

SINGLE-STAGE, SLURRY-CATALYZED CO-PROCESSING DEVELOPMENTS

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INTRODUCTION

UOP is currently in the sixth year of a co-processing research program sponsored by the U. S. Department of Energy (DOE). Earlier work, under completed contract DE-AC22-84PC70002, has been reported in a series of papers and reports (1-7). The overall objectives, to evaluate the technical feasibility of the co-processing concept and to establish a co-processing process data base, were met. The concept of single-stage, slurry-catalyzed co-processing was successfully demonstrated in laboratory batch experiments (1). The concept was further extended to include continuous bench-scale operations (2). Good long-term operability of the process was demonstrated in the continuous pilot plant for nearly 2,000 hours on stream (3). Typical yields and conversions from this run are shown in Table 1. A method of recovering the catalyst was developed and demonstrated on the laboratory scale. Catalyst recovery exceeded 95%. On the basis of the long-term operability and catalyst recovery studies, a conceptual commercial design was completed for a co-processing unit integrated with a 100,000 BPSD conventional refinery (3,4).

The overall objective of the current contract, DE-AC22-87PC79818, is to extend and optimize the single-stage, slurry-catalyzed co-processing scheme. Specific objectives are to improve and define catalyst utilization and costs, determine the process response to changes in resid composition and different coals, investigate the process response to changes in key operating variables, define optimum operating conditions, and reassess the economics of co-processing.

Catalyst economics play a major role in determining the overall profitability of slurry-phase co-processing. Consequently, much work has been devoted to exploring new catalyst systems and improving catalyst activity, dispersion, and recovery techniques. A new catalyst that is more active than the previous reference catalyst was identified in autoclave screening tests. This molybdenum-based catalyst is currently being evaluated in the continuous bench-scale unit. A study of the effect of catalyst concentration and increased process severity on product yields and plant operability has recently been completed and is the subject of this paper.

EFFECTS OF CATALYST CONCENTRATION AND INCREASED PROCESS SEVERITY

Program Objective

The overall objective of the current work is to study the interaction of catalyst concentration and increased process severity in the continuous bench-scale unit. A specific objective is to determine the optimum conversion level required to produce high liquid yields by selective catalytic conversion as opposed to thermal conversion. This study should lead to a better understanding of how the catalyst

functions and how it can best be utilized in co-processing to accelerate reactions and decrease intrinsic activation energy. Previous experience has indicated that optimum operation is achieved at less-severe operations, where undesirable regressive recombination reactions are minimized.

Continuous Bench-Scale Operations

A simplified block diagram of the pilot plant is shown in Figure 1. The unit contains many of the essential features of the commercial flow scheme and is equipped to quantitatively measure the hydrogen consumption in the operations. The slurry feed (finely ground coal, petroleum vacuum resid, and catalyst) is combined with a hydrogen-rich recycle gas and is preheated before it enters the bottom of an upflow reactor. The products from the reactor are separated into gas and oil streams in the high-pressure separator (HPS). The gas stream from the HPS is combined with makeup hydrogen before being recycled back to the incoming fresh feed. A portion of the oil stream from the HPS is recycled back to the incoming fresh feed, and the remainder is sent to a stripper. The lighter hydrocarbon stream from the stripper is sent to a debutanizer, where it is separated into C_4 and C_5+ products. The heavier hydrocarbon stream from the stripper is sent to a vacuum fractionator to recover an overhead stream (light oil and vacuum gas oil) and a bottoms stream containing catalyst, coal minerals, insoluble carbonaceous material, and nondistillable hydrocarbons.

Feedstocks

The feedstocks used for this study were reference feedstocks, Lloydminster vacuum resid, designated as R10, and Illinois No. 6 coal designated as C1.4. Feed properties are given in Tables 2 and 3.

Lloydminster vacuum resid (950°F⁺, 120-150 Pen.) was obtained from a commercial refinery in Canada.

Illinois Coal No. 6 was obtained by the Kentucky Center for Energy Research Laboratory from the Burning Star Mine. Grinding (thru 200 mesh) and drying were done by Empire Coke Company of Holt, Alabama. The preparation procedure and equipment have been previously described (5).

Process Conditions

For each given catalyst concentration, a temperature survey was conducted with a 2:1 mixture of resid to coal, at 3000 psig and base WHSV. The reactor temperature was increased in a stepwise manner from 420°C until evidence of thermal degradation or reactor fouling was observed. Heptane insoluble conversion, which is primarily controlled by catalytic effects, was monitored to determine the process response to temperature. Three catalyst concentrations, 0.50, 0.12 and 0.05 wt-% Mo, were studied.

0.50 wt-% Mo Catalyst Temperature Study

The first study was made with 0.50 wt-% molybdenum (Mo) catalyst, measured on a metal per moisture and ash free feed (MAFF) basis. The run was started at 422°C, and the temperature was increased in a

stepwise manner. Six test conditions (422, 427, 440, 451, 457, and 467°C) were run. The plant operated well, even at the higher processing temperatures and showed no evidence of either thermal degradation or reactor fouling. Surprisingly, the conversions showed a steady increase with temperature, with no sign of decrease even at 467°C. The unconverted coal (toluene insolubles less ash) did not show the characteristic increase that is typically observed as a result of coking at higher temperatures (Figure 2). Heptane insoluble conversion also showed a steady increase with temperature (Figure 3). Previous studies showed a rapid decline in heptane insoluble conversions at temperatures greater than about 430°C and coking and plugging problems limiting plant operability above about 435°C (2). The decline in conversions and increase in coking with increased temperature may be attributed to retrograde reactions in which asphaltenes in the petroleum feedstock and those formed by thermal breakup of the coal polymerize and eventually form coke. In the presence of an effective hydrogenation catalyst and hydrogen, these reactive intermediates may be preferentially converted to stable lower-molecular-weight products. However, at high temperatures, the rates of the retrogressive thermal reactions possibly exceed those of the beneficial catalytic reactions, and pitch and coke are formed at the expense of the more-desirable lighter liquid products.

