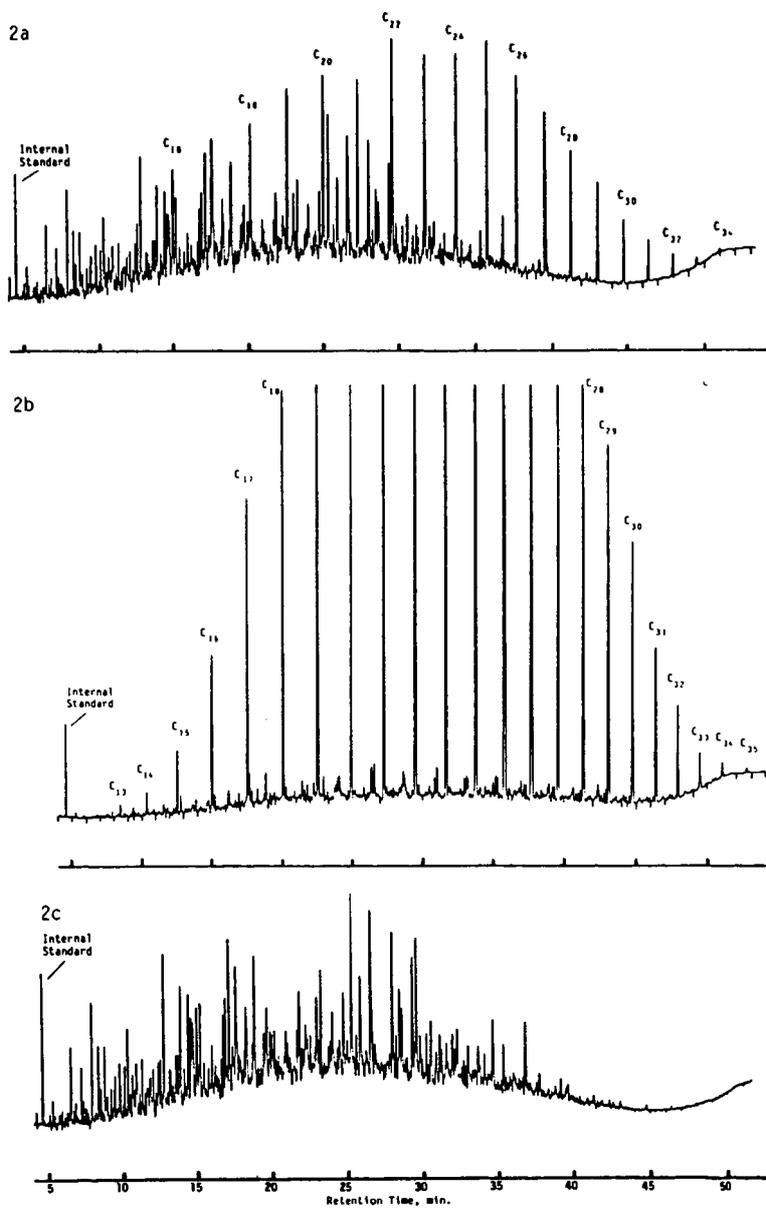


Figure 2. Gas chromatograms of samples from experiment 5. (a) feed oil, (b) wax, (c) dewaxed oil. (internal standard, n-decane)

PERFORMANCE OF THE LOW TEMPERATURE FIRST STAGE OF  
HRI'S CATALYTIC TWO-STAGE LIQUEFACTION PROCESS

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ABSTRACT

Hydrocarbon Research, Inc. (HRI), under the sponsorship of the U. S. Department of Energy (DOE), is developing a catalytic two-stage coal liquefaction process. The process consists of two direct-coupled ebullated-bed reactors in series, with the first stage operated at lower temperatures (<800°F) than typically used in direct liquefaction. Studies of both bituminous and sub-bituminous coals in a nominal 50 lb/day continuous, integrated recycle bench unit have shown considerable improvements in both distillate yield and product quality over other processes. In order to better understand the chemistry of the unique first-stage reactor conditions, a special on-line sampling system was added to the bench unit. Samples obtained over a wide range of operating conditions indicate that the first stage is an efficient hydrogenation system, achieving balanced rates of coal conversion and dissolution, solvent to coal hydrogen transfer, solvent regeneration, and liquefaction product upgrading and stabilization. Differences in responses of the two coals studied are noted and discussed.

INTRODUCTION

Hydrocarbon Research, Inc. (HRI) has long been actively involved in the development of coal liquefaction process technology. The H-Coal® Process, featuring a single-stage ebullated-bed catalytic reactor, was successfully developed and demonstrated through operation of a 200 ton per day pilot plant at Catlettsburg, Kentucky, in the early 1980's.<sup>(1)</sup> In 1981-1982, HRI conducted a series of laboratory investigations to evaluate various two-stage liquefaction concepts which featured a thermal first-stage reactor followed by a closely coupled, ebullated bed, catalytic second stage.<sup>(2-6)</sup> The results of these programs formed the basis for the current Catalytic Two-Stage Liquefaction (CTSL) concept, which features two direct-coupled, ebullated-bed reactors in series. Under DOE sponsorship, HRI has been conducting a development program for the CTSL Process since 1983. Program results have been reported<sup>(7-11)</sup> with C<sub>4</sub>-975°F distillate yields of 65 W % MAF coal achieved for both Illinois No. 6 and Wyodak coals. The process economics have been shown to be favorable in comparison with other two-stage approaches by an independent contractor's study<sup>(12)</sup> for both coals.

## PROCESS FEATURES

The salient features of the CTSL Process are listed in Table 1. The key feature which distinguishes this from other single- or two-stage processes is the operation of a low temperature (<800°F) first-stage liquefaction reactor which contains an effective hydrogenation catalyst. Here, coal is converted by dissolution in the recycle solvent at a controlled rate, allowing the catalytic hydrogenation reactions important for solvent regeneration and liquefaction product stabilization to keep pace with the rate of coal conversion. The second stage, operating at conditions more similar to the single stage H-Coal® Process (but still less severe), finishes the job of coal conversion while converting primary liquefaction products to high quality distillates. Overall, the process produces higher yields of better quality distillate products than competing technologies.

It is generally recognized that coal conversion to liquids is a thermal process (involving hydrogen transfer from donor compounds in the recycle solvent), and that the function of a catalyst in a direct liquefaction system is to hydrogenate the solvent to provide those donor compounds, as well as to upgrade the thermal liquefaction products. As a result, two-stage liquefaction concepts were developed which featured a thermal first-stage liquefaction reactor, followed by a catalytic second stage for solvent hydrogenation and product upgrading. These are represented by the Integrated Two Stage Liquefaction (ITSL) processes developed at Lummus-Crest<sup>(13)</sup> and the Wilsonville Advanced Coal Liquefaction Pilot Plant,<sup>(14)</sup> and the Direct Coupled Two-Stage Liquefaction system (DC-TSL) developed at HRI. These processes rely on production of a high quality recycle donor solvent, produced at low (<800°F) catalytic stage temperatures which favor hydrogenation over cracking. One primary drawback to this sequential approach is that solvent donor compounds are depleted in the non-catalytic liquefaction reactor, so that the final "spent" solvent quality is much poorer than the inlet recycle solvent. Also, the lack of catalytic product stabilization leads to undesirable regressive recombination reactions at the conditions necessary to achieve complete coal conversion.

The CTSL Process avoids these drawbacks by conducting liquefaction at a much slower rate in the low-temperature first stage. The first stage conditions provide a very efficient hydrogenation atmosphere so that hydrogen shuttling compounds in the solvent can be effectively regenerated and reused over and over again. Thus the solvent does not become "spent". Primary liquefaction products are also efficiently hydrogenated as they are formed, reducing the tendency for regressive reactions. By conducting conversion and hydrogenation functions simultaneously rather than sequentially, the "lifetime" of unstable thermal products is reduced. The second stage then completes the coal conversion at more typical liquefaction temperatures in the presence of a much higher relative concentration of high quality solvent. Second-stage conditions are chosen to optimize coal and residuum conversion and heteroatom removal, without approaching a thermal severity where dehydrogenation of first-stage products become significant. This paper presents data to support each of the first-stage functions listed in Table 1, which in turn provide the basis for the observed overall performance benefits of the two-stage concept.

## BENCH UNIT DESCRIPTION

Process development studies have been conducted in HRI's continuous two-stage Bench Unit 227, shown in Figure 1. It is necessary to study the process in a continuous unit with self-sustained recycle solvent generation in order to fully understand the results and avoid the pitfalls of smaller batch or once-through experimental units. The unit features two 2000cc ebullated-bed reactors in series. A special high-pressure, on-line sampling system was adapted to the first-stage reactor to obtain the data required to independently assess the effectiveness of the two reactor stages. Prior to this, it was necessary to attempt to interpret the effects of first-stage variables based on overall results only. Since the reactors are direct-coupled, and the desired sample quantities represent a significant fraction of the first-stage reactor inventory, the design and operation of the sampling system is critical to obtain representative samples while minimizing unit disruption. The data presented in this paper are based on analyses of the first-stage samples. A continuous atmospheric still was also added to the unit during this program to provide accurate control of recycle solvent cut points. The atmospheric still bottoms are subjected to further batch filtration and/or vacuum distillation operations to study various recycle oil preparation techniques. System inventories are minimized in order to provide a rapid lineout response to condition changes.

## PROGRAM HISTORY

A summary of bench unit operations conducted through February 1986 is shown in Table 2. The first year of the program was dedicated to Illinois No. 6 coal, and the second year to Wyodak sub-bituminous coal. Following renewal of the contract for two additional years in 1985, additional studies are being conducted with Illinois No. 6 coal. Each of these coals has been studied in previous single- and two-stage operations, so that an extensive data base for comparison of CTSL results exists. The implementation of the first-stage sampling system, late in the original Illinois coal program, greatly enhanced the understanding of the observed favorable performance, and first-stage sample analyses were used extensively in all subsequent work.

## FIRST-STAGE PERFORMANCE

### Coal Conversion Rate

One of the primary benefits of the lower temperature liquefaction stage is that coal is converted at a controlled rate, allowing a balance between thermal and catalytic reaction rates to be maintained. Figures 2 and 3 show the relationship between coal conversion (to quinoline solubles) and both temperature and residence time for several sets of data for both coals. In each case, the connected data points represent studies where all other parameters (second-stage conditions, solvent/coal ratio, etc.) are held constant. Comparisons of non-connected points should not be made since other parameters are different as well. Note that increasing severity by both parameters always results in an increased coal conversion, indicating kinetic rate control. It should also be noted that

overall process conversions were in all cases substantially higher, and tended to correlate with first-stage conversions. In the case of the Illinois No. 6 coal, it appears that "maximum" coal conversions (95-96%, typically) are being approached at 750-775°F, while the Wyodak coal is much slower to convert and requires additional thermal severity (90-93% conversion typically achieved in second stage).

#### Hydrogen Transfer Efficiency

Figure 4 shows the atomic hydrogen/carbon ratio of THF insoluble IOM from both first- and second-stage samples as a function of coal conversion for Wyodak coal. Surprisingly, this ratio stays quite high (at or above the original coal level) over a wide range of first-stage conversions. It would be expected that the most reactive components of the coal would be the most hydrogen-rich, and would leave behind a residue of depleted hydrogen content. This in fact does occur in higher temperature, thermal processes. However, the controlled conversion rate in CTSL allows for efficient hydrogen transfer to the coal as it reacts. A similar relationship has been noted for the Illinois No. 6 coal. Only at the more severe thermal conditions of the second stage does the hydrogen transfer appear to drop off, as evidenced by the lower H/C ratios for the high conversion samples.

No attempt has been made here to distinguish "unreacted coal" from IOM formed by regressive reaction. However, the combination of the observed kinetic response, residue analyses, and mild severity conditions indicate that regressive reaction should be minimal in the first stage. While residue analyses are interesting, they are of limited utility, particularly since the overall coal conversions achieved in CTSL are no better than in the single-stage H-Coal® Process. Of more importance are the analyses of the liquids which are formed at first-stage conditions, which are substantially different than those produced in other direct liquefaction processes.

#### Solvent Hydrogenation

Since the coal is liquefied in the presence of a catalyst at conditions which favor hydrogenation, donor species present in the solvent can be regeneratively rehydrogenated. This is illustrated for a typical condition for each coal in Table 3, which compares properties of first-stage oil and pressure filter liquid (PFL), which is both the second-stage oil and process recycle solvent. Note that even though substantial coal conversion has occurred in the first stage in each case, there is no indication of solvent quality deterioration - in fact, the solvent quality, as measured by standard microautoclave tests, has improved. This is due to simultaneous solvent hydrogenation, as indicated by the improved hydrogen content and lower aromatics level in the first-stage liquid. This is a key difference from other two-stage processes, where solvent quality is depleted in the liquefaction stage due to more severe thermal conditions and the lack of an effective hydrogenation catalyst. One positive benefit of this effect on the overall process is that the feed solvent/coal ratio can be set at a minimum pumpable level, without concern for available donor hydrogen levels. Bench unit operations on Illinois No. 6 coal have been conducted at feed slurry solvent/coal ratios as low as 1.1, and still lower ratios may well be possible on a larger scale. This has a large favorable impact on process economics.

### Recycle Residuum Hydrogenation

Residuum in the recycle solvent is upgraded by hydrogenation in the first stage, making it more reactive for cracking to lighter distillates in the second stage. This is indicated in Table 4, which shows net positive yields of residuum components in the first stage, and net conversion to distillates in the second stage. As a result, the overall 975°F+ yields are quite low, and the quality (as indicated by high oil and low preasphaltene contents) is also quite good.

### Catalytic Stabilization/Upgrading of Primary Liquefaction Products

The discussion above had highlighted the effect of first-stage conditions on recycle solvent properties. In fact, the oil properties presented are for liquids which are a blend of recycle solvent and direct first-stage products. Depending on feed solvent/coal ratio and net first-stage reactions, the first-stage oil content is estimated to be 20-50% directly produced from coal, with the remainder derived from recycle solvent. (Of course, in an integrated operation all of the material is ultimately coal-derived; here the distinction is being made to specifically include material which has not yet been exposed to second-stage conditions.) With this in mind, the level of hydrogenation is even more notable since the primary liquefaction products should be of substantially lower quality than the recycle solvent.

### COAL COMPARISON

Evidence has been presented for both Illinois No. 6 and Wyodak coals which support the process concept of first-stage hydrogenation, resulting in improved overall liquid yields and product qualities. However, the response of the two coals - and hence the optimum process conditions for each - are quite different. As has been noted in Figure 2, the sub-bituminous coal is much slower to convert, and probably requires a first-stage temperature of at least 750°F to achieve enough coal conversion for the catalytic treatment to be effective. The bituminous coal liquefies much more readily, but (as noted in Table 4) gives much higher net residuum yields. Work to date has indicated optimum performance at 750-775°F, but it is probable that this can be reduced by the appropriate combination of catalyst, space velocity, etc. This objective is being pursued in the present program. Other items being investigated include optimization of liquid yield distribution, particularly the extinction conversion of all 650°F+ products, and operation at lower second-stage temperatures to improve product quality and extend catalyst life.

### ACKNOWLEDGEMENTS

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- (6) "Two-Stage Liquefaction Study Using Illinois No. 6 Coal and Equal Volume Reactors - Run 227-7", Hydrocarbon Research Inc., FE-10152-92, September 1982. (Not Issued)
- (7) "New Technology Concept for Two-Stage Liquefaction of Coal - Illinois No. 6 Coal", Hydrocarbon Research, Inc., DE-60017-TOP-1, August 1985.
- (8) "New Technology Concept for Two-Stage Liquefaction of Coal - Wyoming (Wyodak) Coal Study", Hydrocarbon Research, Inc., DE-60017-TOP-3, February 1986.
- (9) "New Technology Concept for Two-Stage Liquefaction of Coal - Final Summary Report", Hydrocarbon Research, Inc., DE-60017-10, February 1986.
- (10) "HRI's Catalytic Two-Stage Liquefaction Process - Performance Comparison For Illinois No. 6 and Wyodak Coals", McLean, J. B., A. G. Comolli, and J. B. MacArthur. Presented at the American Chemical Society's Division of Petroleum Chemistry Symposium, September 1985.
- (11) "The Catalytic Two-Stage Liquefaction Process", McLean, J. B., A. G. Comolli, J. E. Duddy and T. O. Smith. Department of Energy's Direct Liquefaction Contractors' Conference, November 1985.
- (12) "Technical and Economic Impacts of Staged Liquefaction Configurations", Mitre Corporation, Contract No. 21-5262 (Final Report to be issued April 1986).
- (13) "Recent Developments With The Lummus-Crest Integrated Two-Stage Liquefaction Process", M. Peluso, et al. Proceedings of 9th Annual EPRI Contractors' Conference on Coal Liquefaction, May 1984.
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TABLE 1

HRI'S CATALYTIC TWO STAGE LIQUEFACTION PROCESS

FIRST STAGE

"Low" Temperature (<800°F)  
Hydrogenation Catalyst (e.g. Amocat 1C, NiMo)

Functions: Coal Conversion (controlled rate)  
Hydrogen Transfer to Reacting Coal  
Solvent Hydrogenation - Regenerative  
Recycle Residuum Hydrogenation  
Catalytic Stabilization/Upgrading of Primary Liquefaction Products

SECOND STAGE

"High" Temperature (>800°F)  
Hydroconversion Catalyst (e.g. Amocat 1A, CoMo)

Functions: Complete Coal Conversion (Thermal in an improved solvent environment)  
Residuum Conversion to Distillate Products  
Heteroatom Removal  
Avoid Dehydrogenation

OTHER PROCESS FEATURES

Reaction Stages are Direct-Coupled  
Ebullated Bed Technology Scaleable Based on H-Coal®/H-Oil® Experience  
Highest Conversion to Distillates of any Direct Liquefaction Process  
More Aliphatic/Petroleum-Like Products than other Direct Liquefaction Processes