Two major differences between this study and the earlier temperature studies were observed, and these differences may account for the improved high-temperature conversions and plant stability. The catalyst was changed from a catalyst based on vanadium (V) to a more-active Mo-based catalyst, and a liquid recycle stream from the bottom of the HPS to the reactor inlet was included. Space velocity was maintained constant in each study, but the addition of the liquid recycle stream (5:1 recycle to fresh feed) resulted in greater mixing and higher velocity through the reactor. The improved high-temperature conversions and plant stability may be due to better contacting of the reactive fragments with hydrogen and catalyst (as a result of increased reactor backmixing), or to the decreased relative contact between the coke precursors and the hot reactor walls due to greater superficial liquid velocities in the reactor. Hydrodynamic differences from the recycle may have also affected the flow regime, heat transfer characteristics, or gas void fraction in the reactor. How much of the improved high-temperature conversion and operability is due to the catalyst and how much is due to improved hydrodynamics resulting from use of liquid recycle is not known at this time. Further reactor modeling studies are required to thoroughly understand these phenomena.

The greatest impact of the higher temperature was the 40 wt-% increase in nondistillable conversion (Figure 4), without significant carbon loss to retrograde reactions, and only about 6% increase in light-ends yields (Figure 5). Table 4 compares the yields and product properties at 427, 451, and 467°C. The product distribution gives the expected trends with increasing temperature: an increase of lighter fractions (C₁-C₄, C₅-177°C, and 177-343°C) and a decrease of heavier fractions (343-510°C and 510°C+). The quality of the liquid product improved with increasing temperature. The API gravity and hydrogen content of the product increased, and heptane insolubles, sulfur, and nitrogen levels decreased.

0.12 wt-% Mo Catalyst Temperature Study

This run was started at 427°C, and as in the previous run, the temperature was increased in a stepwise manner. Six test conditions (427, 432, 438, 446, 451, and 459°C) were run. Plant operations were again reasonably good, and there was no evidence of thermal degradation or reactor fouling. As in the prior run, all of the conversions continued to increase with temperature over the range studied. The unconverted coal showed a steady decrease with temperature (Figure 6), and the heptane-insoluble conversion increased with temperature (Figure 7). The yields and product properties at 427, 446, and 459°C are compared in Table 5. The yields of lighter fractions (C₁-C₄, C₅-177°C, and 177-343°C) increased and the heavier fractions (343-510°C and 510°C+) decreased with increasing temperature. The increases in nondistillable conversion (Figure 8), and light-ends yields (Figure 9) were comparable to the 0.50% Mo case. The quality of the liquid product improved with increasing temperature. The API and hydrogen content increased, and heptane insolubles, sulfur, and nitrogen levels decreased, though to a lesser extent than in the 0.50% Mo case.

0.05 wt-% Mo Catalyst Temperature Study

The third temperature study was conducted with a 0.05 wt-% Mo catalyst concentration. The objective of this run was to determine the low-concentration and high-temperature operability limits of the plant. Four test conditions (428, 447, 456, and 462°C) were run. Even with this low catalyst concentration, the plant operations were reasonably good, and there was no evidence of either thermal degradation or reactor fouling over the temperature range studied. As in the previous runs, all of the conversions continued to increase with temperature, and the yields and product properties follow similar trends. The yield of unconverted MAF coal, heptane insolubles, and nondistillable conversions and light-ends yield versus temperature are shown in Figures 10-13. Yields and product properties at 428, 447, and 462°C are compared in Table 6.

Effect Of Catalyst Concentration

An understanding of the effect of catalyst concentration at increased process severity is important to the co-processing concept. Increased conversion of petroleum resid and coal to lighter products can be achieved by increasing process severity. However, at these high conversion levels, increased hydrogen consumption and the nonselective production of light ends also occur. Degradation reactions and the fouling and coking tendency of the resid-coal mixture also tend to increase at high-severity conditions. At very high severities, thermal effects greatly predominate over catalytic effects and further accelerate the problems associated with yield loss, product stability, and coking. A wide range of nondistillable conversion levels can be achieved, merely by increasing the reactor temperature. The more-difficult task and an important part of UOP's program is to determine the optimum conversion level that produces high liquid yields by selective catalytic conversion, as opposed to thermal conversion, and reduces the problems associated with high severity operation.

Nondistillable conversion, which increased with increasing

temperature, was about the same for the different catalyst concentrations over the entire temperature range investigated (Figure 16). This result indicates that nondistillable conversion is primarily controlled by thermal effects and is not catalytically induced. Coal conversion (Figure 14) and heptane insoluble conversion (Figure 15) were more responsive to catalyst concentration, indicating that catalyst plays a role in coal and heptane-insoluble conversion. The 0.05 wt-% Mo catalyst gave slightly higher heptane insoluble conversion (Figure 15) than the 0.12 wt-% Mo. The liquid product properties were also equal to or better than the properties of the 0.12 wt-% Mo catalyst. This can be accounted for by improved catalyst dispersion for the 0.05 wt-% Mo catalyst. The effect of catalyst concentration was more pronounced at temperatures below about 440°C. At the higher temperatures, the effect of catalyst concentration diminishes, and virtually identical performance is obtained irrespective of catalyst concentration. The fact that the effect of catalyst concentration was more pronounced at the low temperature and its effect diminished at the high temperature indicates that hydrogenation, which is catalytically induced and is favored at low temperature, is being promoted by the catalyst. The catalyst provides hydrogen in an active form for stabilization of the coal-derived free radicals at the onset of coal dissolution and for the conversion of asphaltenes to thermally stable oil-soluble products. Thus, the catalyst beneficially effects the ultimate conversion and product distribution. The liquid-product properties (Tables 4, 5, and 6) followed the same trends as the coal and heptane-insoluble conversions; i.e., they improved with higher catalyst concentration, and the improvement diminished with increasing temperature. Increases in API, hydrogen content, conversion of asphaltenes, and removal of heteroatoms are primarily controlled by catalytic effects that predominate at the lower temperatures.

Two questions may be asked: what is the role of the catalyst at the higher temperature, and is it indeed needed? To answer these questions, UOP has planned a run with no catalyst. This run will provide a baseline for determining whether improved high temperature operability was due solely to improved hydrodynamics resulting from the use of liquid recycle, or whether the catalyst also plays an important role, even at very low concentrations.

CONCLUSIONS

The beneficial effects of increased catalyst concentration were more pronounced at lower temperatures (below about 440°C). The advantage of high catalyst concentration diminished at higher temperatures, where thermal effects dominate over catalytic effects. High nondistillable conversions, without excessive carbon loss to retrograde reactions and light-ends yields, were demonstrated. The improved operability of co-processing at high temperatures represents an important advance that may significantly improve the process economics.

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Table 1

Run 19 Long-Term Operability Study

<u>Conditions:</u>	<u>Yields, wt-% MAF Coal and Resid</u>
Coal: Ill. No. 6 (C1.2)	H ₂ S 2.2
Resid: Lloydminster Vacuum Resid (R8)	NH ₃ 0.4
Catalyst: 1.0 wt-% V (K1.0)	H ₂ O 5.0
Resid-Coal: 2:1	C ₂ -C ₄ 2.7
Temperature: 425°C	C ₅ -371°C 28.5
Pressure: 3,000 psig	371-510°C 26.3
	510+°C 33.7
	Unc. MAF Coal ^a 3.7
	H ₂ Consumption (2.5)
	100.0
 <u>Conversions, wt-%</u>	
MAF Coal	89.3
Heptane Insolubles	79.5
510+°C Nondist.	56.8
371+°C Nondist.	35.7

Table 2
Petroleum Resid Analysis

<u>Resid</u>	<u>Lloydminster Vacuum Resid (R10)</u>
API Gravity	6.6
Specific Gravity	1.0246
Distillation, °C	
IBP, vol-%	379
5	455
10	473
20	509
EP	512
Vol-% over at EP	22.0
Analysis, wt-%	
Carbon	83.6
Hydrogen	10.3
Sulfur	4.77
Nitrogen	0.59
Heptane Insolubles	13.56
Carbon Residue (MCRT)	17.39

Table 3
Coal Analysis

<u>Coal</u>	<u>Illinois No. 6 (C1.4)</u>
Proximate Analysis	
(AR Basis), wt-%	
Volatile Matter	38.84
Fixed Carbon (1)	45.80
Moisture	4.08
Ash	11.28
Ultimate Analysis	
(AR Basis), wt-%	
Carbon	66.75
Hydrogen (2)	4.66
Sulfur	2.91
Nitrogen	1.34
Oxygen (1)	8.98
Ash	11.28
Moisture	4.08

- (1) By difference
(2) Corrected for moisture

Table 4
Effect of Severity on Yields and Product Properties

0.50 wt-% Mo Catalyst

Temperature, °C	427	451	467
Yields, wt-% MAFF			
H ₂ O + CO _x	2.20	4.22	6.11
H ₂ S	2.26	3.11	3.11
NH ₃	0.21	0.63	0.22
C ₁ -C ₄ (Light Ends)	2.33	6.75	8.91
C ₅ -177°C (Naphtha)	5.90	17.17	25.46
171-343°C (Distillate)	17.61	31.54	32.59
343-510°C (VGO)	26.52	22.12	15.90
510°C+ (Resid)	40.82	15.27	8.37
Unc. MAF Coal	4.51	2.87	2.95
H ₂ Consumption	(2.37)	(3.66)	(3.61)
TOTAL	100.00	100.00	100.00
C₅+ Total Liquid Product			
MAFF, wt-%	90.85	86.10	82.32
API Gravity	13.3	24.4	28.6
Carbon, wt-%	86.36	86.99	85.76
Hydrogen, wt-%	10.38	11.04	11.23
Sulfur, wt-%	1.66	0.61	0.47
Nitrogen, wt-%	0.79	0.57	0.84
Heptane Insolubles, wt-%	8.64	4.61	3.38
MCRT, wt-%	12.84	7.36	6.36

Table 5
Effect of Severity on Yields and Product Properties

0.12 wt-% Mo Catalyst

Temperature, °C	427	446	459
Yields, wt-% MAFF			
H ₂ O + CO _x	6.7	4.0	4.3
H ₂ S	1.6	3.3	3.5
NH ₃	0.2	0.4	0.8
C ₁ -C ₄ (Light Ends)	2.5	5.5	9.1
C ₅ -177°C (Naphtha)	5.4	12.0	14.5
177-343°C (Distillate)	17.6	24.0	36.0
343-510°C (VGO)	29.2	26.1	22.9
510+°C (Resid)	34.0	24.2	10.3
Unc. MAF Coal	5.6	3.6	2.3
H ₂ Consumption	<u>(2.8)</u>	<u>(2.9)</u>	<u>(3.6)</u>
TOTAL	100.0	100.0	100.0
C ₅₊ Total Liquid Product			
MAFF, wt-%	86.2	86.3	83.7
API Gravity	12.9	17.0	19.9
Carbon, wt-%	84.7	84.0	84.4
Hydrogen, wt-%	10.0	10.3	11.0
Sulfur, wt-%	2.1	1.4	1.1
Nitrogen, wt-%	0.9	0.8	0.4
Heptane Insolubles, wt-%	9.8	9.1	3.1
MCRT, wt-%	12.7	11.2	6.2