FIGURE 1

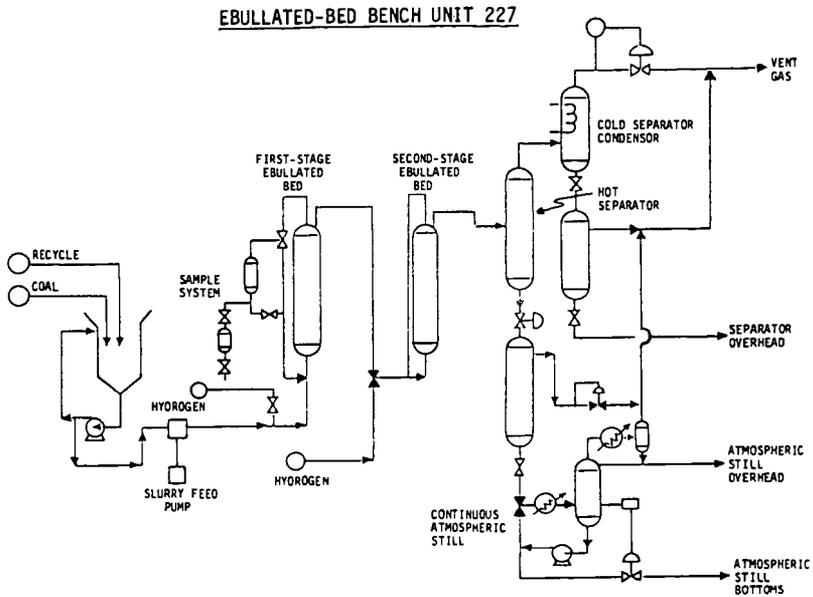


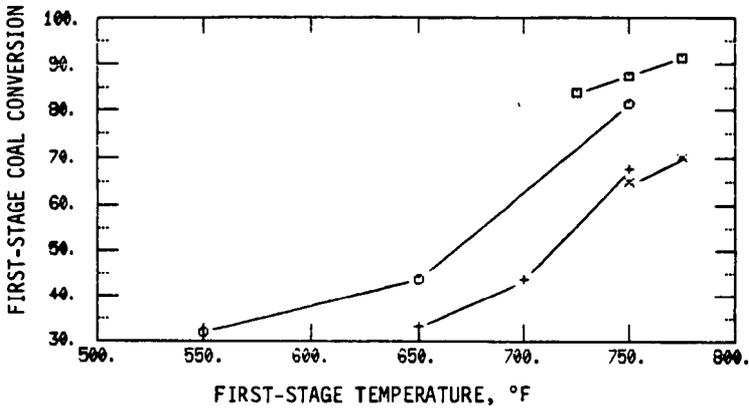
TABLE 2

**CATALYTIC TWO STAGE LIQUEFACTION PROCESS DEVELOPMENT**  
History of Bench Unit Operations (through February 1986)

	Number of		Conditions	First Stage Samples
	Runs	Days		
<u>Illinois No. 6 Coal (1983-1984)</u>				
Process Variable Studies	8	149	38	-
First Stage Sampling	1	12	4	4
Process Demonstration	1	25	1	-
Total Illinois No. 6 (1983-1984)	10	186	43	4
<u>Wyodak Sub-bituminous Coal (1983-1985)</u>				
Process Variable Studies	3	80	25	18
Process Demonstration	2	44	3	8
Total Wyodak Coal	5	124	28	26
<u>Illinois No. 6 Coal (1985-1986)</u>				
Process Variable Studies	2	57	16	15

FIGURE 2

FIRST-STAGE COAL CONVERSION (W % MAF)  
VERSUS TEMPERATURE



- o Illinois No. 6 (Run 227-18)
- Illinois No. 6 (Run 227-32)
- + Wyodak, Run 227-22 (Conditions 4, 5 and 6)
- x Wyodak, Run 227-22 (Conditions 7 and 9)

FIRST-STAGE COAL CONVERSION (W % MAF) VERSUS TIME

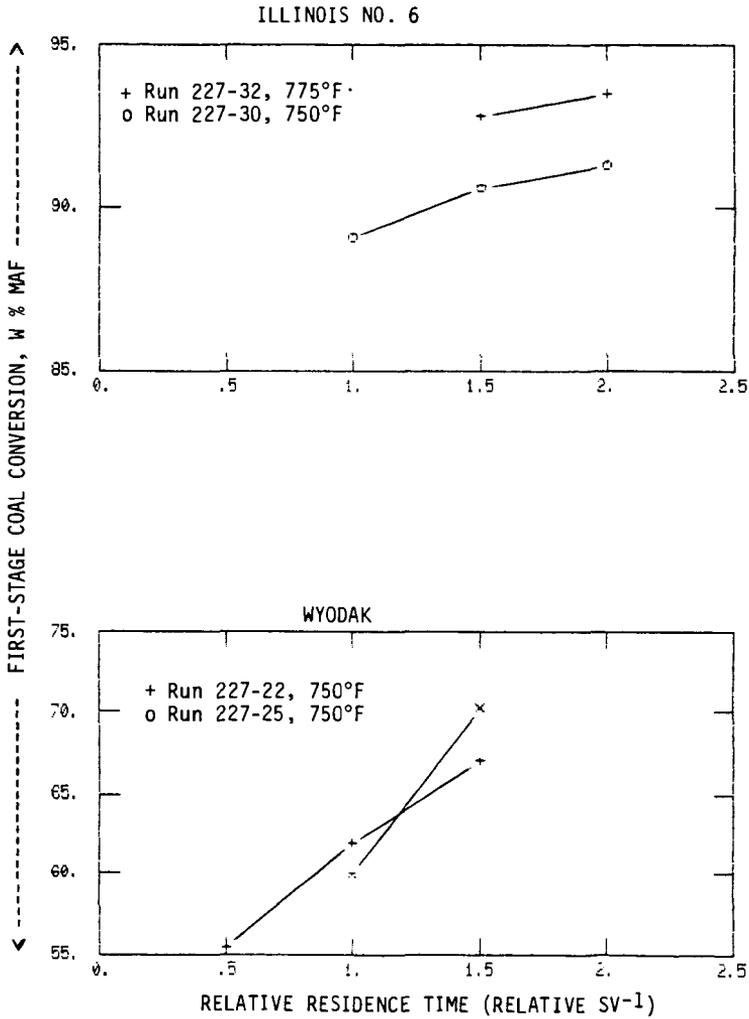




TABLE 3

COMPARISON OF FIRST-STAGE OIL AND PFL PROPERTIES

	<u>ILLINOIS NO. 6 COAL</u>		<u>WYODAK COAL</u>	
	<u>Run No. 227-18-12</u>		<u>Run No. 227-25-16</u>	
	<u>&lt;----- S T A G E S -----&gt;</u>			
	<u>FIRST</u>	<u>SECOND</u>	<u>FIRST</u>	<u>SECOND</u>
	<u>OIL</u>	<u>PFL</u>	<u>OIL</u>	<u>PFL</u>
Bench Unit Coal Conversion, W % MAF	87.1	92.7	73.6	91.6
Microautoclave Solvent Quality Test, W % THF Conversion				
HRI(1)	83.3	76.6	54.5	52.0
Conoco(2)*	82.9	79.9	64.5	64.0
H/C Ratio - 650-850°F	1.28	1.25	1.40	1.40
850-975°F	1.19	1.13	1.34	1.24
975°F+	0.95	0.91	1.06	0.98
Proton* NMR - % Aromatics				
850°F- Distillate	14.6	15.7	11.0	10.6
850°F+ Residuum	29.2	31.4	19.3	25.3

(1) HRI procedure uses matched coal and solvent.

(2) Conoco procedure uses Indiana V coal.

\* Data provided by CONOCO.

TABLE 4

975°F+ RESIDUUM PROPERTIES

	<u>ILLINOIS NO. 6</u>		<u>WYODAK</u>	
	<u>Run 227-32-9</u>		<u>Run 227-25-16</u>	
	<u>&lt;----- S T A G E S -----&gt;</u>			
	<u>First</u>	<u>Second</u>	<u>First</u>	<u>Second</u>
W % 975°F+ In Oil	39.5	32.1	12.1	9.0
<u>975°F+ Properties</u>				
H/C Ratio	1.03	0.99	1.06	0.98
% Nitrogen	0.65	0.53	0.79	0.73
% Oil	64.5	71.9	75.3	84.7
% Asphaltenes	28.6	23.5	24.1	15.0
% Preasphaltenes	6.9	4.6	0.6	0.3
Estimated Net 975°F+ Yield - W % MAF Coal				
Oils	9.6	-3.2	2.4	-0.2
Asphaltenes	9.3	-7.2	2.2	-1.8
Pre-Asphaltenes	<u>3.3</u>	<u>-2.9</u>	<u>0.1</u>	<u>-0.1</u>
TOTAL	22.2	-13.3	4.7	-2.1

## TRANSPORTATION FUELS FROM TWO-STAGE LIQUEFACTION PRODUCTS

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### INTRODUCTION

For several years, Chevron Research Company under a contract with the US Department of Energy has been studying the refining of coal liquids. Detailed results are given in a series of DOE Interim Reports (1). The earlier work emphasized upgrading of products from single-stage processes: SRC-II, H-Coal, and EDS. More recently, we have been studying products from two different two-stage processes: the Integrated Two-Stage Liquefaction (ITSL) Process and the Catalytic Two-Stage Liquefaction (CTSL) Process.

The purpose of this paper is to compare results for syncrudes from single-stage and two-stage processes, from different two-stage processes, from different coals [Illinois No. 6 (bituminous) and Wyodak (subbituminous)], and of different boiling ranges from a given coal and process.

The ITSL process, developed by Cities Service and Lummus Crest, Inc., operates with a high temperature (over 800°F) first stage with no added catalyst. The product is then deashed, and sent to a second-stage that operates at lower temperatures (typically below 800°F) with an ebullated catalyst bed (2).

The CTSL process, developed by Hydrocarbon Research, Inc. (HRI), operates with two catalytic ebullated-bed stages. In contrast to the ITSL process, the CTSL first stage operates at a lower temperature (below 800°F) than the second (which operates above 800°F) (3).

Depending upon how each liquefaction process is operated, the end point (EP) of the net whole-liquid product will vary. Typically, part or all of the vacuum gas oil (VGO) made by the process is used as recycle solvent for the coal. Some or all of it is ultimately converted to lower boiling products. Thus, the net whole-liquid product can have an EP ranging from below 650°F to over 850°F. As we will see, the ease or difficulty of upgrading is affected to a large extent by product EP. The 650-850°F VGO is relatively difficult to upgrade, but is reported to be an excellent recycle solvent. Therefore, there may be both upstream and downstream advantages to recycling this VGO, as shown for example, by MacArthur et al (4). Ultimately, of course, the costs and yields of both liquefaction and upgrading must be used to determine the optimum EP.

In this paper, we will use results for upgrading products from the H-Coal process (1, 5) as our primary basis for comparison with single-stage processes.

### FEEDSTOCKS

Key factors that determine how easy or difficult a particular syncrude is to refine are EP, boiling range, hydrogen content, and heteroatom content. Also, hot-heptane insoluble compounds (low-solubility polycyclic-aromatic and polar compounds, asphaltenes, and ash) can make syncrudes difficult to processes.

Table I shows properties of pairs of H-Coal and ITSL syncrudes derived from Illinois coal. Table II shows properties of pairs of H-Coal, CTSL, and ITSL syncrudes derived from Wyodak coal. In each case, the syncrude identified as "A" had a higher EP than that identified as "B". The A syncrudes were blended from components supplied HRI and Lummus in ratios recommended by DOE to represent, as nearly as possible, "net whole-liquid products" from these processes. [Note: the heavy fractions of Illinois ITSL A and Wyodak CTSL A, as-received, contained large quantities of hot-heptane insolubles and metals that presumably would not be part of the commercial net product. Therefore, the heavy fractions were redistilled to remove these impurities before the syncrude blends were prepared.] The B syncrudes were either fractions provided by DOE to represent product from lower-cut-point operation (Illinois ITSL B, Wyodak CTSL B), or redistilled from higher-boiling syncrudes (Illinois H-Coal B, Wyodak H-Coal B, Wyodak ITSL B). [Note that part of the front end was missing from the Wyodak ITSL oils.]

The distillation curves for the Illinois syncrudes are shown in Figure 1. The contrast between the boiling ranges of H-Coal and ITSL oils is quite striking. The H-Coal oil was quite low boiling--roughly 50% boiled below 400°F. The ITSL oil was considerably higher boiling--less than 20% boiled below 400°F, 70-75% boiled between 400 and 700°F.

Table I  
SYNCRUDES FROM ILLINOIS NO. 6 COAL

Process	<----H-Coal----->		<-----ITSL----->	
Sample Identification	A	B	A	B
LV% of As-Received Oil	100	87	95	69
<b>Inspection</b>				
Gravity, °API	25.8	28.1	13.6	17.6
Sulfur, ppm	2000	1400	865	700
Nitrogen, ppm	4600	3300	1050	730
Oxygen, ppm	18000	19600	2600	1800
Hydrogen, Wt %	11.29	11.44	10.19	10.68
Carbon, Wt %	86.25	86.13	89.35	88.99
Hot-Heptane Insolubles, ppm	3500	54	375	290
<b>TBP Distillation, °F (ASTM D2887)</b>				
St/5	56/177	56/170	97/275	97/214
10/30	213/333	200/310	375/532	314/471
50	404	380	602	560
70/90	476/588	440/508	665/745	609/676
95/99	654/765	538/589	793/859	703/763
<b>Boiling Range, LV%</b>				
St-400°F	49	57	12	18
400-700°F	48	43	69	76
700°F+	3	0	19	6

Table II  
SYNCRUDES FROM WYODAK COAL

Process	<-----H-Coal----->		<-----CTSL----->		<-----ITSL----->	
Identification	A	B	A	B	A	B
LV% of As- Received Oil	100	96	93	62	100*	52*
<b>Inspections</b>						
Gravity, °API	35.1	35.1	29.0	36.1	8.8	15.8
Sulfur, ppm	410	250	140	88	580	305
Nitrogen, ppm	1700	1500	1230	935	1670	1020
Oxygen, ppm	8500	6700	1500	1400	4600	3900
Hydrogen, Wt %	12.74	12.97	12.14	12.65	9.35	10.48
Carbon, Wt %	86.20	86.20	87.35	87.11	89.76	89.00
Hot-Heptane Insol., ppm	680	<10	216	54	180	80
<b>TBP Dist., °F (ASTM D2887)</b>						
St/5	53/156	52/165	69/184	56/179	295/353	295/340
10/30	173/261	178/269	216/375	206/312	449/587	363/538
50	354	356	478	397	653	587
70/90	429/535	424/509	566/706	470/539	710/790	623/668
95/99	602/785	542/603	771/858	571/634	840/941	689/731
<b>Boiling Range, LV%</b>						
St-400°F	60	57	34	51	**	**
400-700°F	38	43	55	49	8 (17)	13 (25)
700°F+	2	0	11	0	57 (58)	84 (73)
					35 (25)	2 (2)

\* Much of the front end (500°F-) was missing from the Wyodak ITSL oils. The missing fraction represented 24 LV% of the net liquid product for Syncrude A; 38 LV% for Syncrude B.

\*\* Numbers in parenthesis were corrected for the missing front end.

Figure 2 shows the distillation curves of the Wyodak oils. [Wyodak H-Coal B is omitted, because only 4% was removed by distillation. Therefore, its curve would lie close to that Wyodak H-Coal A, except for the EP which was much lower--603°F instead of 785°F.] Based on information supplied by Lummus, the ITSL curves were corrected to include the missing front end. As with the Illinois oils, the Wyodak H-Coal oil contained large amounts of naphtha; the Wyodak ITSL oil much more middle distillate. The CTSL oils were intermediate in boiling range and had a more even distribution than either the H-Coal or ITSL oils.

In general, the two-stage products contained fewer nitrogen- and oxygen-containing compounds than the single-stage products. [Exception: Wyodak ITSL A and Wyodak H-Coal contained about the same amounts of nitrogen.] The H-Coal oils contained considerably more hydrogen than the ITSL oils, and slightly more hydrogen than the

comparable CTSL oils. Probably, the higher hydrogen content was a result of the higher severity required for the single-stage process. In contrast, Figure 3 shows that within a given boiling range, the two-stage products had higher hydrogen contents than comparable H-Coal oils. Together, these two sets of observations may seem to present a paradox. However, the results are explained by the boiling distributions--the H-Coal oils contained more of the comparatively hydrogen-rich low-boiling components than the two-stage oils.

#### HYDROTREATING PILOT PLANT TESTS

**Discussion.** The major goals of the hydrotreating runs were either (1) to make specification jet fuel or diesel fuel and a naphtha suitable for catalytic reforming in a single hydrotreating step; or (2) to make a product suitable for hydrocracking in a second step.

To meet either goal, almost all of the heteroatom contaminants--sulfur, nitrogen, and oxygen--had to be removed by the hydrotreatment. Typically, the control target for product nitrogen content was 0.5 ppm or below. Sulfur is relatively easy to remove compared to nitrogen, and therefore was of little concern in this study. [Although sulfur is much easier to remove than nitrogen, the equilibrium concentrations of sulfur are somewhat higher than nitrogen in products hydrotreated in a single stage.] Oxygen-containing compounds can be as hard or harder to remove than nitrogen compounds. However, when the nitrogen was removed to 0.5 ppm, organic oxygen content was also removed to less than 10 ppm (based on limited analytical results). Most of the reported 50-100 ppm oxygen in the products was dissolved water.

In addition to removing the heteroatoms, it is necessary to hydrogenate most of the aromatics compounds in these fractions if finished jet fuel or diesel are to be the main products from a single hydrotreating step. One of the purposes of this work was to show the degree of aromatics saturation needed for specification diesel and jet fuel. The amount of hydrogen consumed will be determined by the hydrogen contents of the feed and products, and the amounts of heteroatoms removed.

If the hydrotreated product is to be hydrocracked, the hydrotreating severity can be somewhat less severe than if jet and diesel fuels are to be finished product. Additional hydrogen will be added in the second-stage hydrocracker.

**Catalyst Activity.** Table III briefly compares results of hydrotreating results for the syncrudes. The tests were made with a single catalyst, Chevron's commercial ICR-106 catalyst, at three different liquid hourly space velocities (LHSV): 0.5, 1.0, and 1.5 volumes of feed per volume of catalyst per hour, and a variety of hydrogen partial pressures and catalyst temperatures. The syncrudes are listed in approximate order of difficulty (easiest to hardest). All of the oils were not tested at a single set of conditions; therefore, some of the rankings were estimated using results of other tests described in our DOE reports (1). All of the first five syncrudes listed were comparatively easy to hydrotreat, and some rankings were close to one another.