Table 6

Effect of Severity on Yields and Product Properties

0.05 wt-% Mo Catalyst

Temperature, °C	428	447	462
Yields, wt-% MAFF			
H ₂ O + CO _x	1.67	2.00	3.64
H ₂ S	2.51	3.28	3.64
NH ₃	0.34	0.49	0.42
C ₁ -C ₄ (Light Ends)	2.75	5.68	9.10
C ₅ -177°C (Naphtha)	5.69	13.69	23.43
173-343°C (Distillate)	11.04	25.65	27.92
343-510°C (VGO)	30.65	24.47	17.92
510°C+ (Resid)	40.66	24.03	14.66
Unc. MAF Coal	6.76	3.67	2.62
H ₂ Consumption	(2.07)	(2.96)	(3.35)
TOTAL	100.00	100.00	100.00
C ₅₊ Total Liquid Product			
MAFF, wt-%	88.04	87.84	83.93
API Gravity	11.4	18.7	25.4
Carbon, wt-%	84.4	84.8	85.0
Hydrogen, wt-%	10.4	10.9	11.3
Sulfur, wt-%	2.4	1.5	0.9
Nitrogen, wt-%	0.7	0.7	0.7
Heptane Insolubles, wt-%	7.0	5.6	3.1
MCRT, wt-%	13.5	10.6	8.7

FIGURE 1
CO-PROCESSING PILOT PLANT

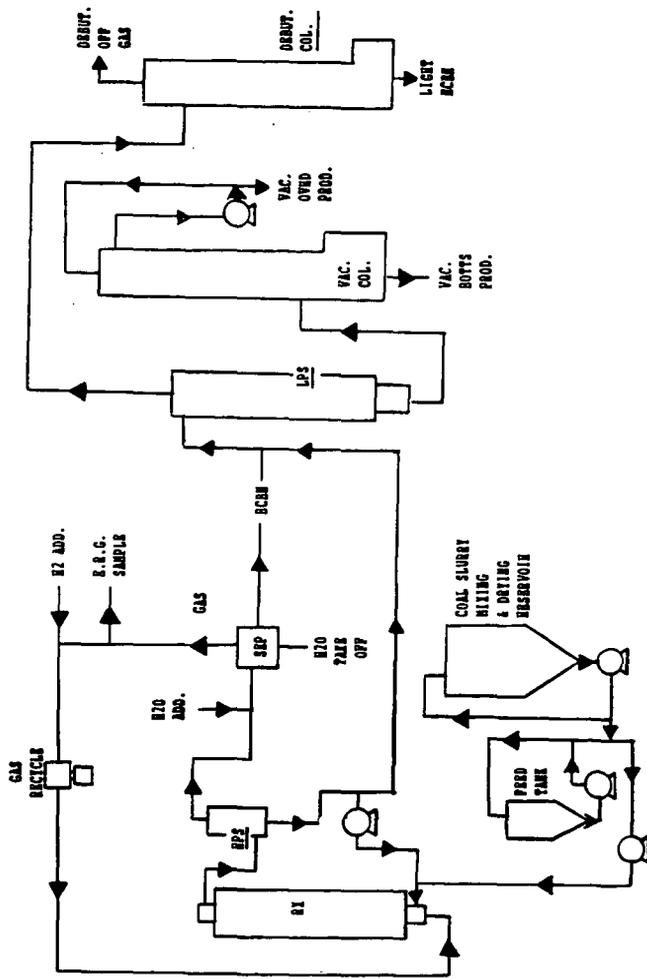


Figure 2
Unconverted Coal Yield
vs. Temperature

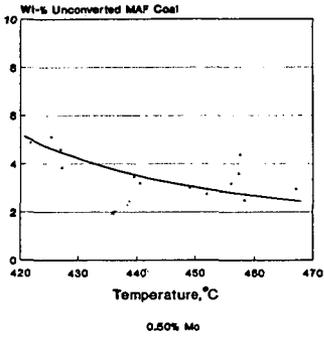


Figure 3
Hept. Insol. Conversion
vs. Temperature

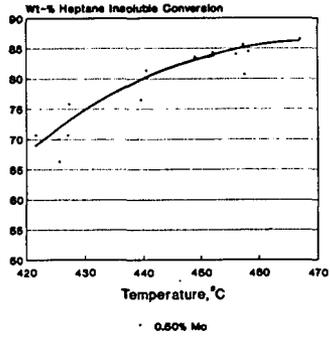


Figure 4
Nondistillable Conversion
vs. Temperature

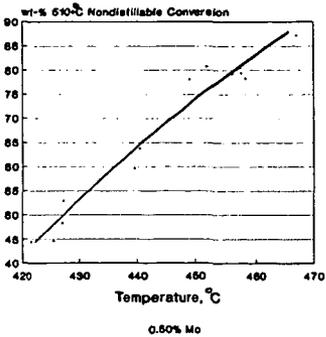


Figure 5
Light Ends Yields
vs. Temperature

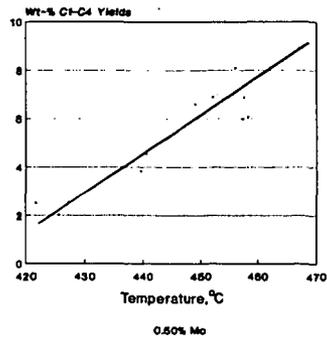


Figure 6

Unconverted Coal Yield
vs. Temperature

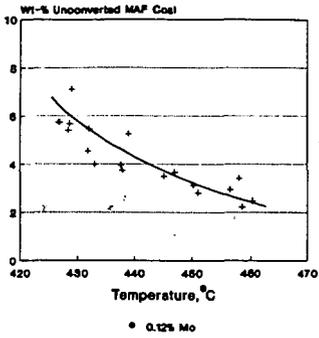


Figure 7

Hept. Insol. Conversion
vs. Temperature

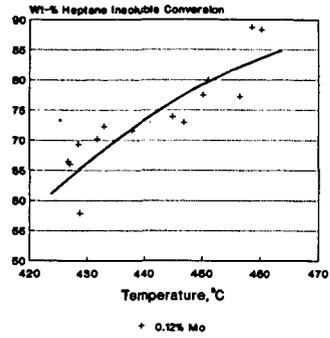


Figure 8

Nondistillable Conversion
vs. Temperature

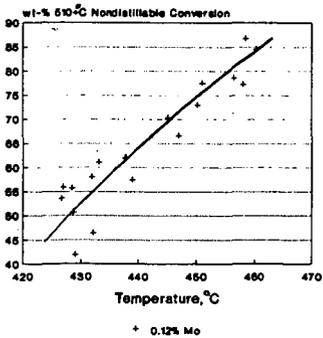
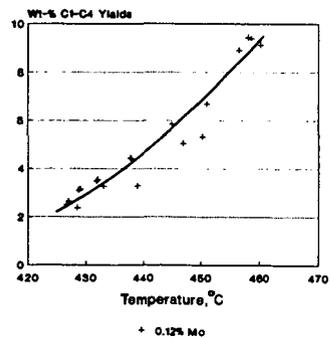


Figure 9

Light Ends Yields
vs. Temperature



CO-PROCESSING OF NEW MEXICO COAL WITH HONDO RESIDUUM

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KEYWORDS: coal liquefaction, co-processing, synfuels

INTRODUCTION

Hydrocarbon Research, Inc. (HRI) has developed a process for co-processing coals with heavy petroleum crudes and residua. The process utilizes one or more ebullated bed reactors in series and brings together experience in resid processing (H-Oil process) and coal liquefaction (H-Coal and CTSL processes). Co-processing has been demonstrated with bench-scale and PDU-scale tests.

During last few years, HRI has assessed co-processing performance of several coal and petroleum feedstock combinations. Coals of varying rank including Texas lignite, Black Thunder (Wyoming), Forestburg (Alberta), New Mexico (McKinley mine), and Taiheiyo (Japan) subbituminous coals, Ohio 5/6, Lingan (Nova Scotia) and Westerholt (Germany) bituminous coals were tested. Petroleum residua tested include Maya (Mexico), Orinoco (Venezuela), Cold Lake (Canada), and Hondo (California).

This paper presents results obtained on co-processing of New Mexico coal with a vacuum residuum from Hondo heavy crude. This feedstock combination was found to be particularly reactive in co-processing. Some results on comparative reactivities of Hondo, Maya, and Cold Lake residua, using Texas lignite as a reference coal, are also presented.

EXPERIMENTAL

The bench tests were conducted in a 50 lb/day (nominal size) continuous unit equipped with two close-coupled ebullated bed reactors. Both reactors were charged with commercial NiMo hydroprocessing catalyst which was sulfided during start-up. Unlike commercial operation, each bench test was conducted with a fixed charge of catalyst with no intermediate catalyst additions and withdrawals.

Table 1 shows the analyses of New Mexico (McKinley mine) subbituminous coal and Texas lignite (cleaned, from Homer city). Analyses of Hondo, Cold Lake, and Maya vacuum resids are also shown in Table 1.

RESULTS AND DISCUSSION

New Mexico coal was co-processed with Hondo vacuum resid according to the run plan indicated in Table 2. Condition 1 was the baseline condition at the base space velocity, base reference (internal reactor) temperature of 810°F in both reactors, 33 W % coal concentration in feed, and once-through operation. Coal concentration, space velocity and reactor temperatures were varied over conditions 2 through 4. In condition 2, with coal concentration at 50 W % of fresh feed, atmospheric bottoms were used as recycle (to reduce the feed viscosity) at recycle-to- fresh-feed ratio of 0.5. Condition 5 was identical to condition 1 and was used to assess the extent of catalyst deactivation.

The process performance obtained in co-processing of New Mexico coal with Hondo vacuum resid is shown in Table 2 and in Figures 1 and 2. The product yields are based on ASTM distillations. Coal conversion was calculated based on solubility in quinoline. Residuum (975°F+) conversion was calculated from D-1160 distillation on product vacuum-still-bottoms. Hydrodesulfurization (HDS) and Hydrodenitrogenation (HDN) were calculated from heteroatom contents of the products and the total feed (including ash). Demetallization was based on the metals (Ni + V) content of the liquid product. Net C₄-975°F yield was calculated by subtracting the gas oil content of the feed from the C₄-975°F content of the product and expressing it as a percentage of the feed 975°F+ (MAF) content. Hydrogen efficiency is defined as the ratio of net distillate produced to hydrogen consumption.

Coal conversion for New Mexico coal ranged from 91.0 to 93.1 W % (MAF). There was virtually no effect of catalyst deactivation on coal conversion. Coal conversion dropped from 93.1 W % in condition 1 to 92.5 W % in condition 5. The lowest coal conversion (91.0 W %) was obtained in condition 3 (at high space velocity), however, the decrease was small. Residuum (975°F+) conversion ranged from 85.9 to 93.2 (MAF) W %. There was a small effect of catalyst deactivation, 975°F+ conversion dropped from

93.2 W % in condition 1 to 91.1 W % in condition 5. Again, the lowest conversion was obtained in condition 3. The effect of high space velocity was more pronounced on 975°F+ conversion than on coal conversion, with 975°F+ conversion dropping to 85.9 W % in condition 3.

Hydrodesulfurization (HDS) level was very high throughout the run, ranging from 96.7 W % to 97.7 W %. In conditions using oil-to-coal ratio of 2, more than 95% of the sulfur content of the feed was associated with Hondo. The extremely high level of HDS is an indication of the high reactivity of Hondo. Hydrodenitrogenation (HDN), unlike HDS, was very dependent upon catalyst age, decreasing from 87.4 W % in condition 1 to 67.3 W % in condition 5. High level of demetallization, over 96 W %, was obtained throughout the run.