Table III  
 HYDROTREATING TESTS WITH ICR 106 CATALYST  
 Syncrudes listed in increasing order of hydrotreating difficulty

LHSV	0.5	1.0	1.5	1.5	1.5	1.5
H <sub>2</sub> Pressure, psia.	2300	2300	2300	1800	1400	1000
<b>Wyodak CTSL B (EP=634°F)</b>						
Temperature, °F	680	705	715	715	715	715
H <sub>2</sub> Consumption, SCF/B	775	725	725	690	450	180
Product Nitrogen, ppm	0.5	<0.3	<0.3	<0.3	<0.3	<0.3
Product Aromatics, LV%	3	3	4	6	14	25
<b>Wyodak H-Coal A (EP=603°F)*</b>						
<b>Illinois H-Coal B (EP=589°F)</b>						
Temperature, °F		750	750			
H <sub>2</sub> Consumption, SCF/B		2000	1950			
Product Nitrogen, ppm		<0.3	<0.3			
Product Aromatics, LV%		2	5			
<b>Wyodak ITSL B (EP=731°F)</b>						
Temperature, °F	683					
H <sub>2</sub> Consumption, SCF/B	1650					
Product Nitrogen, ppm	<0.3					
Product Aromatics, LV%	14					
<b>Wyodak H-Coal A (EP=785°F)</b>						
Temperature, °F		750	750			
H <sub>2</sub> Consumption, SCF/B		1225	950			
Product Nitrogen, ppm		<0.3	<0.3			
Product Aromatics, LV%		3	13			
<b>Illinois ITSL B (EP=763°F)</b>						
Temperature, °F	710	730	745	745		
H <sub>2</sub> Consumption, SCF/B	1600	1400	950	600		
Product Nitrogen, ppm	<0.2	<0.2	0.4	6		
Product Aromatics, LV%	10	26	38	58		
<b>Illinois H-Coal A (EP=765°F)</b>						
Temperature, °F	750	750	750	750		
H <sub>2</sub> Consumption, SCF/B	2150	1600	1275	825		
Product Nitrogen, ppm	<0.3	0.3	10	50		
Product Aromatics, LV%	2	20	35	45		
<b>Wyodak CTSL A (EP=858°F)</b>						
Temperature, °F	750					
H <sub>2</sub> Consumption, SCF/B	825					
Product Nitrogen, ppm	0.3					
Product Aromatics, LV%	24					
<b>Illinois ITSL A (EP=859°F)*</b>						
<b>Wyodak ITSL A (EP=941°F)</b>						
Temperature, °F	750					
H <sub>2</sub> Consumption, SCF/B	1825					
Product Nitrogen, ppm	4					
Product Aromatics, LV%	42					

\* Rank estimated from tests at other conditions (Reference 1).

Some generalizations can be made, based on the ease of hydrotreating and feed properties:

(1) For a given boiling range, syncrudes from two-stage liquefaction are easier to upgrade than those made in one-stage--that is, lower hydrotreating severity is needed for a given product quality in upgrading. This result appears to be the effect of the lower heteroatom contents of two-stage syncrudes.

(2) For syncrudes from a given liquefaction process, relatively small increases in EP can make the syncrudes much harder to upgrade. For example, a good correlation (roughly linear) was found between required catalyst temperature and syncrude EP for a group of ITSL oils, regardless of coal source. For example, Wyodak ITSL B (EP = 634°F) could be hydrotreated at a temperature about 100°F lower than Wyodak ITSL A (EP = 941°F) for the same degree of heteroatom removal. [See Figure 4, Reference 6.]

Not surprisingly, the easiest oils to process were the three syncrudes with EPs below 650°F--Wyodak CTSL light oil (B), and the two redistilled H-Coal (B) oils. The CTSL appears to be the easiest of the three. Although it had a slightly higher EP than the others, it had the advantage of a lower heteroatom content.

Of the four oils with EPs between 700°F and 800°F, Wyodak ITSL oil B had the lowest EP and was easiest. Next is Wyodak H-Coal B. Although it had a slightly higher EP than the oils in this group, it had a much lower average boiling range. Illinois ITSL B ranked next. It was much easier than Illinois H-Coal A, which had about the same EP but a much higher heteroatom content.

Finally, of the three oils with EPs above 800°F, Wyodak CTSL oil A was clearly the easiest. Although its EP was about the same as Illinois ITSL A, it had a lower average boiling range and lower heteroatom content. Of all the oils, Wyodak ITSL A was the most difficult to process. It contained the most 700°F+ material of any of the syncrudes, and had the highest EP (941°F).

Catalyst Stability. The length of specific tests varied from several days to several months. With one exception and within the limits of the tests, ICR-106 catalyst appeared to stable for heteroatom removal during all of the tests shown in Table III. The exception: With Illinois H-Coal A, the catalyst lost about 20°F of activity during 1100-hr at 1.5 LHSV and 1800 psia hydrogen partial pressure. In contrast, Illinois ITSL B (with about the same EP as Illinois H-Coal A) was stable during a 900-hr test at the same conditions. The difference was probably due to the lower heteroatom and hot-heptane insolubles contents of the ITSL oil. [The higher EP oils were not tested at this pressure, but would be expected to cause appreciable catalyst deactivation also.]

#### YIELDS

For syncrudes with EPs below 800°F, there was relatively little cracking during hydrotreating, and the feed boiling range determined product boiling range (except for some EP reduction due to hydrogenation). As an example, Table IV contrasts yields of products from Illinois H-Coal A and Illinois ITSL B, two oils that have about the same EP but widely different boiling ranges.

Table IV  
HYDROTREATING TO 0.2 PPM NITROGEN (0.5 LHSV, 2300 psia H<sub>2</sub>)

Syncrude	H-Coal	ITSL
Catalyst Temperature, °F	750	710
Yields, Based on Fresh Feed		
C1-C4, Wt %	0.3	0.2
C5-250°F, LV %	20.4	7.0
250-350°F, LV%	26.3	6.8
350-550°F, LV%	57.7	53.6
550°F+, LV%	6.4	40.6
Total C5+, LV%	111	108
Chemical H <sub>2</sub> Consumption, SCF/B	2150	1600
Product Aromatics, LV%	2	12

For higher EP syncrudes, higher hydrotreating severities were required and more cracking occurred. Still, C1-C4 yields were low (2 LV% or below), indicating efficient use of the hydrogen.

#### PRODUCT PROPERTIES

General Comments. After hydrotreating, products of similar boiling ranges from the different liquefaction processes and different coals were quite similar. After removal of heteroatom-containing compounds, the products mainly consisted of cyclic hydrocarbons. The severity of hydrotreating determined the amount of hydrogenation of aromatics to naphthenes. There were, however, some differences. Products from subbituminous coals contained more paraffins than those from bituminous coals.

Naphtha. Hydrotreated and hydrocracked naphthas from coal liquids are excellent feeds for catalytic reformers because of the high content of cyclic compounds. Paraffin contents of all the hydrotreated naphthas were low, although the Wyodak naphthas contained somewhat more paraffins than those from Illinois coal as shown by Table V.

Table V  
PARAFFIN CONTENTS OF TYPICAL 150-350°F HYDROTREATED NAPHTHAS

<u>Feed Source</u>	<u>Paraffins, LV%</u>
Wyodak H-Coal	23
Wyodak ITSL	23
Wyodak CTSL	18
Illinois H-Coal	11
Illinois ITSL	7

At the higher hydrotreating severities, the cyclics in the naphthas were almost all hydrogenated. The naphthenes, however, could be dehydrogenated to high-octane aromatics by catalytic reforming at relatively mild conditions compared to those required for typical petroleum naphthas. Or, when reformed at higher severities, these naphthas would make extremely high octane products for gasoline blending or for chemicals production (benzene, toluene, and xylene). In the reforming process, much of the hydrogen consumed during hydrotreating would be recovered. [We have not performed catalytic reforming studies on naphthas from the two-stage processes, but

results would be expected to be similar to those previously reported for naphthas from single stage processes (7).]

**Jet.** To make jet fuel meeting the ASTM smoke point specification of 20 mm (minimum), most of the aromatics in the coal liquids had to be hydrogenated.

Figure 4 is a plot of smoke point versus aromatic content of kerosene jet fuels from the various syncrudes. The results fall into two rough groups, those from Wyodak coal and those from Illinois coal. At a given aromatics content, those from Wyodak coal had smoke points 2-3 mm higher than those from Illinois coal, a consequence of the higher Wyodak paraffin content. [The Wyodak jet contained about 10 LV% paraffins; the Illinois jet, 1-3 LV%.] The Illinois jet fuels met the jet smoke specification of 20 mm at 10% aromatics or lower; the Wyodak jet fuels met the specification at about 16 LV% aromatics. [Some of the scatter in results for products from a given coal was due to different boiling distributions. Those jet fuels containing more low boiling material had somewhat higher smoke points.]

Jet fuels from coal offer some unique advantages over those from petroleum. Because they contain high concentrations of naphthenes, they are very dense and have high heating values by volume. Therefore, they could have specialized uses, such as for military fuels. For example, Figure 5 shows the densities of narrow boiling fractions of hydrotreated ITSL oil. Jet fuel of a desired density could be made by adjusting the boiling range. The ASTM specification for jet fuel gravity is 37°API (minimum). However, this specification is probably unnecessary for aircraft with modern flow controllers, and lower gravity (higher density) fuels could be acceptable. Also, these jet fuels have unusually low freezing points, because of low normal paraffin contents.

**Diesel.** Diesel products from both single-stage and two-stage processes met typical ASTM specifications. A relatively high degree of hydrogenation was needed to meet the cetane-number specification of 40 (minimum).

Figure 6 shows the relationship for cetane number versus aromatics content for products from single-stage and two-stage processes. With the two-stage oils, the specification was met with an aromatics content of about 20 LV%; with single-stage oils, an aromatic content of less than 10 LV% was needed. These differences, however, were not necessarily the result of single-stage versus two-stage processing. Rather, they appear to be due to changes in boiling ranges of the diesels. For example, Table VI compares pairs of samples of different boiling ranges. The aromatics and paraffin contents within a given pair were about the same. Within each pair, the higher boiling sample had the higher cetane number. Also, in other comparisons (1), the more paraffinic diesels had higher cetane numbers, when other properties were about equal.

As with the jet fuels described above, these coal-derived diesel fuels had excellent cold weather properties, and high volumetric energy contents.

Table VI  
EFFECT OF BOILING RANGE ON CETANE NUMBER

Source	Initial, °F (TBP)	Midpoint, °F (TBP)	Cetane No.	Aromatics, LV, %	Paraffins, LV%
Wyodak CTSL	250	414	44.2	3.9	9.5
	350	454	48.7	4.6	7.7
Illinois ITSL	250	520	43.1	9.8	<1
	350	538	45.3	11.7	<1
Illinois H-Coal	250	393	35.9	15.6	3.6
	350	438	37.7	18.5	3.7

#### HYDROCRACKING RUNS

If the feed EP is below 775°F and if diesel fuel is a desired product, further cracking conversion of hydrotreated coal syncrude will probably not be necessary. The EP will be lowered somewhat due to hydrogenation, and little or no hydrotreated product will boil above the diesel range. However, if the feed EP is higher than 775°F or the desired products are either all-gasoline or a combination of gasoline and jet fuel, further conversion may be necessary. In a other papers (8, 9), we discussed in detail the hydrocracking of hydrotreated H-Coal and ITSL oils. Hydrocracking is a flexible process that can be varied to make only naphtha or a combination of gasoline and middle distillate. The products from hydrocracking coal oils are similar to those obtained from hydrotreating; the quantities of each can be varied, depending upon demand.

The liquid yields from hydrocracking were greater from ITSL syncrudes than those from H-Coal or CTSL syncrudes. This is because of the larger fraction of high boiling material in the ITSL syncrude, the lower hydrogen content, and--as a result--the greater volume expansion during hydrocracking. For example, the yield of C5+ naphtha was 115 LV% (based on fresh feed to the first-stage hydrotreater) when Illinois ITSL B was hydrocracked at 350°F recycle cut point, compared to 108 LV% from Illinois H-Coal A. Thus, 7 LV% more liquid was made from a given volume of ITSL syncrude than from H-Coal syncrude.

#### TWO-STAGE HYDROTREATING OF HIGH EP SYNCRUDES

Specification jet and diesel fuels were made from all of the syncrudes with EPs below 775°F in a single-step by hydrotreating at relatively severe conditions. However, with the three high EP feeds listed at the bottom of Table III, the jet and diesel were either marginal or too aromatic to meet specifications directly--even at 0.5 LHSV and 2300 psia hydrogen pressure.

A series of experiments with Wyodak ITSL A (the most difficult syncrude), suggested an alternative upgrading route.

First, it was shown that the aromatic content increased rather than decreased when the catalyst temperature was increased from 750°F to 775°F. Then, it was shown that the aromatic content remained about the same when the LHSV was reduced by a factor of two (to 0.25 LHSV) and the temperature held constant. Together, these results indicated

that the equilibrium was unfavorable for hydrogenation of some of the high-boiling polycyclic-aromatic compounds at the run conditions.

Therefore, we tried a two-step approach: (1) Hydrotreat at relatively high temperature (e.g., 750°F) to remove most of the heteroatoms. (2) Further hydrogenate at lower temperatures (e.g., 600-650°F) for further aromatics saturation.

In the next test, product from the initial experiment (750°F, 0.5 LHSV, 2300 psia H<sub>2</sub>), which contained 42 % aromatics, was hydrotreated a second time using the same catalyst. The LHSV and pressure were kept the same, but the temperature decreased to 650°F--100°F lower than previously. Due to the more favorable equilibrium at 650°F, product aromatics were reduced to 12%. The jet and diesel fractions, respectively, exceeded smoke point and cetane number specifications. Also, enough EP reduction was achieved so that less than 5% of the product boiled above the diesel range.

When the temperature was further decreased to 600°F, the aromatic content of the product did not decrease further, but increased to 20%. [The rate of hydrogenation was lower, although the equilibrium was even more favorable than at 650°F.] The diesel fraction still met the cetane number specification, however.

The results show that two-step hydrotreating [with the second hydrotreatment at a relatively low temperature] is an alternative to the hydrotreating/hydrocracking route for upgrading high EP syncrudes, provided diesel fuel is a desired product.

#### CONCLUSIONS

Coal liquids produced in the ITSL and CTSL processes with EPs from about 600°F to over 900°F were hydrotreated to make diesel and jet fuels, and naphthas suitable for catalytic reforming to gasoline. Specific conclusions are as follows:

(1) Oils from two-stage processes were easier to upgrade than comparable boiling-range products from single-stage processes, due to lower nitrogen and oxygen contents. However, as with products from single-stage processes, relatively small increases in EPs made the oils much harder to upgrade.

(2) Except for modest differences in paraffin contents, properties of finished products of given boiling ranges from both Wyodak and Illinois coals, and both one- and two-stage processes studied were fairly similar, and mainly consisted of cyclic hydrocarbons. Products from Wyodak coal were somewhat more paraffinic than those from Illinois coal.

(3) Product boiling ranges were different, depending upon the liquefaction process and the cut point used in that process. The single-stage processes made more naphtha than the two-stage processes at a given cut point; the two-stage processes made more middle distillate. The ITSL process made more middle distillate than the CTSL process. Diesel products from two-stage processes had higher cetane numbers at a given aromatic content than those from single-stage processes. At least in part, this was due to product boiling range differences.

(4) In all cases studied, the jet fuel and diesel products had high densities and, therefore, high volumetric-energy contents.

(5) Wyodak CTSL light oil had a higher hydrogen content and lower heteroatom content than the other oils. These factors, plus its low EP, made it easier to upgrade than the other syncrudes studied.

(6) For high EP syncrudes, an attractive upgrading route is a two-step process--hydrotreating to remove most of the heteroatoms, followed by low-temperature hydrogenation to saturate aromatics.

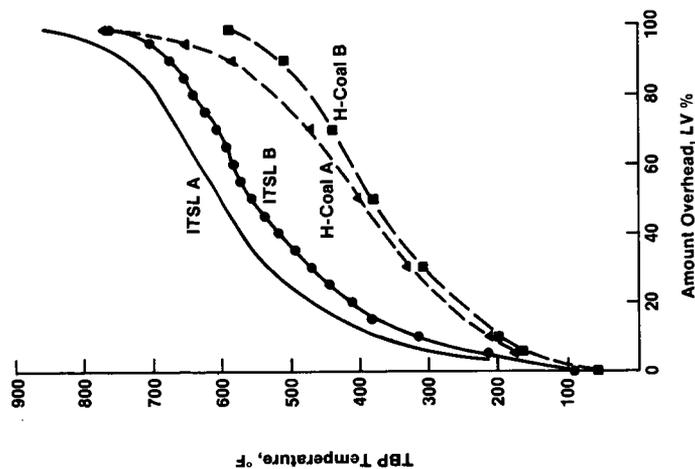
#### ACKNOWLEDGMENT

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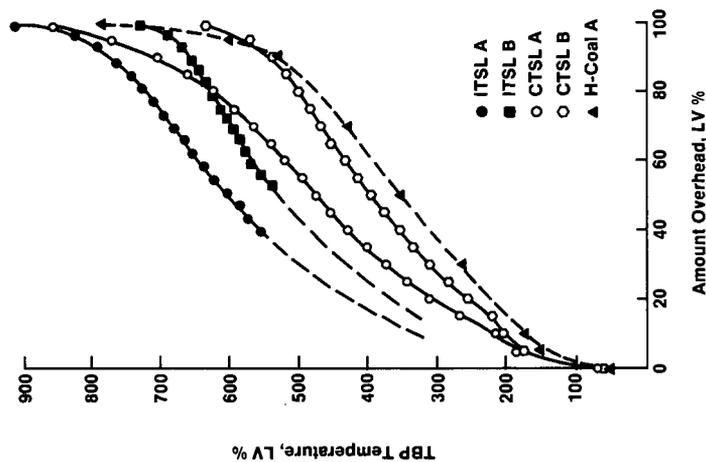
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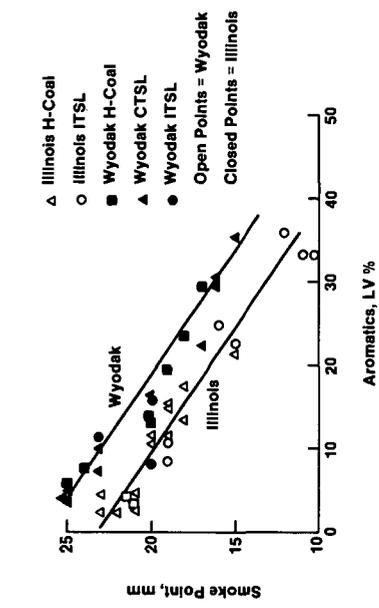
**FIGURE 1**  
**TBP DISTILLATIONS OF**  
**SYNCRUDES FROM ILLINOIS NO. 6 COAL**