The net yield of C₄-975°F product was high and ranged from 72.6 W % to 77.9 W % (expressed as percentage of 975°F+ MAF content of feed). The lowest yield was obtained in low-severity (high space velocity) condition. Excluding this condition, the yield range was quite small with very low effect of catalyst deactivation.

The effect of coal concentration on process performance can be assessed by interpolating the performance at condition 1 and condition 5 to condition 2 and comparing it with that observed in condition 2. It is, however, difficult to use this method to assess the effect on HDN due to high, non-linear deactivation effect on HDN performance. The effect of coal concentration on coal and 975°F+ conversions was slightly negative, with that on 975°F+ conversion a little more pronounced. Higher coal concentration also gave a lower net yield of C₄-975°F distillate and showed lower hydrogen efficiency. The latter was caused due to lower hydrogen content of the feed and higher gas (C₁-C₃) and water yields obtained using higher coal concentration. As shown in Table 2, the yield of vacuum gas oil (VGO) (650-975°F) fraction in the product slate was lower in condition 2. However, when yields are calculated on a net basis (by subtracting VGO portion of the feed), the distillate selectivity for condition 2 is not much different from that in condition 1. In both cases, the net yield of VGO was quite small indicating the reactive nature of New Mexico coal and Hondo vacuum resid.

In condition 3, low severity was employed by increasing the space velocity from the base value by 60%. Consequently, lower process performance was obtained. As mentioned earlier, coal conversion decreased by a small amount and the 975°F+ conversion and net C₄-975°F yield decreased by a greater amount. The hydrogen consumption fell considerably.

The reference reactor temperature was increased by 15°F in condition 4 maintaining the high space velocity. The increased severity increased process performance to the high levels obtained in the baseline condition. Hydrogen efficiency in condition 4, although lower than that in condition 3 due to higher gas yield, was still quite high. The effect of temperature and space velocity on net distillate selectivity is shown in Figure 3. In condition 3 (base temperature, high space velocity), the net selectivity of VGO was quite high - 14.5 W % (of C₄-975°F product) versus less than 2 W % in condition 5 (base temperature, base space velocity). When the temperature was increased in condition 4 by 15 F, the net selectivity of VGO dropped to 3.1 W % giving a very light product slate. The selectivity in condition 4 was very similar to that in condition 5. The results indicate that the operating variables used in condition 4 would produce a more economical product as compared to the baseline conditions (1/5) due to lower capital cost arising from higher space velocity. Higher temperature operation usually results in higher gas make-up and higher catalyst deactivation. However, the above results suggest that these factors are of small consequence for New Mexico/Hondo feedstock combination.

A noteworthy feature of this test was the effect of catalyst deactivation on performance. The effect of deactivation on coal conversion and HDS was negligibly small. It affected 975°F+ residuum conversion, however, the magnitude was quite small. HDN and hydrogen consumption, especially the former, were markedly affected by catalyst deactivation. Table 3 shows the analyses of the product TBP cuts. All distillate products had very low sulfur contents. There is a significant effect of deactivation on the product quality of heavier cuts. For instance, the 975°F+ liquid portion obtained on day 21 had very low hydrogen content and higher sulfur, nitrogen, and metals contents as compared to that obtained on day 5. It is very interesting to note that there is a large effect on the sulfur content (0.07 W % on day 5 versus 0.48 W % on day 21) although the effect on HDS level is very small (97.7 W % on day 1 versus 96.7 W % on day 21). This is due to very low yields of 975°F+ liquid product.

The small effect on catalyst deactivation on coal and residuum conversions and HDS might be hypothesized as due to predominantly thermal character of these reactions. This is quite true for coal conversion and partly true for residuum conversion. It is quite unlikely that the desulfurization of the thiophenic components typically found in heavy oils would occur by a thermal path. A possible explanation of the behavior observed here might be the non-uniform deactivation of catalyst sites. It is known that hydrotreating catalysts such as the one used here have distinct hydrogenation and hydrogenolysis sites. The former type of sites might have deactivated while the latter type relatively unaffected. HDS rate is dependent upon hydrogenolysis and does not require hydrogenation. HDN reactions require hydrogenation prior to hydrogenolysis and could get affected by deactivation of hydrogenation sites depending upon the limiting step in the reaction network.

Co-processing of New Mexico coal with Hondo vacuum resid gave very high level of demetallization (based on metals (Ni + V) content of the liquid product). Figure 4 shows the mode of demetallization. In all conditions, the total demetallization was in high 90's (W %). In condition 1, catalytic demetallization accounted for more than 80%. The balance was achieved through deposition on coal solids. During the course of the run, as the catalyst deactivated, the relative amount of catalytic demetallization dropped. In condition 5, it accounted for just over 55 W %, the balance was achieved by coal solids. Although this decline in catalytic activity towards demetallization is significant, it is our experience that the above retained activity is higher than that typically observed for a similarly aged catalyst.

The recovered first-stage catalyst had lower carbon content and higher contaminant metals than the second-stage catalyst. This is the usual behavior, however, the first-stage carbon content was lower than that usually found. This perhaps is the cause for higher retained activity towards 975°F+ conversion, HDS and demetallization.

The extremely high HDS level indicated that Hondo vacuum resid was very reactive. In order to compare its reactivity with other residua tested in this program, Texas lignite was co-processed with Maya, Hondo, and Cold Lake. Texas lignite was the reference coal for the program. The run plan and the results are shown Table 4 and in Figure 5. The residuum conversion with Hondo was 92.7 W % versus 90.3 W % with Maya and 88.1 W % with Cold Lake. Similarly, HDS level was higher with Hondo. The product distribution as reported in Table 4 did not show much variation, however, considering Hondo contained substantial amount of VGO, the net distillate product slate with Texas lignite - Hondo combination was more selective towards lighter products.