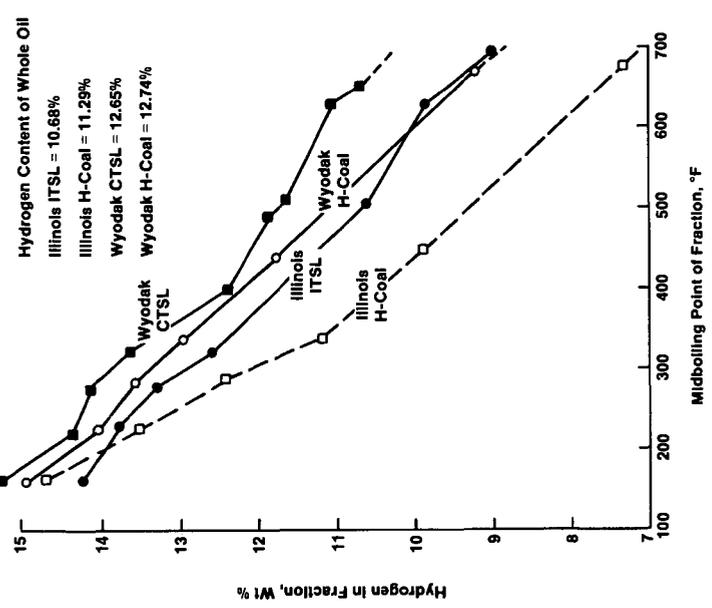
**FIGURE 2**  
**TBP DISTILLATIONS OF**  
**SYNCRUDES FROM WYODAK COAL**



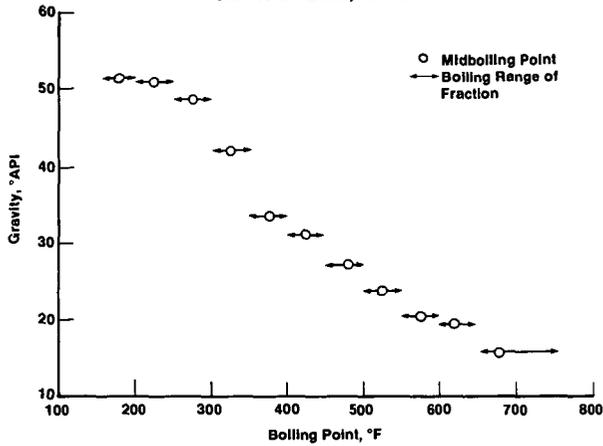
**FIGURE 4**  
**EFFECT OF AROMATICS ON**  
**SMOKE POINT OF JET FUELS FROM**  
**HYDROTREATED COAL-DERIVED FEED**  
**Boiling Range = 250-550°F or 250-600°F**



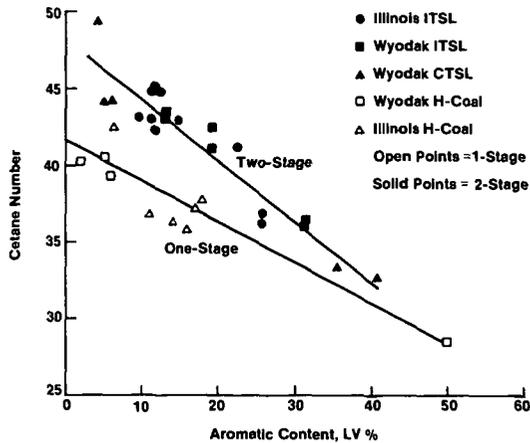
**FIGURE 3**  
**HYDROGEN CONTENT OF SYNCRUDE**  
**FRACTIONS VERSUS BOILING RANGE**



**FIGURE 5**  
**API GRAVITIES OF NARROW BOILING**  
**FRACTION OF HYDROTREATED ILLINOIS ITSL OIL**  
**Total Aromatics, 11 LV %**



**FIGURE 6**  
**EFFECT OF AROMATICS ON THE**  
**CETANE NUMBER OF DIESEL**  
**FUELS FROM HYDROTREATED COAL-DERIVED OILS**



## INTEGRATED TWO-STAGE LIQUEFACTION: THE LEGACY AND THE UNFINISHED WORK

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### INTRODUCTION

The Integrated Two-Stage Liquefaction (ITSL) concept has received considerable attention by many laboratories and has emerged as one of the most promising technology in direct coal liquefaction.

DOE/Lummus/Cities Service, EPRI/Kerr McGee, the Wilsonville teams, Chevron and Exxon (1) have been in one way or another involved in processes conforming to the ITSL concept, each one with a somewhat different approach or processing scheme. Recently, HRI (2) has developed another staged liquefaction concept which recently has received DOE support for extended continuous bench-scale testing.

Major achievements were obtained during the development of the ITSL process at Lummus, from May 1980 to June 1985, which have changed substantially our approach to coal liquefaction techniques and inspired new thoughts in unraveling the mechanism of direct coal liquefaction at low severity operations. These novel mechanistic considerations need to be supported with further studies using suitable model compounds, some of which have been recently proposed (3).

Several papers have reported the early development of the ITSL process and related projects (4-8). This paper has the objective to divulge the most recent achievements of an evolved ITSL process, pointing out the unfinished work, and to expand the concept of the low-severity staged approach which resulted from the evolved ITSL process and emerged as the most desirable pathway for the direct production of marketable liquid fuels from coals. The ultimate objective is to interest the researchers dedicated to fundamentals of coal liquefaction toward the technological needs and the understanding of reaction mechanism, kinetics and thermodynamic limitations residing with the novel, low-severity staged coal liquefaction approach.

### THE ITSL LEGACY

Major accomplishments obtained at low-severity operations in a 3/4 ton/day ITSL process development unit at Lummus and from related bench-scale studies in various laboratories, include:

Low severity produced extracts are low in heteroatoms and more easily hydrogenatable, consistently yielding excellent equilibrium donor solvent (9).

No high viscosity gel region is apparent over the 280-350°C temperature range for a slurry of bituminous coal and ITSL solvent, as was the case for slurries prepared with the same coal and other types of solvent (10).

Low severity processing forms mostly reactive low molecular-weight fragments. Conversely, single stage thermal and thermal/catalytic processing produce high-molecular weight products thought to be actually condensation products of such smaller fragments and consequently, less reactive (11).

Proton NMR analysis, modified to provide data on ITSL distillate and non-distillate fractions, has been shown to be useful in the development of a kinetic model for coal extract hydroprocessing, thus enabling us to distinguish catalytic hydrogenation and cracking reactions, and to predict the solvent donor capability as well as the yield structure of the upgraded products (12).

A mixture of condensed aromatics, hydroaromatics, paraffins and their respective heteroatom derivatives is produced during coal liquefaction. This mixture tends to be unstable because of the incompatibility between polar heteroatom compounds and hydrocarbons, as well as between condensed aromatics and paraffins. Condensed hydroaromatics, having closer affinity for both aromatics and paraffins, tend to keep them in solution, thus contributing to the stability of the coal extract. Low severity coal extraction yields a larger quantity of hydroaromatics and small amounts of high heteroatom, condensed aromatics and paraffins (12).

Best catalysts tested are those modified to suppress the hydrocracking activity and enhance hydrogenation functionality (9).

Coal derived transportation fuels, produced by refining of distillate from low severity operations, possess inherent high quality which is due mostly to their hydroaromatic (naphthenic) nature. Coal derived naphthas contain large quantities of highly alkylated cyclohexanes which, by reforming, convert to the corresponding benzenes and in the process, recover a large portion of the hydrogen to make the overall coal liquefaction approach economically more attractive. Alkylated benzenes are the major contributors to the high octane gasoline thus formed. Coal derived middle distillate is constituted mostly of di- and tri-hydroaromatics and corresponding aromatics.

Further refining has been successfully employed to convert some of the aromatics to meet marketable jet and diesel specifications of smoke point and cetane number, respectively (13).

From the operation of the process development unit (PDU) at Lummus (9) the following important results were obtained:

Subbituminous coal was demonstrated to be an attractive feed for direct liquefaction: The distillate yield was slightly lower (2.9 bbl/ton of moisture-ash-free coal compared to 3.2 for bituminous coals) but its lower cost, higher reactivity in the second stage and its ease in being converted to a lighter product

are over-riding features in its favor. In addition, ITSL with Wyodak coal demonstrated good operability in both reaction stages and was easily deashed.

When the deasher is placed after the LC-Fining reactor, the distillate yield was increased seven percent. More importantly, the LC-Fining catalyst was unaffected by ash feed and reactor volume is unchanged.

Most of the LC-Fining reactor volume could be replaced by a fixed bed hydrocracking unit. This resulted in an equally good yield of -650°F product with no loss in hydrogen efficiency. The -650°F product contained less than 100 ppm sulfur and less than 500 ppm nitrogen, making this a clean, light and environmentally acceptable product. Furthermore, this flow configuration reduces the second stage reactor volume by at least 18 percent and may also greatly simplify and reduce the cost of the deashing section.

The SCT reaction was operated at 500 and 1000 psig, with no adverse effect on yields or hydrogen usage. This leaves the LC-Fining as the only high pressure section of the process.

Analysis of the results indicated that a commercial SCT reactor can be designed to retain all the important features of the PDU. There is every reason to believe that SCT can be scaled to commercial size.

Deasher bottoms were coked to produce additional liquid products. The liquid yield was about 20 percent of the organic matter in the ash-rich feed.

Low temperatures of about 700°F, do not provide sufficient hydrogenation to replenish solvent quality, while at 800°F the solvent contains insufficient transferable hydrogen. Therefore, the optimum temperature for both conversion and regeneration of recycle solvent is about 724-750°F (9).

In antisolvent deashing experiments, THF-insoluble/quinoline-soluble preasphaltenes precipitate consistently with the mineral matters, whereas the THF-soluble preasphaltenes do not. This indicates that THF-insoluble preasphaltenes may be the major cause of mineral matters agglomeration, increasing their diameter and causing the particles to settle faster (14).

#### THE UNFINISHED WORK

The most significant achievements of the ITSL program came into focus during the last part of the ITSL project and of the related projects before they ceased operation. In this particular period, those who closely monitored the overall program, gathered the large set of data made available, and structured them for suitable process engineering and economic evaluation,

became aware of an evolutionary trend in coal liquefaction processing. The major factors contributing to this novel trend were: 1) the better understanding of the very sensitive interdependency between the stages of coal extraction, of the coal extract upgrading and hydrogen donor recycle solvent requirements, which emerged only from the data produced in a continuous, integrated recycle mode of operations, and 2) the more favorable results of low-severity operations, practically solving, in an easy and elegant manner, most if not all the problems encountered by using high-severity operations which were practiced in earlier processes, i.e. German, H-Coal, SRC-II, etc.

But perhaps more important to the fundamental research community is the fact that the large set of ITSL data under scrutiny for process development, lacks the fundamental data to support the profound changes in the mechanism and kinetics occurring at low-severity coal liquefaction.

Some of the concepts and technology needs are outlined below.

Preservation of highly reactive, small fragments in the coal extract is of utmost importance in producing an excellent donor solvent and high quality distillate fuel products. For this purpose, the fragments should be withdrawn from the extraction reactor as soon as they are formed. The unconverted coal can be further converted by recycling it with the preasphaltenes as part of the recycle solvent.

Better preservation of the reactive small fragments can be achieved by increasing the donatable hydrogen level and decreasing the heteroatom content of the recycle solvent. It is important for the superior hydrogen donor solvent to penetrate the less reactive macerals. Consequently, it is advisable to allow for a thermal soaking treatment, i.e., at 250-350°C temperature range for 10-30 minutes, prior to the short contact time (SCT) reaction of rapid heating (two minutes) to the 450°C exit temperature. It is evident that all the above activities are interdependent and the improvements maximized in an integrated recycle process.

It is extremely difficult to capture in research bench scale units the essence of the results produced in the integrated recycle process, because most of the key benefits, i.e., coal conversion and enhanced donor solvent quality, are obtained only after several cycles of the integrated staged operations. Bench scale researchers could avoid the long and tedious recycle operations by applying the aforementioned kinetic model for coal extract hydroprocessing (12) and using proton-NMR data of the coal extract to predict solvent donor capability and yield structure of the upgraded products.

Proton-NMR analysis is rapid, requires small samples, is highly reliable and has excellent reproducibility.

Removal of the heteroatoms in the early stage of coal extraction is desirable and ought to be sequential, removing first the more abundant oxygen and thus making easier the subsequent nitrogen removal.

Complementary fundamental studies on C-O and C-N bond scission should be emphasized over the current C-C bond cracking effort.

Most of the sulfur is converted to hydrogen sulfide during the two above sequences, and the H<sub>2</sub>S must be kept in the system as catalyst itself and as "activator" of transition metal catalysts.

It is essential that the ITSL technology be pursued to the completion of the evolutionary trend which became almost dormant with the termination of most of the ITSL projects. It is up to the fundamental research community to fill-up the gap of supportive fundamental research through studies of thermodynamics, kinetics and reaction mechanisms involved in low-severity operations which are part of the ITSL process. Of particular interest would be the matching of reaction kinetics of dehydrogenation of the hydrogen donor solvent with the hydrogen acceptancy of coal extracts.

Those of us involved in these efforts are optimistic about the future of low-severity direct coal liquefaction and the quite similar coal/oil co-processing as the practical approaches in helping to alleviate an increasingly energy-deficient world.

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## Comparative Economics of Two-Stage Liquefaction Processes

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### Background

It has been recognized in research and development carried out by Lummus-Crest (1), that two stage liquefaction provides an attractive route to coal liquefaction by optimizing the discrete stages in conversion of solid coal to distillate. While improvements in process efficiency, product yield and quality have been demonstrated, the current limited knowledge of coal structure and liquefaction chemistry still necessitates empirical testing of process alternatives.

A number of promising process alternatives have been developed and are under current investigation at a bench or process development unit (PDU) scale by a number of contractors under DOE sponsorship. The contractors include Lummus-Crest, Southern Services (Wilsonville) (2), Hydrocarbon Research Inc., (3) and Amoco (4). The process variations under current investigation are as follows:

- Production of a major part of the distillate product in Stage 1 versus Stage 2.
- Catalytic first and second stage versus thermal first stage and catalytic second stage.
- Critical Solvent Deashing versus Anti-Solvent Deashing.
- Direct coupling of Stages 1 and 2 without intermediate deashing.

DOE requested that MITRE undertake a comprehensive technical and economic analysis of all the two-stage coal liquefaction configurations currently under development in order to quantify the improvements made in the production of high quality distillates from coal. Table 1 lists the processes that were analyzed in this task.

The methodology used to perform this analysis was as follows:

- Review test data. Select most representative run for each process using both Illinois #6 and Wyoming coals.
- Scale test data to develop material balances for conceptual commercial plants processing 30,000 tons per day of moisture free coal to the liquefaction units.
- Identify unit operations for commercial plants.
- Compute coal and energy requirements for plant balance.
- Estimate capital and operating costs for commercial plants.

- Compute annual revenue requirements based on consistent economic assumptions.
- Compute product costs required to satisfy revenue required.

### Results and Discussion

Table 2 shows the characteristics of the commercial-scale plants for both Illinois No. 6 and Wyoming coals. Plants with high yields and/or high hydrogen consumption require large quantities of additional coal for steam and hydrogen production.

The construction costs of the conceptual commercial plants were estimated using an 1981 UOP/SDC (5) commercial design of the Lummus Integrated Two-Stage Liquefaction (ITSL) plant as a basis for costs of unit operations, where possible. Costs of unit operations not addressed in this report were obtained from other sources. Operating and maintenance costs were estimated using a standard procedure developed by UOP/SDC. The annual revenue requirements for these plants were then calculated based on the capital recovery and operating costs developed from use of consistent economic assumptions.

Since each process configuration produces a syncrude having a different quality, it was decided to account for this product quality difference. In order to do this, MITRE has calculated the hydrogen requirements and volume gain which occur when the C<sub>4</sub>-850°F raw output of each plant is hydrotreated to produce a heteroatom-free, 35°API, 13-percent hydrogen product. The cost of this hydrotreatment is calculated based on the assumption that the cost of hydrogen production and addition is \$1.00/pound.

Product costs were then computed to satisfy the annual revenue requirements based on the following assumptions. It was assumed that heavy products (i.e., 850°F+ products) were valued at one-half of the value of a barrel of C<sub>4</sub>-850°F liquid product. For the hydrocarbon gases (C<sub>1</sub>-C<sub>3</sub>), it was assumed that 12x10<sup>6</sup> Btus were equivalent in value to one barrel of C<sub>4</sub>-850°F product.

Figure 1 shows comparisons of the annual revenue requirement, equivalent product yield, and required selling price of products from the conceptual commercial plants when operated with Illinois No. 6 coal. All values are shown as percentages of the Lummus Integrated Two-Stage Liquefaction (ITSL) base case. For comparative purposes two conceptual plants based on single-stage processes (H-Coal (6) and EDS (7)) are included.

The bars depicting annual revenue requirements are divided into four sections, to illustrate the relative contribution of capital recovery, coal, operating and hydrotreating costs. The capital recovery costs for the two-stage plants vary by about 2 percent, indicating a similarly small variation in the capital costs of the plants. Capital costs of the single-stage plants are 5.4- and 9.5-percent lower than the Integrated Two-Stage Liquefaction (ITSL) base case for H-Coal and EDS, respectively.

The variation in hydrotreating costs reflects variation in both the quality of the raw product and the quantity of the C<sub>4</sub>-850°F fraction. Hydrotreating costs of EDS are lower than the other systems, because of the relatively low yield and high API quality of the raw EDS product. The total annual revenue requirements vary from a low of 89.7 percent of base for EDS, to a high of 107.5 percent of base for CTSL.

The equivalent barrels of yield show a much wider variation than the annual revenue requirements. EDS yield is lowest at 84.6 percent of base, while CTSL is highest at 115.7 percent.

The lower portion of Figure 1 compares the required selling price of hydrotreated products from the conceptual plants. The prices vary from 105.9 percent of base for EDS to a low of 92.9 percent of base for CTSL, a spread of 13 percent. The most advanced systems, e.g., modified Lummus, Wilsonville RITSL, and CTSL, offer the lowest product prices. All these systems catalytically treat an ash-containing extract. It is doubtful that the one-percent difference between CTSL and RITSL is significant. However, the slight superiority of these systems relative to the modified Lummus is believed to be significant and is traceable to the higher rejection of soluble material which is inherent in the deashing system employed at Lummus. Lummus has suggested that the additional liquids in the deashed overflow could be recovered by coking.

Figure 2 shows economic comparisons for plants operated with Wyoming coal. Capital recovery cost variations between the plants are very similar to those observed in the Illinois No. 6 plants. The total revenue requirements vary from 93.8 to 100 percent of base for the two-stage plants, but are much lower at 89 and 83.3 percent of base for the single-stage H-Coal and EDS plants, respectively.

Plant yields show a much greater variation than was observed in the plants processing Illinois No. 6 coal. Yields vary from a low of 91.6 percent of base for EDS to a high of 141.5 percent of base for CTSL.

The required selling prices also show a wide variation. The Lummus ITSL shows the highest selling price at 100 percent of base, while CTSL offers the lowest price at 68.9 percent of base. The single-stage H-Coal and Wilsonville DITSL processes offer similar prices of 80.3 and 80.7 percent of base, respectively.

The results with both Illinois No. 6 and Wyoming coals indicate that the additional cost and complexity of two-stage processing is justified by the increases in yield and product quality which can be obtained.

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FIGURE 1: COMPARISONS OF ILLINOIS NO. 6 COAL PLANTS

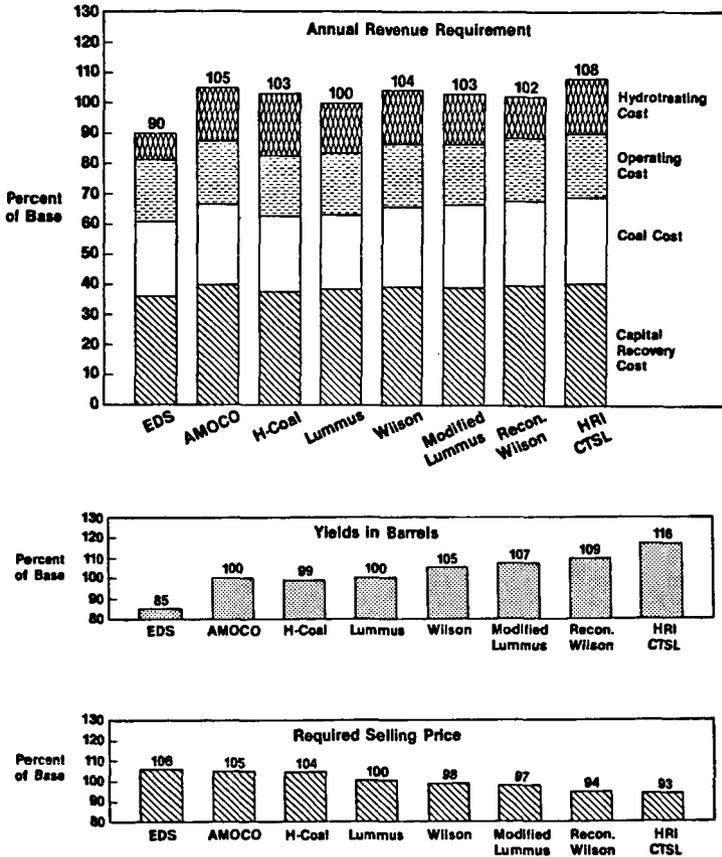


FIGURE 2: ECONOMIC COMPARISONS OF WYOMING COAL PLANTS

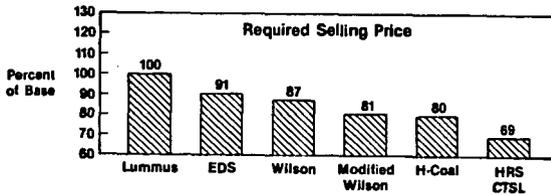
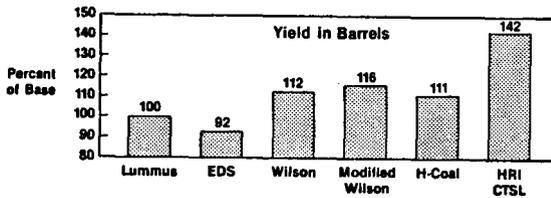
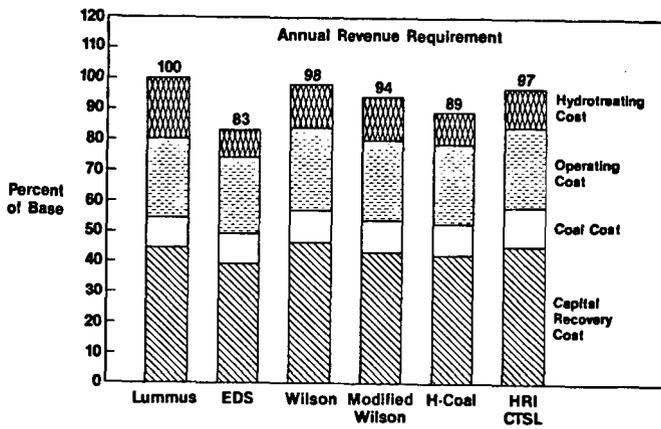


TABLE 1: TWO-STAGE PROCESSES

<u>Process</u>	<u>Scale</u>	<u>Stage I</u>	<u>Deashing</u>	<u>Stage II</u>
<b>Lummus-Crest Integrated Two-Stage Liquefaction (ITSL)</b>	<b>600 Lb/Day</b>	<b>Thermal</b>	<b>Anti-Solvent</b>	<b>Catalytic</b>
<b>Wilsonville Two-Stage Liquefaction</b>	<b>3 T/Day</b>	<b>Thermal*</b>	<b>Critical Solvent Deashing</b>	<b>Catalytic</b>
<b>Hydrocarbon Research, Inc. Catalytic Two-Stage Liquefaction (CTSL)</b>	<b>50-100 Lb/Day</b>	<b>Catalytic</b>	<b>No Deashing Between Stages</b>	<b>Catalytic</b>
<b>AMOCO Thermal/Catalytic Two-Stage Liquefaction</b>	<b>50-100 Lb/Day</b>	<b>Thermal</b>	<b>No Deashing Between Stages</b>	<b>Catalytic</b>

\*Sometimes Slurry Catalyst Used

TABLE 2: CONCEPTUAL COMMERCIAL PLANT SUMMARIES

ILLINOIS NO. 6 COAL FEED

<u>Process:</u>	<u>Lummus ITSL</u>	<u>Wilsonville ITSL</u>	<u>Wilsonville RITSL</u>	<u>Modified Lummus ITSL</u>	<u>AMOCO</u>	<u>CTSL</u>
<b>Input</b>						
Steam Coal, TPD (MF)	2,000	2,000	2,000	3,000	3,000	3,000
Gasifier Coal, TPD (MF)	0	3,000	4,000	2,000	2,000	4,000
Total Plant Coal, TPD (MF)	32,000	34,000	37,000	35,000	35,000	37,000
<b>Output</b>						
SNG, MMSCFD	0	0	12	11	60	25
Raw C <sub>4</sub> + Liquid, BPSD	90,000	105,000	105,000	95,000	94,000	108,000
Total Liquid Yield after Hydrotreatment, BPSD	101,000	114,000	113,000	108,000	100,000	117,000

WYOMING COAL FEED

<u>Process:</u>	<u>Lummus ITSL</u>	<u>Wilsonville ITSL</u>	<u>Wilsonville DITSL</u>	<u>CTSL</u>
<b>Input</b>				
Steam Coal, TPD (MF)	3,000	2,000	2,000	4,000
Gasifier Coal, TPD (MF)	0	3,000	4,000	9,000
Total Plant Coal, TPD (MF)	33,000	36,000	36,000	43,000
<b>Output</b>				
SNG, MMSCFD	33	28	6	3
Raw C <sub>4</sub> + Liquid, BPSD	70,000	90,000	97,000	114,000
Total Liquid Yield after Hydrotreatment, BPSD	80,000	94,000	98,000	119,000

## Temperature-Staged Catalytic Coal Liquefaction

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### Abstract

Coal liquefaction has been investigated under conditions where reaction is conducted in successive stages of increasing temperature and in the presence of a dispersed sulfided Mo catalyst. This sequence leads not only to high conversions but also greatly increases the selectivity of the products to oils at the expense of asphaltenes, with only marginal increase in gas make. The product distribution is strongly influenced by the solvent composition and the reaction conditions in the two stages. Examination of the liquefaction residues from the liquefaction of a bituminous and a subbituminous coal has provided supporting evidence to show that the temperature-staged reaction sequence favors hydrogenative processes. Moreover, the choice of reaction conditions for optimum performance is rank-dependent; for example, low-rank coals appear to require a lower first stage temperature than bituminous coals in order to minimize the potential for regressive reactions.

### Introduction

In some earlier reported research (1,2) a bituminous and a subbituminous coal were pretreated by dry catalytic hydrogenation, using a molybdenum catalyst at 350°C for 1 h, following which they were mixed with naphthalene (2:1 solvent to coal ratio) and reacted at 425°C for 10 min. The results showed that the low-temperature pretreatment improved both the net coal conversion, based upon solubility in tetrahydrofuran, and the product distribution. Notably, the oil to asphaltene ratio was substantially increased with only marginal additional gas make.

Based upon these findings, further research has been directed to investigating the chemistry and the potential of temperature-staged coal liquefaction. The results of this research are presented in this paper. Similar studies are being conducted on a larger scale by Hydrocarbon Research Inc. (3).

### Experimental

#### Coal Preparation

Samples of bituminous and subbituminous coal were provided by the Penn State Coal Sample Bank for use in this research. The coals were obtained undried and in lump form about 12 mm size and were crushed in a glove box under oxygen-free nitrogen to 0.8 mm top size. The crushed coals were subdivided by riffing into a number of 10 g representative samples and sealed in vials under nitrogen. Properties of the coals are shown in Table 1.

The coals were impregnated with Mo catalyst by slurring with an aqueous solution of ammonium tetrathiomolybdate in the concentration necessary to attain a loading of 1% wt Mo on a dmmf basis. The quantity of coal impregnated was sufficient for a complete series of experiments. After slurring, the excess water was removed by vacuum freeze-drying.

#### Liquefaction

The impregnated coal was mixed in a ratio of 1:2 with liquefaction solvent. In most of the experiments, naphthalene was selected as the solvent because, at least

at the onset of reaction, no H-donor would be present, which would allow the effects of added catalyst and low-temperature coal pretreatment to be more clearly discerned. Approximately 0.1 g of CS<sub>2</sub> was added to the reaction mixture to ensure that the molybdenum was maintained in the fully sulphided state.

Reactions were carried out in tubing bomb reactors of about 30 cm<sup>3</sup> capacity which were heated by immersion in a fluidized sandbath. More detailed descriptions of the experimental procedures have been given elsewhere (4). Reactions were conducted either at 425°C for 10 min or under these same conditions after first pretreating at 350°C for 60 min. The initial hydrogen pressure (cold) for both pretreatment and the higher temperature reaction was 7 MPa.

When the low-temperature pretreatment was carried out, the bombs were quenched to room temperature at the end of the reaction period and the yields of light gases were determined by volumetric measurement and gas chromatographic analysis. The main purpose of the cooling and venting procedure was to ensure that there was a high partial pressure of hydrogen in the reactor at the beginning of the higher temperature stage. The rationale for choosing a short reaction time for the high-temperature stage (10 min at 425°C) was the same as that used for solvent selection; namely to accentuate the effects which would be caused by the low-temperature reaction.

Following high-temperature reaction, the gas yield and composition were determined and the solid and liquid products were worked-up to obtain the yields of insoluble residue (tetrahydrofuran, THF) asphaltenes (hexane-insoluble, THF-soluble) and oils (hexane-soluble). In these calculations, it was assumed that the naphthalene reported to the hexane-solubles. Despite extensive precautions, some of the lighter liquefaction products were lost during product work-up and especially during the removal of solvents. Oil yields are therefore calculated from the mass balance assuming that most of the mass balance deficit is attributable to the loss of light ends.

A further factor, which is not accounted in the product distribution, is the yield of water produced by reaction. It is not anticipated that this will constitute more than a few percent of the liquid yields, even with the subbituminous coal, although firm estimates have not yet been made. Because of the method of calculation of the oil yield, any water which is produced is considered as oil. Consequently, the actual oil yield will be somewhat lower than reported.

A few experiments were conducted to explore the effects of extended reaction time at 425°C and the influence of a more reactive solvent than naphthalene. In the latter instance, the solvent was a process-derived recycle solvent fraction (454+°C) obtained from the Lummus Integrated Two-Stage Liquefaction (ITSL) process, when operating on Wyodak subbituminous coal.

In determining the product distribution, quantities of oil and asphaltene, equivalent to those present in the original solvent, were subtracted from the product yields in order to obtain the net yields attributable to coal.

#### Residue Microscopy

The dried liquefaction residues (THF insolubles) were embedded in epoxy resin and polished with a series of alumina slurries. Examination was undertaken with a polarizing reflected-light microscope under oil immersion at a magnification of 625; a rotatable compensation plate was used as an aid in distinguishing between isotropic and anisotropic materials. Some observations were made in blue-light irradiation, in order to observe the proportions of liptinite macerals present.

## Results and Discussion

### Reactions in Naphthalene

The conversions and product distributions obtained by the liquefaction of the subbituminous and bituminous coals under various combinations of pretreatment and liquefaction reactions are summarized in Tables 2 and 3. Similar trends are apparent for both of the coals. Reaction in the presence of the catalyst produced higher net conversions than the 'thermal' experiments, as would be expected. However, the combination of low-temperature catalytic pretreatment followed by the higher temperature catalytic reaction had the greatest influence in improving the product selectivity concomitant with attaining the highest conversion. In particular, the highest oil yields were obtained without any attendant increase in the production of light hydrocarbon gases.

An examination of the liquefaction products by gas chromatography showed that there was no significant conversion of naphthalene to tetralin (less than 1%) in any of these experiments. While this finding does not exclude the possibility that the catalyst may promote liquefaction through the successive generation and dehydrogenation of donor solvent, it does suggest that other reaction pathways are operative and may be more important.

The addition of catalyst, without pretreatment, significantly increased the conversion of both coals over that obtained in the thermal experiments. At the same time, these conditions produced the lowest oil yields and the lowest ratios of oils to asphaltenes. The pretreatment evidently allows the catalyst to perform certain functions which ultimately lead to higher oil yields and these functions appear to be not as readily performed during a short catalytic reaction at the higher temperature of 425°C.

### Microscopic Examination of Liquefaction Residues

There were notable differences in the appearance of the residues from the bituminous and subbituminous coals. The bituminous coals hydrogenated in the absence of catalyst showed clear evidence of the development of plasticity, i.e., rounded particle outlines and the formation of spheres of vitroplast. Vitroplast is a low-reflecting, isotropic, pitch-like material, usually derived from vitrinite, that occurs as spheres and agglomerates (5). The vitroplast observed in this study is the type which Shibaoka (6) has referred to as a primary vitroplast, being derived directly by softening of vitrinite.

In contrast, the residues derived from the catalytically hydrogenated bituminous coals had apparently undergone more extensive reaction. There was no evidence of simple melting, and the vitrinite-derived material was considerably reduced in volumetric proportion relative to that of other macerals. The reflectance of this vitrinite-derived material was lower than either that of the vitrinite in the feed coal or that of the vitroplast in the residues of uncatalyzed runs. These observations are consistent with the action of the catalyst being instrumental in the hydrogenation and breakdown of the vitrinite structure. An unexpected feature of the residues was the large proportion of remaining, although not necessarily unchanged, liptinite (sporinite and cutinite) present in samples from the catalysed experiments with bituminous coal.

None of the residues from the subbituminous coal contained vitroplast or showed other evidence of plasticity during treatment. Rather, the residues of the vitrinite (huminite) consisted of tattered skeletons of the structures present in the original coal. However, the vitrinite reflectance was significantly higher in the residues than in the parent coal; that of the residue from the catalysed and pretreated coal was judged to be somewhat lower than that of other residues. This

run also resulted in more particle disintegration than was observed in the other residues.

The microscopic studies of the liquefaction residues reflect the trends shown by the yield data in confirming that the staged catalytic liquefaction produced the conditions most conducive to coal hydrogenation and liquefaction.

From the residue analysis for the subbituminous coal, it appears that the temperature selected for the low-temperature stage was too high as shown by the increase in reflectance of the vitrinite-derived materials in the residues relative to the vitrinite (huminites) in the untreated coal. In contrast, the residues from catalysed bituminous coal hydrogenation display the predominance of hydrogenation reactions as evidenced by the lower vitrinite reflectance compared to the parent coal. Without catalyst, the very obvious development of plasticity indicates the dominating effect of thermal treatment.

#### Effect of Other Reaction Conditions

The data presented above have illustrated the potential advantages to be derived by liquefying coals in stages of increasing temperature and in the presence of a catalyst. Verification of these phenomena has been demonstrated more comprehensively and on a larger scale by Hydrocarbon Research Inc. (3).

In the laboratory scale studies, no systematic attempt has yet been made to investigate how independent variables such as the reaction conditions in the first and second stages, the solvent composition and the catalyst type and concentration affect the performance attainable in such a reaction sequence. Some preliminary data are presented in Figure 1 which show the comparative effects on the product distribution for the subbituminous coal (PSOC-1401) due to (i) increasing the high temperature residence time from 10 to 45 min while employing naphthalene as solvent and (ii) using the more reactive process solvent and the 45 min high-temperature residence time.

With naphthalene, increasing the reaction time at high-temperature is evidently advantageous in promoting further interconversion of oils to asphaltenes (the oil to asphaltene ratio increased from 0.8 to 2:1) with some simultaneous increase in gas make; the CO<sub>x</sub> yield increased from 7.9 to 9.8% and the yield of C<sub>1</sub>-C<sub>4</sub> hydrocarbons increased from 0.8 to 3.0%. As in the other experiments using naphthalene as solvent, there was no significant conversion of naphthalene to tetralin.

A much more dramatic change in product selectivity was achieved by using the process solvent when the oil to asphaltene ratio increased to approximately 14:1. To offset this gain there was a more significant increase in gas make; the CO<sub>x</sub> and C<sub>1</sub>-C<sub>4</sub> yields being 12.2 and 4.7%, respectively. Quite evidently, the composition of the solvent is an important parameter even in the presence of an active catalyst.

#### Acknowledgements

Three of the authors, Derbyshire, Epstein, and Stansberry, wish to acknowledge the financial support of the Department of Energy, Grant No. DE-FE22-83PC60811 and Contract No. DE-FG-22-84PC7003. Frank Derbyshire wishes to acknowledge Dr. Frank Burke of Conoco Coal Research for his helpful discussions and contributions and Dr. Eneo Moroni for his steadfast support.

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TABLE 1

Coal Properties		FSOC-1266	FSOC-1401
Penn State Sample Bank No.			
Seam	L. Kittanning	Lower Wyodak	
County	Mahoning	Cambell Co.	
State	Ohio	Wyoming	
Province	Eastern	Northern Great Plains	
ASTM rank class	hVAb	sub. B. (apparent)	
Moisture content, % wt (a.r.)	3.4	16.3	
Mineral Matter, % wt dry coal	6.1 <sup>†</sup>	6.6*	
<u>Elemental Composition % dmmf</u>			
C	83.2	74.3	
H	5.0	5.2	
O**	8.6	19.3	
N	2.1	1.1	
S	0.5	0.2	
<u>Maceral Analysis, % vol</u>			
Vitrinite	91	85	
Exinite	3	2	
Inertinite	6	13	
<u>Sulfur Forms (% dry coal)</u>			
Organic	0.46	0.19	
Pyritic	0.79	0.01	
Sulfate	0.02	0.00	
Total	1.27	0.20	

<sup>†</sup> By low-temperature ashing; \* Reported as ASTM "Ash"; \*\* By difference

TABLE 2

Product Yields from the Liquefaction of Subbituminous Coal (PSOC 1401)

Conditions		Product Yields (% dmmf)									
Pretreatment	Liquefaction	Conversion	Asphaltenes	Oils <sup>1</sup>	CO <sub>2</sub> <sup>2</sup>	CO <sub>2</sub>	C <sub>1</sub> -C <sub>4</sub> <sup>2</sup>	CO <sub>3</sub>	CO <sub>2</sub> <sup>3</sup>	C <sub>1</sub> -C <sub>3</sub>	C <sub>1</sub> -C <sub>4</sub> <sup>3</sup>
a)	None	Thermal	42.5	4.7	28.8	--	--	--	0.6	7.9	0.5
b)	Thermal	Thermal	41.9	9.9	22.1	0.2	7.3	0.1	0.4	9.3	0.2
c)	None	Catalytic	66.7	41.8	17.6	--	--	--	0.5	6.3	0.5
d)	Catalytic	Catalytic	90.7	46.7	35.3	0.3	6.5	0.3	1.1	6.8	0.8

TABLE 3

Product Yields from the Liquefaction of Bituminous Coal (PSOC 1266)

Conditions		Product Yields (% dmmf)									
Pretreatment	Liquefaction	Conversion	Asphaltenes	Oils <sup>1</sup>	CO <sub>2</sub> <sup>2</sup>	CO <sub>2</sub>	C <sub>1</sub> -C <sub>4</sub> <sup>2</sup>	CO <sub>3</sub>	CO <sub>2</sub> <sup>3</sup>	C <sub>1</sub> -C <sub>3</sub>	C <sub>1</sub> -C <sub>4</sub> <sup>3</sup>
a)	None	Thermal	58.1	42.8	13.7	--	--	--	0.3	0.9	0.4
b)	Thermal	Thermal	59.0	47.3	10.2	0.03	0.9	0.05	0.2	1.1	0.24
c)	None	Catalytic	72.6	66.7	4.8	--	--	--	0.2	0.6	0.3
d)	Catalytic	Catalytic	77.3	36.8	38.8	0.09	0.5	0.06	0.3	0.8	0.6

Conditions: 2/1 solvent (naphthalene) to coal (dmmf); catalyst MoS<sub>2</sub>, 1% wt dmmf; pretreatment 350°C, 1 h, 7 MPa H<sub>2</sub> (cold); liquefaction 425°C, 10 min 7 MPa H<sub>2</sub> (cold).