The reactivity of various coal/residuum combinations towards 975°F+ residuum conversion were modelled by the equation:

$$k = k_0 \cdot \exp(-E/RT) \cdot (1+C)^a \cdot \exp(-d \cdot A)$$

where,

- k = first-order rate constant calculated assuming two CSTRs in series,
- k₀ = constant representing initial reactivity at 0 W % coal
- E = activation energy
- R = gas constant
- T = temperature
- C = fractional coal concentration
- a = exponent indicating effect of coal concentration
- d = deactivation parameter
- A = catalyst age

This model fits the experimental data obtained under the entire program very well. Table 5 shows a comparison of the model parameters obtained for various feedstock combinations. New Mexico - Hondo combination was the most reactive feedstock and had very low deactivation rate.

CONCLUSION

New Mexico subbituminous coal was co-processed with Hondo vacuum resid in a continuous bench unit employing HRI's Coal/Oil Co-processing Technology. This feedstock was very reactive and gave high yield of distillate product. The hydrodesulfurization was extremely high. The effect of catalyst deactivation on residuum conversion, HDS, and net distillate yield was quite small, however, the effect on HDN was more pronounced. A separate test done on co-processing of Texas lignite with Maya, Hondo, and Cold Lake VSB showed that Hondo was the most reactive residuum.

ACKNOWLEDGEMENTS

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TABLE I
ANALYSES OF FEEDSTOCKS

COALS	New Mexico		Texas Lignite	
Moisture, W %	7.6		9.4	
Ultimate Analysis, W % (Dry)				
Carbon	69.3		64.7	
Hydrogen	5.2		4.4	
Nitrogen	1.3		1.3	
Sulfur	0.5		1.3	
Ash	9.8		12.6	
Oxygen (Difference)	13.9		15.7	
PETROLEUM VACUUM RESIDUA	Hondo	Cold Lake	Maya	
API Gravity	7.8	2.6	3.1	
Elemental Analysis, W %				
Carbon	82.8	83.5	83.4	
Hydrogen	10.6	9.9	9.9	
Nitrogen	0.8	0.7	0.7	
Sulfur	5.4	5.7	5.1	
Metals, WPPM				
Nickel	108	137	105	
Vanadium	277	348	562	
IBP, °F	750	882	835	
IBP-975°F, W %	31.9	9.1	9.6	
975°F+, W %	68.1	90.9	90.4	

TABLE 2
CO-PROCESSING OF NEW MEXICO COAL
WITH HONDO VACUUM RESIDUUM

Condition No.	1	2	3	4	5
Days	1-5	6-9	10-13	14-17	18-21
Relative Space Velocity	1.0	1.0	1.6	1.6	1.0
Reactor Temperature, °F	810	810	810	825	810
Coal Concentration in Fresh Feed, W %	33	50*	33	33	33
Yields (W % Fresh Feed)					
C ₁ -C ₃	6.1	6.3	4.6	6.3	6.4
C ₄ -350°F	16.0	17.2	13.7	18.4	18.0
350-650°F	40.9	38.2	33.0	38.2	38.5
650-975°F	23.2	19.7	29.2	23.1	22.2
975°F+ Liquid	3.0	4.1	7.9	3.5	4.4
Coal (IOM) + Ash	5.3	8.7	6.3	5.7	5.8
CO + CO ₂	0.3	0.4	0.5	0.6	0.2
NH ₃ + H ₂ S + H ₂ O	9.7	10.3	8.4	8.4	8.7
Total (100 + H ₂ Consumption)	104.5	104.9	103.5	104.1	104.0
Coal Conversion (W % MAF)	93.1	92.3	91.0	92.9	92.5
975°F+ Conversion (W % MAF)	93.2	90.3	85.9	92.5	91.1
HDS, W %	97.7	97.1	97.1	97.1	96.7
HDN, W %	87.4	77.4	66.5	67.6	67.3
DEMET, W %	99.1	98.4	99.9	97.6	96.6
C ₄ -975°F Yield (W % Dry Fresh Feed)	80.2	75.1	75.9	79.7	78.7
Net C ₄ -975°F Yield (W % 975°F+ MAF)	77.9	74.9	72.6	77.6	76.2
Hydrogen Efficiency (Net C ₄ -975/H ₂ Consumed)	13.0	12.2	15.4	14.3	14.3

* Atmospheric Bottoms were used as recycle (50 W % Fresh Feed) to facilitate pumping

TABLE 3
PRODUCT PROPERTIES
CO-PROCESSING OF NEW MEXICO COAL WITH HONDO VACUUM RESIDUUM

Condition No.	1	2	3	4	5
Day	5	9	13	17	21
IBP-350°F					
API Gravity	51.4	54.8	54.8	54.3	54.8
Carbon, W %	86.5	85.5	86.1	85.5	85.1
Hydrogen, W %	13.9	14.7	14.6	14.5	14.5
Sulfur, W %	0.01	0.01	0.01	0.01	0.01
Nitrogen, W %	0.02	0.11	0.12	0.12	0.11
350-650°F					
API Gravity	32.3	31.0	31.8	31.0	31.8
Carbon, W %	87.6	87.1	87.0	87.5	87.6
Hydrogen, W %	12.8	12.9	12.9	12.6	12.4
Sulfur, W %	0.01	0.01	0.01	0.03	0.02
Nitrogen, W %	0.14	0.22	0.31	0.35	0.24
650-975°F					
API Gravity	22.8	20.1	19.3	20.2	20.3
Carbon, W %	87.4	87.9	87.6	88.0	88.1
Hydrogen, W %	12.0	11.7	12.2	11.8	11.8
Sulfur, W %	0.03	0.02	0.10	0.08	0.11
Nitrogen, W %		0.55	0.45	0.50	0.49
975°F+ Liquid					
API Gravity	4.0	-1.3	-2.2	-8.2	-6.8
Carbon, W %	88.0	89.3	88.7	90.4	89.8
Hydrogen, W %	11.1	9.1	9.0	7.8	7.9
Sulfur, W %	0.07	0.17	0.42	0.30	0.48
Nitrogen, W %	0.51	0.91	1.05	1.27	1.31
Ni, WPPM	0.2	9	25	30	32
V, WPPM	2	5	4	12	4