<sup>1</sup> By difference; <sup>2</sup> After pretreatment; <sup>3</sup> Net yield (pretreatment + liquefaction)

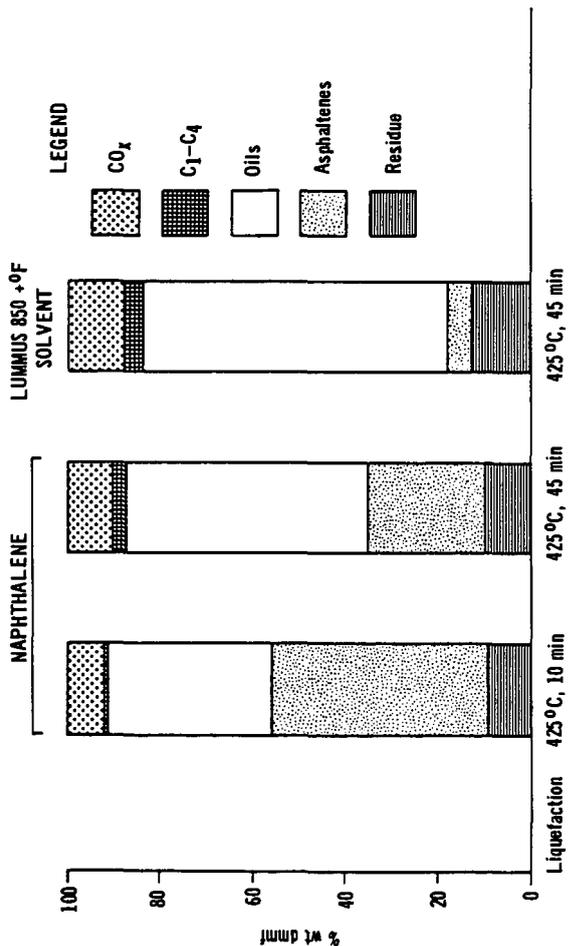


Figure 1. INFLUENCE OF LIQUEFACTION CONDITIONS AND SOLVENT COMPOSITION ON TEMPERATURE STAGED CATALYTIC LIQUEFACTION; SUBBITUMINOUS COAL, WYODAK (PSOC-1401)

Pretreatment 350°C, 1h, 7 MPa H<sub>2</sub>, 1% wt MoS<sub>2</sub>

## TWO-STAGE COAL LIQUEFACTION WITHOUT GAS-PHASE HYDROGEN

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### INTRODUCTION

Current two-stage direct coal liquefaction processes require the use of high-pressure purified hydrogen to hydrogenate either the solvent or a coal/solvent slurry. This paper describes techniques to eliminate the direct use of hydrogen gas in the solvent production and primary coal liquefaction stages. The approach employs the water-gas shift (WGS) reaction to generate liquefaction hydrogen-donor solvents at low temperatures and pressures in a catalytic solvent production stage, followed by reaction of the solvent with coal, in the absence of hydrogen, in a thermal primary liquefaction stage.

Previous researchers (1,2) have used mixtures of carbon monoxide and steam to convert coal in single-stage processes operated at high temperatures (380 to 475°C) and pressures (to 5000 psi). Although pilot tests with high-reactivity, low-rank coals achieved moderate conversions to benzene-soluble products, yields of distillate oils were low (3).

In an initial portion of this study it was proposed (4) that a significant improvement in coal liquefaction using CO/H<sub>2</sub>O mixtures may be realized by separating, or staging, the WGS-solvent production and coal liquefaction reactions, allowing each to be performed at an optimum temperature. Results of thermodynamic calculations and preliminary experiments proved that use of low temperatures (<300°C) favors solvent hydrogenation via the WGS reaction, thus allowing the use of low pressure (500 psi). In contrast, high temperature kinetically favors the reactions involved in coal liquefaction--coal molecule bond rupture and transfer of hydrogen from donor solvent compounds to coal moieties. This paper describes the results of flow reactor experiments to produce a liquefaction solvent at space velocities comparable to actual processes, and use of this solvent to liquefy coal. Both of these steps have been accomplished without the use of hydrogen feed gas, and high conversions of a bituminous coal have been achieved.

### EXPERIMENTAL

Two series of experiments, described briefly here and in more detail in the following sections, were performed. The first consisted of production of a coal liquefaction solvent, rich in hydroaromatics, via the WGS reaction in a catalytic flow reactor at low temperature and pressure. In the second set of experiments coal was thermally liquefied in batch microreactors without gas-phase hydrogen using the solvent produced in the flow reactor.

## Materials

Feeds to the WGS-solvent production reactor consisted of carbon monoxide, deionized water and a nearly saturated mesitylene solution of polynuclear aromatic hydrocarbons (weight basis PAH's: 11.6% phenanthrene, 12.0% pyrene and 16.7% fluoranthene). Mesitylene was chosen as the solvent for the PAH's because of its relatively low vapor pressure (75 psi at 240° C), its ability to dissolve large amounts of PAH's at room temperature, and its stability under high temperature coal liquefaction conditions. Extrudates (0.8 mm diameter by 4 mm length) of Shell 324M, a 2.8 wt. % Ni, 12.4 wt. % Mo on alumina catalyst, were used in the WGS-solvent production reactor. Prior to use, the catalyst was presulfided, in-situ for six hours, with 10 mole % H<sub>2</sub>S in H<sub>2</sub> at 385° C and atmospheric pressure.

Liquefaction reactions were performed with a bituminous coal, Illinois #6 (Burning Star Mine--proximate analysis: 3.7% moisture, 9.4% ash, 34.5% volatile and 52.4% fixed carbon; dry basis ultimate analysis: 72.5% C, 4.7% H, 1.0% N, 0.1% Cl, 2.9% S, 9.8% ash, and 9.0% O by difference; mineral matter content: 13.7%).

## Apparatus and Procedure

WGS-solvent production was performed in a concurrent flow trickle-bed reactor consisting of six 1.0 cm ID by 15 cm long catalyst-filled stainless steel tubes connected in series. Each tube was filled with 10.5 g of catalyst. The reactor was contained in a forced-air convection oven thermostatted to ±1.0° C. Reactor pressure was controlled with a precision back-pressure regulator and gas and liquid products were sampled subsequent to pressure letdown. After pressurizing to 500 psig with CO, the reactor temperature was ramped to 240° C at 10° C/min and water flow was initiated. Upon detection of conversion of CO/H<sub>2</sub>O to CO<sub>2</sub>/H<sub>2</sub>, PAH solution flow was started. Carbon monoxide, water and the PAH solution were delivered to the reactor at weight hourly space velocities of 0.124, 0.079, and 0.48 g-feed/hr/g-catalyst, respectively. For the WGS reaction, the amount of water delivered was one percent in excess of that required by stoichiometry to ensure that conversion was limited only by thermodynamic equilibrium. It was estimated from the reactor void volume and fluid flow rates that the residence time of the gas was two minutes and that of the liquid phase was approximately sixty minutes.

Prior to use for the liquefaction reactions, the solvent produced by the flow reactor was concentrated by nearly a factor of two by evaporation of mesitylene under vacuum. This higher concentration, which allowed the use of lower solvent to coal ratios for the liquefaction reactions, could be achieved because of the increased solubility of the hydroaromatics formed in the flow reactor.

Coal liquefaction reactions were performed in batch microautoclaves with slurry capacities of 8 cm<sup>3</sup> and gas volumes 35 cm<sup>3</sup> (5). Four reactors could be operated simultaneously. After the reactors were charged with coal and solvent, they were pressurized to 450 psig with nitrogen. They were then heated to 445° C for 36 min (time at temperature) in a fluidized sand bath while being agitated with a wrist-action shaker at 200 cycles/min. Following the heating

period, the reaction vessels were quenched in water, the final temperatures and pressures were recorded, a gas sample was taken, and the product slurry was quantitatively removed for analysis. All experimental variables for both the flow and batch reactors were monitored and recorded with a computer-controlled data acquisition system.

Four coal liquefaction reactions were performed. To test the impact of amount of donatable solvent hydrogen on coal conversion, three reactions were performed with WGS-produced solvent to coal ratios of 2:1, 3:1, and 4:1. A control experiment, without donatable hydrogen, was performed with a portion of the flow reactor PAH feed solution, which contained no hydroaromatics. The control experiment had a "solvent" to coal ratio of 3:1.

#### Product Analyses

On-line analyses for the partial pressures of CO and CO<sub>2</sub> in the gas stream from the flow reactor were performed with a Hewlett-Packard 5710A gas chromatograph. Prior to analysis, residual water vapor was eliminated from the gas sample with a cold trap. The partial pressure of hydrogen was obtained by the difference between the sum of the CO and CO<sub>2</sub> pressures and the sample pressure. Gas samples from the liquefaction reactions were analyzed for N<sub>2</sub>, H<sub>2</sub>, CO, CO<sub>2</sub>, and C<sub>1</sub>-C<sub>4</sub> hydrocarbons with a Carle series 500 gas chromatograph with a hydrogen transfer system.

The amounts of PAH's and hydroaromatics in the flow reactor feed and liquid product samples were determined with a Hewlett-Packard 5890 capillary column-equipped gas liquid chromatograph. Coupled gas chromatography/mass spectrometry techniques were used to identify the order of elution of the PAH's and hydrogenated PAH's.

Conversion of coal to products was quantified by tetrahydrofuran (THF) and n-heptane (C<sub>7</sub>) solubility. Dry, mineral matter free (dmmf) basis conversions were calculated from the difference between the weight of organic coal and the insoluble organic matter resulting from THF or C<sub>7</sub> extraction of the product. In addition, the C<sub>7</sub> soluble materials, which contained the post-reaction solvent components, were examined by capillary column chromatography to determine the extent of dehydrogenation of solvent hydroaromatics.

## RESULTS AND DISCUSSION

#### WGS Solvent Hydrogenation

The performance of the WGS-solvent production reactor can be evaluated in terms of conversion of CO/H<sub>2</sub>O to CO<sub>2</sub>/H<sub>2</sub>, and the extent of hydrogenation of the PAH's.

From the gaseous product analyses, the conversion of CO/H<sub>2</sub>O to CO<sub>2</sub>/H<sub>2</sub> was observed to be 97%. This is significantly greater than the value of 92% calculated from the initial partial pressures of CO and steam and the pressure equilibrium constant (6) for 240<sup>o</sup> C. The observed larger conversion results from removal of hydrogen due to hydrogenation of the PAH's, which causes an additional shift to

products. Thus, coupling the WGS and solvent hydrogenation reactions promotes efficiency for the WGS reaction.

The extent of hydrogenation of the PAH's can be seen in Figure 1, which shows a comparison of the chromatogram of the feed solution to that of the product. Analysis of the product solution showed that 31% of the phenanthrene, 49% of the pyrene and 92% of the fluoranthene were converted to hydroaromatics. From the amount and distribution of the hydroaromatics and the extent of the WGS reaction, it was calculated that 30% of the hydrogen generated was used to produce hydroaromatics. The liquid product was found to contain 0.52 wt. % donatable hydroaromatic hydrogen. The solvent for the coal liquefaction reactions, concentrated by removal of mesitylene from the flow reactor product, contained 0.87 wt. % donatable hydrogen, a high value by current process standards.

It is notable that almost complete conversion of fluoranthene to hydrofluoranthenes (primarily tetrahydrofluoranthene, which accounted for half of the donatable hydrogen) was achieved, while only half of the pyrene and a third of the phenanthrene were hydrogenated. For pyrene (Py), the limitation for conversion to dihydropyrene ( $H_2$ Py) is a thermodynamic one. The equilibrium ratio of  $[H_2Py]/[Py]$  may be calculated from the reactor outlet hydrogen partial pressure (155 psia) and the pressure equilibrium constant (7) at 240 °C, 0.0042/psia. The calculated value of 0.65 is in agreement with the observed value of 0.66, indicating that the concentration of dihydropyrene was limited by thermodynamics, rather than kinetics. The production of hydrophenanthrenes may also be thermodynamically limited, though no thermodynamic data are available for comparison. Although the WGS-solvent production reactor yielded high concentrations of hydroaromatics, previously reported work (7) indicates that even better performance can be achieved with a more active catalyst at lower temperatures, where formation of hydroaromatics is favored.

### Coal Liquefaction

The effectiveness of the coal liquefaction reactions performed without gas phase hydrogen can be judged by the conversion of the coal to THF and  $C_1$  soluble products, and to  $C_1$ - $C_4$  hydrocarbons; by the amount of hydrogen transferred from hydroaromatic hydrogen donors to the coal; and by the percentage of hydrogen lost from the solvent to the gas phase.

Table 1 presents a summary of the results of the liquefaction experiments. As can be seen, the conversion of coal was dependent on solvent hydrogen availability. For the control experiment (No. 1), containing no donatable hydrogen, the THF and  $C_1$  conversions were very low: 30% and 17%, respectively. However, all the experiments with WGS-produced solvent, containing hydroaromatics, yielded much higher conversions, which increased with increasing solvent to coal ratio. The 4:1 solvent to coal experiment (No. 4), resulted in the highest THF and  $C_1$  conversions, 98% and 48%, respectively. The  $C_1$ - $C_4$  hydrocarbon/gas make for the experiments with the WGS-produced solvent (Nos. 2-4) were low, nominally 3%.

The fate of the donatable hydroaromatic hydrogen in the solvent was determined from the amounts in the solvent before reaction with coal  $H_a$ , that remaining in the solvent after reaction with coal  $H_b$ , and that transferred to the gas phase  $H_g$ . The percentage donated to the coal  $H_c$  can be calculated by difference:

$$H_c = 100 \times \frac{H_b - H_a - H_g}{H_b} .$$

From the values for  $H_g$  in Table 2 it can be seen that the utilization of hydrogen was efficient, as only 10% of the donatable hydrogen was lost to the gas phase, the balance being donated to the coal or remaining with the solvent. It is also noted from the values of  $H_b$  that nearly all of the donatable hydrogen was depleted from the solvent. In fact, experiment No. 2 with a 2:1 solvent to coal ratio was clearly hydrogen starved, resulting in the lowest THF and  $C_7$  conversions for the experiments with WGS-produced solvent. In contrast, experiment No. 4, with a solvent to coal ratio of 4:1 had sufficient donatable hydrogen to achieve high conversions, as evidenced by the 20% donatable hydrogen remaining after completion of the reaction.

#### PROCESS IMPLICATIONS

The results of the experiments presented in this paper clearly demonstrate that coal can be effectively liquified without the use of high-pressure purified hydrogen feed gas. This suggests that substantial economic improvements in direct coal liquefaction can be achieved. Figure 2 shows a schematic flow diagram for a two-stage liquefaction process proposed on the basis of these results. Notable differences between this and current two-stage processes are: 1) elimination of high-pressure purified hydrogen for solvent production; 2) use of low temperature in the solvent production reactor; 3) elimination of gas-phase hydrogen and high pressures in the thermal liquefaction reactor; and 4) selective recycle of solvent components (primarily PAH's). Use of this process would eliminate the requirements for a separate WGS reactor and gas separation units for hydrogen production, and high pressure equipment for solvent production and liquefaction reactors. Because these units account for approximately half of the estimated \$1.5 billion capital investment of a 50,000 barrel/day plant, this process would result in substantial savings in capital costs. Operating costs such as those for compression of gases would also be significantly lower.

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ACKNOWLEDGEMENT

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Figure 1. Comparison of high resolution gas liquid chromatograms of the flow reactor feed and product solutions.

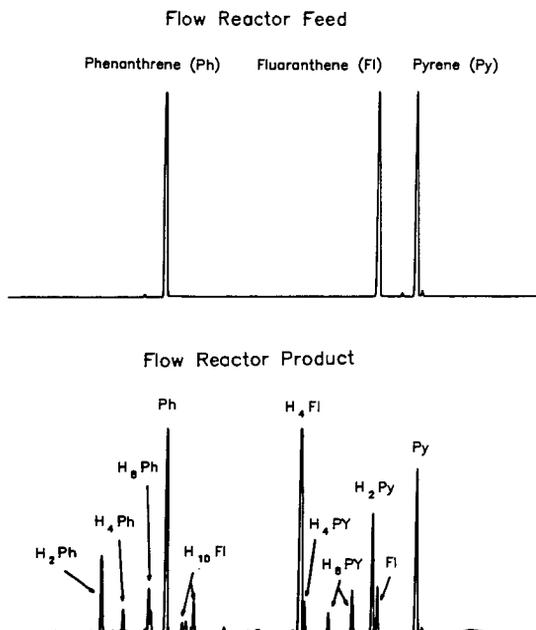


Figure 2. Schematic flow diagram for a two-stage liquefaction process via WGS-solvent production.

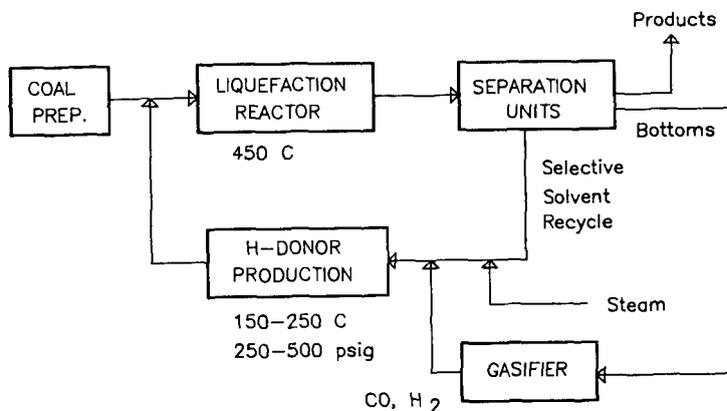


TABLE 1  
Results of Coal Liquefaction Experiments<sup>a</sup>

Exp. No.	Solvent: Coal	Conversions (% dmmf basis)			Solvent Hydrogen Balance (% donatable hydrogen)		
		THF	C <sub>7</sub>	C <sub>1</sub> -C <sub>4</sub>	To Coal	To Gas	Remaining
1 <sup>b</sup>	3:1	30	17	1.6	--	--	--
2 <sup>c</sup>	2:1	91	21	2.9	90	9	1
3 <sup>c</sup>	3:1	97	42	3.1	84	11	5
4 <sup>c</sup>	4:1	98	48	3.1	69	11	20

- a) Reaction conditions for all experiments: 445 C, 36 min, 450 psig cold charge nitrogen. No gas-phase hydrogen used.
- b) Performed with flow reactor feed solution. PAH's only; no donatable solvent hydrogen.
- c) Performed with WGS-produced solvent.

## ENHANCED COAL LIQUEFACTION WITH STEAM PRETREATMENT

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### SUMMARY

A two step process for the liquefaction of coal, in a semi-flow micro reactor, was investigated. The process consisted of pretreating coal with low temperature steam, followed by treatment with supercritical steam. The maximum observed conversion of a Wyodak subbituminous coal, using this two step process, was 40 wt% on a moisture and ash free basis (MAF). The 240 ° C pretreatment step resulted in a 32% increase over the conversion observed with just a 400 ° C treatment. The coal liquid obtained has a number average molecular weight of 325 and a mass average molecular weight of 373, with a narrow molecular weight distribution. The hydrogen and oxygen content of the extract is increased, a significant amount of the oxygen is present as dihydroxyl aromatics. A highly condensed residue of lower hydrogen and oxygen content is obtained which can be of value as a solid fuel.

### INTRODUCTION

Recent investigations have led to the observation (1) that in its native unweathered state coal is a reactive material, far from being the inert solid that it is commonly regarded. Extensive hydrogen bonds connect the poly nuclear aromatic cluster to form a semi-permanent macro molecular structure. The structure is particularly fragile in sub-bituminous coals, and may be subject to rupture with mild treatment to dissociate the hydrogen bonds. Graff and Brandes (2) found that carbon conversion to liquids in pyrolysis at 940 ° C was raised from 23% to over 50% if the coal was exposed to steam for times less than 30 minutes at temperatures between about 320 and 360 ° C. Both pretreatment and pyrolysis were conducted in 50 atm of steam. This result suggests that coal is partially depolymerized by the steam pretreatment, perhaps by the removal of oxygen linkages. If this is indeed the case, improved yields and/or lighter liquids should result if the pretreated coal is liquefied instead of pyrolyzed.

## EXPERIMENTAL

Wyodak coal was pretreated and treated with steam in a semi-flow micro reactor at controlled conditions to exclude oxygen. The apparatus is depicted in Figure 1. The main components are a Milton Roy metering pump (29 to 290cm<sup>3</sup>/hr) which provides a continuous and constant flow of distilled deoxygenated water to the reactor, a Tecam fluidized sand bath (model SBS-4) controlled with a Leeds and Northrup controller (Electromax III), a Helicoid pressure gauge (0 to 3000 PSIG), an autoclave micro metering valve and a micro reactor equipped with a sheathed thermocouple (see Figure 2).

The feed material was an unweathered subbituminous Wyodak coal provided by EPRI in a water slurry kept in a sealed air-tight barrel (#4171). Table 1 shows the elemental analysis of samples taken from this barrel. Samples A and B were taken from the top and middle of the barrel and were suction dried for use. These were the main feed material. About a 50 gm sample of this material was removed from the barrel and vacuum dried; a sample of this material is reported as sample C. A few reactions were carried out with this material.

The suction dried coal was prepared in a Buchner filter, by applying suction to it for about one hour. The top portion of the material was removed from the filter and thoroughly mixed to insure a homogeneous sample for reaction. The moisture content of this material ( $\approx 30$  wt %) was determined by weighing a sample before and after further drying in a vacuum oven at 45 °C for 6 hours. Duplicate samples were used for moisture determinations.

Suction dried Wyodak coal is paste-like, and is messy to handle. A free-flowing coal powder was obtained for reaction experiments by drying the coal in vacuum under mild heating. The vacuum dried coal was prepared by suction drying in a Buchner funnel over nitrogen; the material was then transferred in a jar filled with nitrogen, to a vacuum oven and dried for 72 hours at 45 °C. The experimental reaction procedure for vacuum dried coal was similar to suction dried coal except that the separate moisture determination of the dried coal was no longer necessary.

To prepare for reaction the oven dried micro reactor (see Figure 2) was weighed and then filled with about 4 gm of wet suction dried coal or 3 gm of vacuum dried coal and reweighed for an accurate determination of the quantity of material charged to the reactor. The charged reactor was fitted into the apparatus upon connecting tubings and fittings. The system was purged of air by flushing with nitrogen. Enough water was pumped from the buret into the reactor to raise the pressure to 50 psia, about 10 to 12cm<sup>3</sup> being required. The reactor was lowered into the sand bath, the pressure adjusted to 750 psia with the aid of the micro metering valve, as water was pumped into the system at 0.4cm<sup>3</sup>/min. The steam generated in the heating coil passed through the reactor, was condensed, and collected in an Erlenmeyer flask.

At the termination of an experiment the reactor was removed from the sand bath, and placed in a vacuum oven over night at 45 °C to remove any water. The reactor was then weighed, the contents were removed and placed in a predried and weighed thimble. The reactor was then reweighed, the

change in weight being compared to the weight gain of the thimble.

The coal in the thimble was extracted with toluene for 4 to 6 hours in a Soxhlet apparatus. The thimble was dried over night in a vacuum oven and reweighed to determine the amount of coal extracted. On selected runs the effluent collected in the Erlenmeyer flask was extracted with chloroform and sent to analysis.

The only time the coal sample was exposed to oxygen of the air was during suction drying at ambient temperature. Oxygen was carefully excluded from the reaction system. Feed water to the reactor was deoxygenated by blowing it with nitrogen. From the time of steam pretreatment the reactor remained tightly closed and completely isolated from air until the reactor was cooled down after steam treatment. The only coal that was heated before reaction was that which was vacuum dried at 45 ° C. The suction dried coal was never heated.

#### EXPERIMENTAL RESULTS

Table 2 shows the conversion of Wyodak coal upon pretreatment and treatment with steam at 750 psia. Treatment and pretreatment (if used) steps each lasted 30 minutes. Conversion expresses the fraction of coal that was extracted by the steam from the reactor plus the fraction that was extracted by toluene from the Soxhlet apparatus. The toluene extraction was small, ranging from 0% to less than 3% of the total reported conversion. Toluene extraction was incorporated in our experimental procedure in order to put our experimental results on the same basis with those of other investigators (3,4,5,6) who wash their coal residue with toluene.

With suction dried coal, when not pretreated, treatment with steam at 200 ° C gives a practically zero (2.2%) conversion. Raising the treatment temperature to 400 ° C raises the conversion to 30.5%. Pretreatment with steam at 200 ° C further raises the conversion to 38.5%. Raising the pretreatment temperature to 240 ° C raises the conversion to 40.3%. This is the highest conversion observed in this work, for, upon raising the pretreatment temperature to 320 ° C conversion is lowered to 33.8%. Raising the treatment temperature to 430 ° C further lowers the conversion to 34.2%.

The conversion of vacuum dried coal is reported in the second part of Table 2, and is generally lower than the corresponding results for suction dried coal. Even the mild heating at 45 ° C during vacuum drying made the coal more refractory. Comparison of the results obtained with the two different coal samples convinced us to stop using vacuum dried coal. All other experiments reported here used suction dried coal.

The conversions reported in Table 2 were obtained with 750 psia steam for both the pretreatment and treatment. The effect of steam pressure at the treatment stage was investigated, the results are reported in Table 3. Holding the pretreatment pressure constant at 750 psi, an increase in treatment pressure from 750 to 2500 psia, produced a slight reduction in the observed conversion. Higher pressure apparently increases the rate of retrograde reactions. This effect more than compensates for any increase

in solvent power of the steam at a higher pressure, leading to reduced extraction.

Twenty five experiments were performed in all. The conversions in Tables 3 and 3 represent average values for experiments at the same conditions.

### CHEMISTRY

Extract and residue samples from two experiments, Runs 5 and 27, were analyzed by infrared spectroscopy, NMR and FIMS. Run 5 consisted of a 320 °C pretreatment followed by a 430 °C treatment, while Run 27 was at 200 °C and 400 °C.

Table 4 shows the elemental analyses of the extract and the residue of Run 27. The analysis of the feed coal is also shown for comparison. The extract has a higher H/C ratio (1.28) as compared to the feed coal (0.95), whereas the residue has a lower ratio (0.68). The O/C ratio follows a similar pattern, being higher in the extract (0.32) than in the feed (0.28), and lower in the residue (0.13).

The steam pretreatment/extraction process produces a hydrogen-rich extract which contains oxygenated compounds and heteroatomic species of the original coal, leaving behind a more condensed aromatic residue.

The same trend is indicated for nitrogen and sulfur, being enriched in the extract and reduced in the residue. But here because of the small amounts, especially of nitrogen, accuracy is low.

The infrared spectrum of the steam extract of Run 27 is shown in Figure 3. The IR spectrum is dominated by broad, strong -OH stretching vibrations in the 3400-3100  $\text{cm}^{-1}$  region. The presence of sharp aliphatic -OH bands just below 3000  $\text{cm}^{-1}$  suggests that the extract contains aliphatic material, and reinforces the observed enrichment of H and O in the extract.

Further confirmation is provided by the  $^1\text{H}$  NMR spectrum of the steam extract from Run 5 shown in Figure 4. The ratio of  $\text{H}_{\text{sat}}/\text{H}_{\text{ar}}$  is 1:30. 43% of the  $\text{H}_{\text{sat}}$  hydrogens are associated with methylene, methine, or methyl groups which are not directly bonded to aromatic nuclei. Another 20% of the  $\text{H}_{\text{sat}}$  appearing as a group of signals in the 2-3 ppm region are associated with hydroaromatic structures or associated with methyl, methylene and methine groups directly attached to an aromatic nucleus. The dominant sharp signal at 1.2 ppm is characteristic of long chain polymethylene groups. Thus, one of the major constituents of the hydrogen rich extract is aliphatics present primarily as long chain polymethylenes, either as free species or attached to aromatic/hydroaromatic ring systems.

The  $^{13}\text{C}$  NMR spectrum (Figure 5) is dominated by a number of well resolved lines riding on a spectral envelope in the 15-80 ppm region which is the normal chemical shift region for aliphatic compounds, supporting the presence of significant quantities of aliphatic materials in the steam extract. The most intense signal is at 30.2 which is generally assigned to the internal methylene carbons ( $\text{C}_1\text{-C}_2\text{-C}_3\text{-C}_n$ ) of straight chain alkanes corroborating the presence of long chain polymethylene groups (minimum average carbon chain length;  $n_c \sim 8-10$ ) which may or may not be attached to an

aromatic ring.

The group of signals in the 15-20 ppm region is probably due to the methylene carbons attached to aromatic rings. The presence of a broad spectral envelope in addition to the sharp alkane lines demonstrate the extract's complexity. The spectral complexity is due to the presence of small amounts of polymethylene type compounds. The complex band of carbon signals in the 120-130 ppm region is due to the aromatic and polycyclic aromatic species. Interestingly, a small, but distinctive signal occurs at 179 ppm which is where the carbonyl carbon of a -COOH group appears suggesting the presence of some carboxylic acids in the extract.

Field ionization mass spectrometry (FIMS) is a mass spectrometry technique which uses a soft ionization mode and allows most molecules to be observed as unfragmented molecular ions. The method can provide a true molecular weight profile for any given complex mixture. Figure 6 represents the field ionization mass spectrum of the extract. The extract has a very narrow molecular weight distribution with number average ( $M_n$ ) and weight average ( $M_w$ ) molecular weight of 315 and 373, respectively. Since 75% of the material was volatilized in the FIMS probe the observed molecular weights are a true representation of the extract and the extract is composed of low molecular weight compounds. The most prominent peaks in the spectrum appear at  $m/z$  110, 124, and 138 and can be assigned to dihydroxyl benzene and its methyl and ethyl analogs, respectively. Surprisingly no prominent peaks due to monohydroxyl benzene (phenol) or its C-1 or C-2 analogs are found. The oxygenated compounds present in the extract are best represented by the class of dihydroxyl benzenes and other dihydroxyl aromatics. There are a number of other prominent peaks in the higher molecular weight range which, in all probability, arise from the polymethylenes attached to an aromatic ring (identified by NMR) but the FIMS analysis does not allow ready identification of these compounds.

The presence of reactive components like the polymethylene species, the dihydroxyl benzenes, and the low molecular weight profile of the extract suggests that the coal is very reactive and not a highly condensed, very large molecular weight, intractable molecule. Self condensation and crosslinking reactions of the dihydroxyl aromatics, alkylation of the activated aromatic rings by the polymethylene species in the coal, are some of the retrogressive reactions that these coals can undergo, under the severe processing conditions generally employed.

Pretreatment with steam, at lower temperatures, allows the breaking of hydrogen bonds, loosening up the coal matrix, and stabilizing some of the reactive components in the coal. When the temperature increases during the supercritical extraction step, many of these reactive molecules can be steam volatilized or steam extracted, escaping the loosened coal matrix structure before undergoing retrogressive reactions. This explanation is supported since the introduction of a low temperature pretreatment step before the supercritical steam extraction leads to a 32% increase in conversion.

The presence of reactive dihydroxyl benzenes in the extract is also supporting evidence. Dihydroxyl aromatics have never been reported as occurring in coal liquids obtained under normal coal processing

conditions generally employed. They cannot survive the severe processing conditions. Small amounts of dihydroxyl aromatics have been obtained in flash or fast pyrolysis conditions. The very rapid heating allows the dihydroxyl aromatics to escape the coal matrix before they can undergo retrogressive reactions.

#### CONCLUSIONS

The steam pretreatment-extraction process produces enhanced extractan yields. The extract has a high H/C ratio due to the presence of long chain polymethylene compounds which may or may not be attached to aromatic rings. The extract contains significant amounts of oxygenated compounds, some of which are present as dihydroxyl aromatics. A highly condensed residue (low H/C ratio) is obtained which can be attractive as a solid fuel for combustion.

#### ACKNOWLEDGEMENTS

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TABLE 1

## ANALYSIS OF WYODAK COAL

SAMPLE	A	B	C
	Wet	Wet	Vacuum Dried
Carbon	59.51	59.72	58.17
Hydrogen	4.70	4.13	4.35
Oxygen	17.90	22.44	18.94
Nitrogen	0.70	0.76	0.63
Chlorine	-	-	-
Sulfur	3.07	2.55	3.07
Ash	13.50	13.47	16.46
TOTAL	99.55	103.07	101.62
BTU/lb	10,614	-	10,141

Analysis of samples was performed by Huffman Laboratory.

TABLE 2

## Conversion of Wyodak Coal upon Pretreatment and Treatment with Steam at 750 psig

Pretreatment Temp °C	Treatment Temp °C	% Conversion MAF
Suction dried coal		
None	200	2.2
None	400	30.5
200	400	38.5
210	400	40.3
320	400	33.8
320	430	34.2
Vacuum dried coal		
None	400	27.3
200	400	38.4
240	400	34.0

TABLE 3

## Effect of Pressure of Treatment Steam on Conversion

Pretreatment Treatment	Temperature: 200°C Pressure: 750 psia Temperature: 400°C
Pressure of Treatment Steam, psia	% Conversion MAF
750	38.5
1500	36.6
2500	36.9

TABLE 4

## Elemental Analysis of Extract, Residue, and Feed of Run 37

Wt %	Extract	Residue	Feed
C	54.21	64.97	59.72
H	5.77	3.69	4.13
O	23.42	11.20	22.44
N	4.08	1.01	0.76
S	4.30	2.75	2.55
Ash	8.04	17.55	13.47
Atomic Ratio			
H/C	1.26	0.69	0.95
O/C	0.32	0.13	0.28

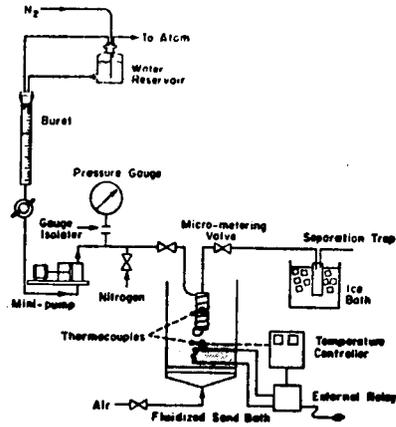


Figure 1: Experimental Apparatus

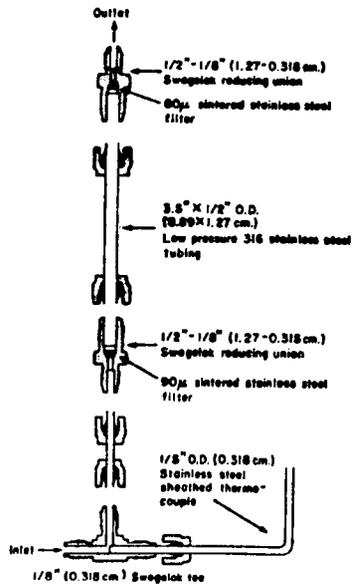


Figure 2: Exploded View of Micro-reactor

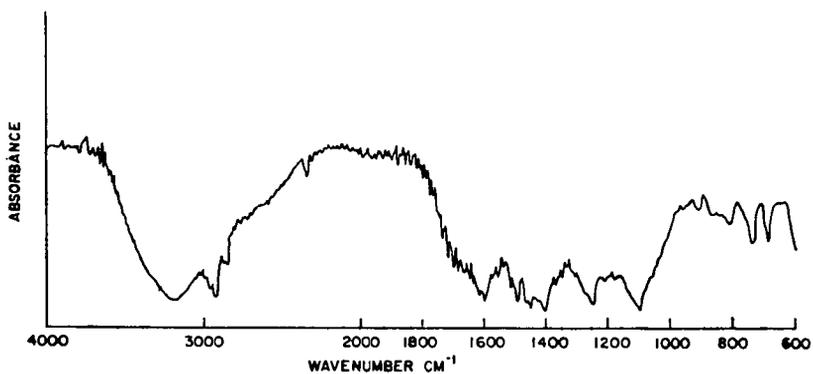


Figure 3: Infrared Spectrum of Steam Extract of Run 27

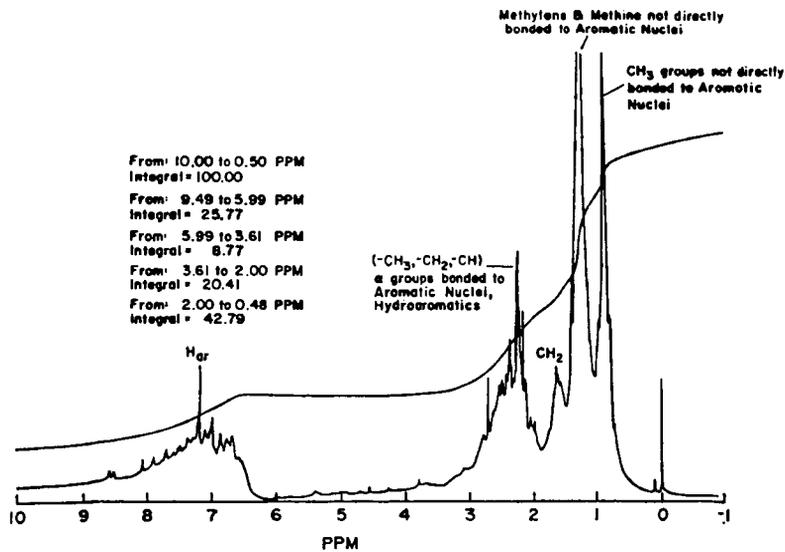
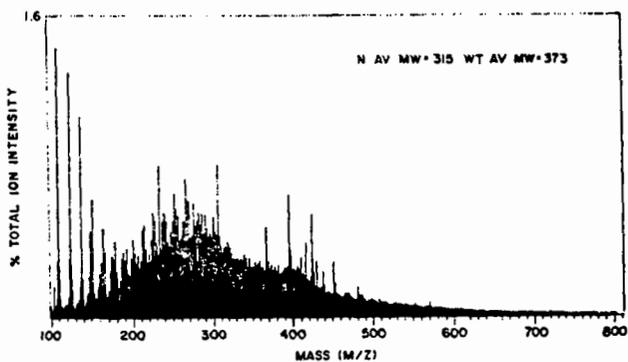
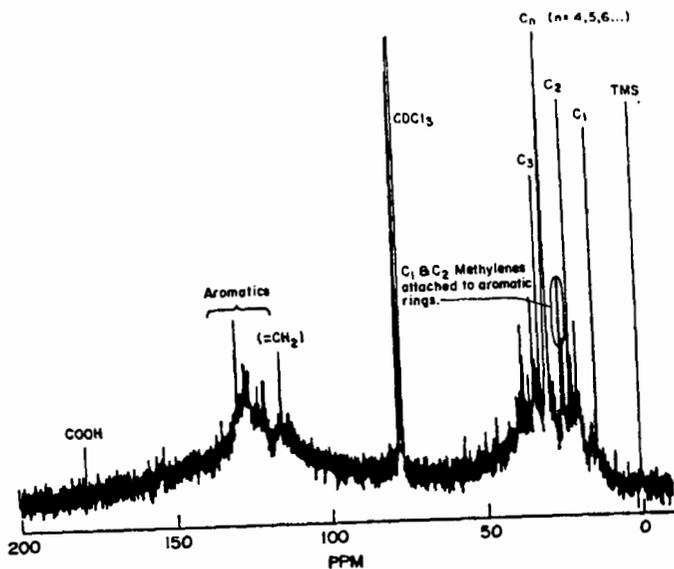


Figure 4: 470 MHz  $^1\text{H}$  NMR Spectrum of Steam Extract of Run 5



## THE EFFECT OF REACTION CONDITIONS ON SOLVENT LOSS DURING COAL LIQUEFACTION

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### INTRODUCTION

The fate of a coal-liquefaction recycle solvent during Integrated Two-Stage Liquefaction (ITSL) and other direct liquefaction processes is a major concern. If the solvent has an inadequate concentration of hydrogen donors or other solvent components that might enhance liquefaction, then the quality of the solvent will be degraded and conversion to liquid products will be adversely affected. Studies using the solvents phenol (1), tetrahydroquinoline (2-4), quinoline (5), and pyridine (6) have shown that these compounds are partially incorporated by covalent bonds, but a relatively large amount is hydrogen bonded to coal-derived products. In other studies using pure  $^{13}\text{C}$ - and  $^{14}\text{C}$ -labeled aromatic or hydroaromatic compounds as solvents (3,6-8), the amount of adduction was determined. Although adduction and hydrogen bonding of solvent components account for solvent loss, other degradative reactions also account for loss of original solvent and solvent quality. Ring contraction of tetralin (9), and octahydrophenanthrene (8,10) under coal-liquefaction conditions reduces the hydrogen-donor concentration and therefore the solvent quality.

The use of a one-component solvent system can be misleading because reactions with coal may be occurring that normally would not occur if other components of a solvent were present. The objective of this study was to examine a multicomponent synthetic solvent and determine if solvent components are preferentially lost or degraded during short-contact-time liquefaction (SCTL), and how solvent loss in SCTL compares with other liquefaction conditions that involve gradual heat-up.

### EXPERIMENTAL

Experiments were performed in a microreactor assembly (11) consisting of a 316 stainless steel 1/2-in. union tee with two end caps. Five grams of a synthetic solvent and one gram of moisture-free Western Kentucky 9/14 coal were added to the microreactor, which was assembled and pressurized to 1100 psig with  $\text{H}_2$ . The synthetic solvent consisted of 4% quinoline, 13% m-cresol, 20% tetralin, 33% 1-methylnaphthalene, 20% phenanthrene, and 10% pyrene. Experiments were conducted with one- and two-component solvents and coal in order to identify unique products from each of the simple solvent systems. The two-component solvent consisted of 20% pyrene and 80% tetralin, or 20% phenanthrene and 80% tetralin. One-component solvents of 1-methylnaphthalene, tetralin, and m-cresol were also used. The microreactor assembly was attached to a wrist-action shaker that moved the reactor through a small arc for adequate mixing of the reactor contents. The shaker was positioned above a vertically moving platform that supported a fluidized sand bath (11).

For SCTL experiments, the bath was heated to an initial temperature of 460°C. When the experiment was initiated, the temperature set point was changed to 425°C and the platform (with bath) was raised, immersing the microreactor. Heat-up to 425°C took approximately 1 min. Reaction time was 3 min at 425°C. For experiments conducted under traditional or severe conditions, the reactor was immersed in the sand bath, which was at room temperature, gradually heated (55 min) to 425°C, and held at reaction temperature for 30 min or 6 hours. At the end of the

reaction, the platform was lowered and the microreactor was cooled with a stream of room-temperature air. The outside of the cooled microreactor assembly was cleaned (to remove sand) with compressed air. Gases were vented, and the microreactor was disassembled.

The reacted suspension was pipetted into a 50-mL volumetric flask containing 0.100 gm durene and 0.100 gm fluorenone, which were the internal standards used for quantitative capillary gas chromatography. The remaining residue and synthetic solvent in the microreactor were removed with tetrahydrofuran (THF) and added to the flask. Aliquots were then analyzed using a 50-meter highly cross-linked phenylmethylsilicone capillary column. Flame ionization was used to detect individual components of the treated synthetic solvent, although in certain instances a mass-selective detector was also used to assist in the identification of products.

Solvent loss of each component was determined by calculating the difference between the original amount of the component and the recovered amount of the component and its reaction by-products. Solvent that was lost and unaccounted for represented adducted or polymerized material. All percentages will be discussed on an absolute basis; therefore, the loss of 10% tetralin would represent 10% of the synthetic solvent and not 10% of the 20% tetralin present in the synthetic solvent. The solvent losses would be five times larger if they were based on the weight of the coal sample, since the solvent:coal ratio was 5:1, i.e., loss of 3% of the solvent by adduction would represent a 15% addition to the weight of the coal.

## RESULTS AND DISCUSSION

The effect of reaction conditions on solvent loss, and specifically on preferential loss of components of the solvent, was examined at three sets of reaction conditions. Experiments were conducted under SCTL conditions (rapid heat-up, 3 min at 425°C), traditional conditions (gradual heat-up, 30 min at 425°C), and severe conditions (gradual heat-up, 6 hours at 425°C). The advantages in using this synthetic solvent are that all components of the solvent are known, its elemental composition is similar to a coal-derived recycle solvent, and the multi-component solvent simulates a recycle solvent better than a one-component solvent does. The use of a synthetic solvent also allows the study of individual components in a more realistic environment.

The objective was to examine solvent recovery with increasing severity of coal-liquefaction reaction conditions. The SCTL stage of an ITS process involves rapid heat-up, followed by a short residence time at reaction temperature. During rapid heat-up, the rate of free-radical production should increase significantly in a SCTL stage. An increase in free-radical concentration was hypothesized, since the demand for hydrogen, with increased free-radical production, would increase and would be less likely satisfied by hydrogen donors and gaseous hydrogen. With an increase in free-radical concentration, a concomitant increase in solvent adduction was hypothesized, since free-radical addition, aromatic substitution, and polymerization reactions involving solvent and coal free-radicals would be likely.

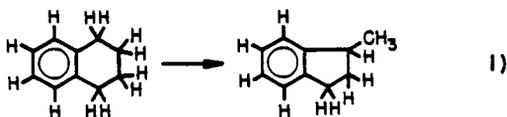
In comparing results obtained under SCTL conditions (Table 1) with results obtained from experiments conducted under traditional liquefaction conditions (gradual heat-up to 425°C, 30 min at 425°C), solvent loss due to adduction should also be occurring under traditional conditions. As the severity of the liquefaction conditions is increased, adducted solvent should undergo cleavage (cracking, hydrogenolysis, etc.) and re-form solvent-like products, resulting in improved solvent balance. While the original components may not be recovered, products having similar structures and chemical properties should be. For example, adduction of phenanthrene with a coal-derived benzylic radical may occur

and may ultimately form methyl-substituted phenanthrene (Figure 1). Based on this hypothesis, severe solvent loss was expected with a SCTL process compared to moderate solvent loss under traditional liquefaction conditions, and if the conditions were severe enough, solvent that was initially adducted, or solvent-like products, could be recovered.

Results from SCTL reactions demonstrated that components of the synthetic solvent were not adducted, degraded, or lost. While 75%-85% of the coal was converted to THF-soluble material, only 2.6% tetralin underwent dehydrogenation. No adduction of m-cresol or quinoline was observed. Results using a synthetic solvent demonstrate that SCTL is a favorable process because solvent balance with little solvent degradation can be achieved. These results were unexpected and suggest that an increased concentration of free radicals in a short period of time does not cause solvent loss or degradation when sufficient readily donable hydrogen is present. The results also imply that free radical production does not play an important role in solvent loss via adduction.

It should also be understood that little, if any, of the recovered, original solvent components are coal-derived. Based on coal experiments performed with one- and two-component solvents, negligible quantities of quinoline, m-cresol, and 1-methylnaphthalene could be considered coal-derived, while a maximum of 0.2% tetralin, 0.3% naphthalene, 0.2% pyrene, and 0.1% phenanthrene were coal-derived.

Experiments conducted using traditional coal liquefaction reaction conditions showed that solvent balance could still be achieved, but degradation of the solvent had started to occur. Results from experiments performed in the absence of coal showed that little, if any, demethylation and decomposition of 1-methylnaphthalene had occurred. Reactions in the presence of coal showed that approximately 3.2% 1-methylnaphthalene had undergone demethylation and decomposition. Some of the demethylated product (2.2%) could be accounted for by the increased amounts of naphthalene. Tetralin reactions included dehydrogenation to naphthalene (6.1%), rearrangement to 1-methylindane (0.5%), and decomposition to butylbenzene (0.1%). The total amount of tetralin and its reaction products is 22.2%; therefore, the additional amount (based on 20% tetralin in the synthetic solvent) could be accounted for by demethylation of 1-methylnaphthalene. It is possible that more than 2.2% 1-methylnaphthalene underwent demethylation to naphthalene if tetralin was being lost via unidentified reactions and not via dehydrogenation to naphthalene. If this occurred, then greater amounts of recovered naphthalene could be attributed to the demethylation of 1-methylnaphthalene and not to the dehydrogenation of tetralin. Methylation was also occurring, and 0.4% dimethylnaphthalene and 0.3% dimethylphenol were produced. Hydrogenation of the aromatic components was also occurring, producing 1.0% methyltetralin, 1.7% dihydrophenanthrene, 0.1% tetrahydrophenanthrene, 0.8% dihydropyrene, and 1.3% tetrahydroquinoline. The production of methyltetralin is most likely occurring via the hydrogenation of 1-methylnaphthalene, since no methylation of tetralin was observed when blank experiments using tetralin as a solvent were conducted. The major degradation reactions occurring were rearrangement of tetralin to 0.5% 1-methylindane (Equation 1) and cracking to butylbenzene (0.1%).



While some of the quinoline was undergoing hydrogenation to tetrahydroquinoline (1.3%), 0.3% could not be accounted for. Solvent balance under traditional liquefaction conditions was quite good. While methylation, demethylation, rearrangement, and cracking reactions have become apparent, 98.6% of the solvent can still be accounted for (less possible coal-derived products) and had not been lost because of adduction with coal-derived products.

Treatment of coal and solvent at more severe conditions resulted in greater rearrangement and degradation of the individual solvent components, although the solvent balance was approximately 97.5%. As much as 16.5% of 1-methylnaphthalene had undergone reaction. At least 12% 1-methylnaphthalene could be accounted for because of demethylation, methylation, and hydrogenation. Extensive dehydrogenation of tetralin was expected, and only 6.3% tetralin was recovered. Rearrangement reactions were significant and again were a major reason for the decrease in solvent quality. Approximately 2.1% tetralin had rearranged to 1-methylindane. Some loss of most components of the solvent had occurred. Methylation and demethylation of m-cresol was greater than observed under traditional liquefaction conditions, and approximately 11.1% was recovered. While quinoline represented the component that was present in the smallest amount, it was preferentially lost, and only 1.8% of quinoline and tetrahydroquinoline could be accounted for. While most of the solvent could be accounted for (approximately 97.5%), only 61.1% was recovered as original solvent and represented a solvent of much poorer quality.

Experiments conducted under these severe reaction conditions have shown that the synthetic solvent has undergone many reactions. Degradation reactions were evident; and greater, not lesser, quantities of solvent were lost. Even under these severe conditions, the overall solvent balance was better than expected.

#### SUMMARY

The effect of reaction conditions on solvent loss was determined. Solvent recovery and solvent balance were better than expected for SCTL and traditional liquefaction conditions. Surprisingly, very little adduction of solvent components was observed. Increased severity of reaction conditions caused an increase in degradation of the synthetic solvent and an increase in adduction (approximately 2.5%). From these results, the extent of solvent adduction under most liquefaction conditions is minimal, and the solvent quality is most affected because of increased degradation with increasing severity.

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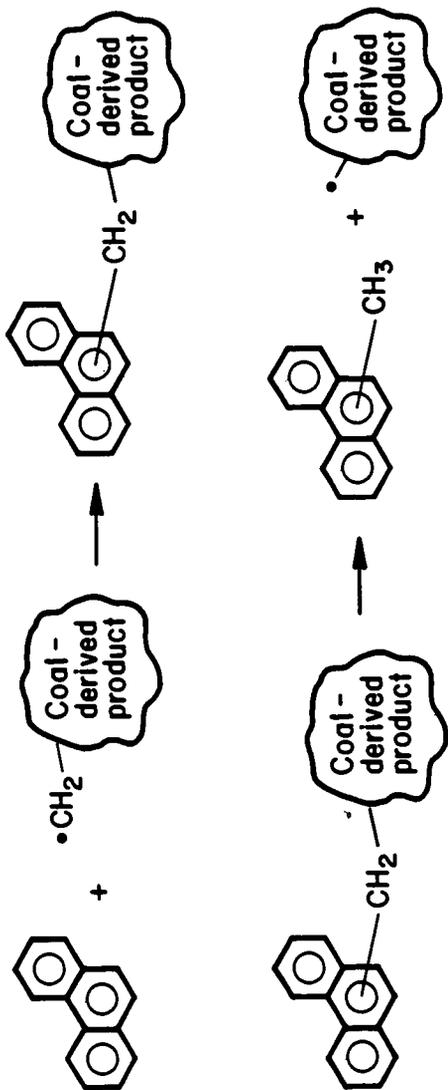
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TABLE 1. Solvent Recovery Values

Components and Percentages in Original Synthetic Solvent	Percentage of Components in Reacted Synthetic Solvent <sup>1</sup>							
	SCTL				Reaction Conditions			
	Solvent	Coal + Solvent	Solvent	Coal + Solvent	Solvent	Coal + Solvent	Solvent	Coal + Solvent
1-Methylnaphthalene	33	33.3	32.8	32.7	28.4	27.9	16.5	16.5
Dimethylnaphthalenes	--	--	--	--	0.4	--	0.6	0.6
Methyltetralins	--	--	--	0.1	1.0	1.2	2.0	2.0
Tetralin	20	20.1	17.5	19.6	15.5	16.6	6.3	6.3
Naphthalene	--	0.1	2.6	0.4	6.1	3.8	20.4	20.4
Ethylbenzene	--	--	--	--	--	--	0.1	0.1
Methylindane	--	--	--	0.2	0.5	1.7	2.1	2.1
Butylbenzene	--	--	--	0.1	0.1	0.2	0.4	0.4
Phenanthrene	20	20.1	19.8	19.4	18.1	17.3	17.3	17.3
Dihydrophenanthrene	--	0.1	0.5	0.8	1.7	2.4	0.8	0.8
Tetrahydrophenanthrene	--	--	--	--	0.7	0.3	0.5	0.5
m-Cresol	13	12.9	12.7	12.7	12.1	11.7	11.1	11.1
Dimethylphenol	--	--	--	--	0.3	--	0.7	0.7
Phenol	--	--	--	--	0.1	0.1	0.3	0.3
Pyrene	10	9.8	9.6	9.2	8.5	8.3	8.4	8.4
Dihdropyrene	--	0.1	0.1	0.7	0.8	1.4	0.5	0.5
Quinoline	4	4.1	4.0	3.3	2.4	1.6	1.5	1.5
Tetrahydroquinoline	--	0.1	0.1	0.8	1.3	1.6	0.3	0.3
Unidentified Solvent-Derived Products	--	--	0.1	0.3	1.2	2.7	4.9	4.9
Unidentified Solvent-Derived and/or Coal-Derived Products	--	--	--	--	1.5	--	2.8	2.8
Total Recoveries		100.7	99.8	100.3	100.1	98.8	97.5	97.5

<sup>1</sup> Values represent average of at least duplicate experiments.



**Figure 1. Methylation of Solvent by Coal**