TABLE 4
CO-PROCESSING OF TEXAS LIGNITE WITH
MAYA, HONDO, AND COLD LAKE VACUUM RESIDUUM

Condition No.	1	2	3
Days	1-5	6-8	9-11
Oil	Maya	Hondo	Cold Lake
Relative Space Velocity	1.0		
Reactor Temperature, °F	810		
Coal Concentration in Fresh Feed, W %	33		
Yields (W % Fresh Feed)			
C ₁ -C ₃	6.4	5.9	6.3
C ₄ -350°F	15.8	16.5	16.4
350-650°F	35.8	38.6	32.1
650-975°F	23.8	23.7	25.0
975°F+ Liquid	6.5	2.6	8.1
Coal (IOM) + Ash	5.8	6.5	6.1
CO + CO ₂	0.1	0.1	0.1
NH ₃ + H ₂ S + H ₂ O	10.6	10.8	10.5
Total (100 + H ₂ Consumption)	104.8	104.6	104.6
Coal Conversion (W % MAF)	92.5	90.6	91.4
975°F+ Conversion (W % MAF)	90.3	92.7	88.1
HDS, W %	95.2	96.7	95.0
HDN, W %	77.9	76.2	67.7
Net C ₄ -975°F Yield (W % 975°F+ MAF)	76.6	76.5	73.4

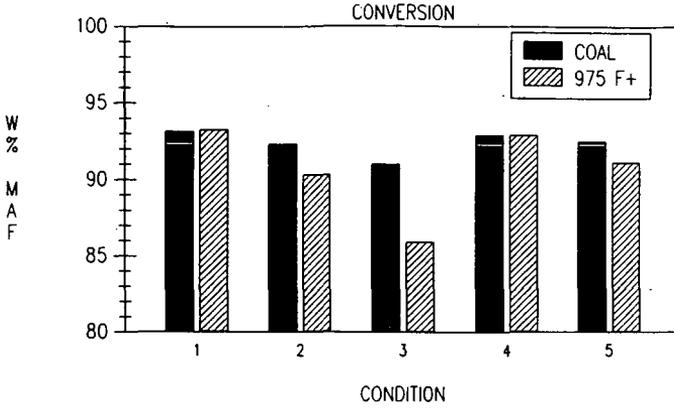
TABLE 5
COMPARISON OF FEEDSTOCK REACTIVITY

Feedstock Combination	Initial Reactivity* at 33 W % Coal	Deactivation* Parameter
Texas Lignite + Maya	1.00	1.00
Texas Lignite + Cold Lake	1.00	-
Texas Lignite + Hondo	1.33	-
Taiheiyo + Maya	0.78	0.42
Westerholt + Cold Lake	0.59	0.75
Forestburg + Cold Lake	0.78	0.71
New Mexico + Hondo	1.29	0.51

* Relative to Texas lignite + Maya combination

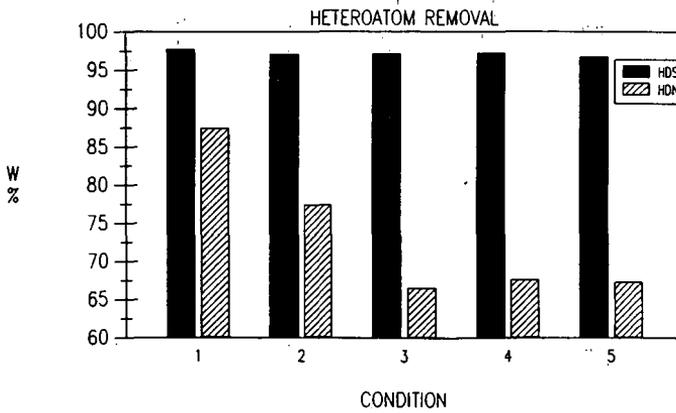
NEW MEXICO COAL PLUS HONDO

FIGURE 1



NEW MEXICO COAL PLUS HONDO

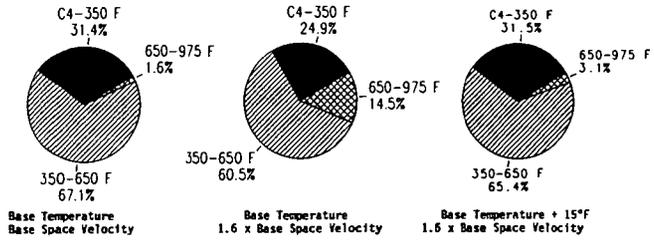
FIGURE 2



NET C4-975 F DISTILLATE PRODUCT

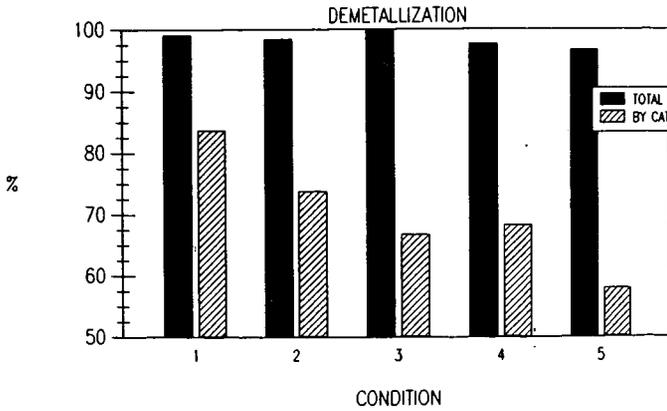
FIGURE 3

EFFECT OF TEMP / SPACE VELOCITY

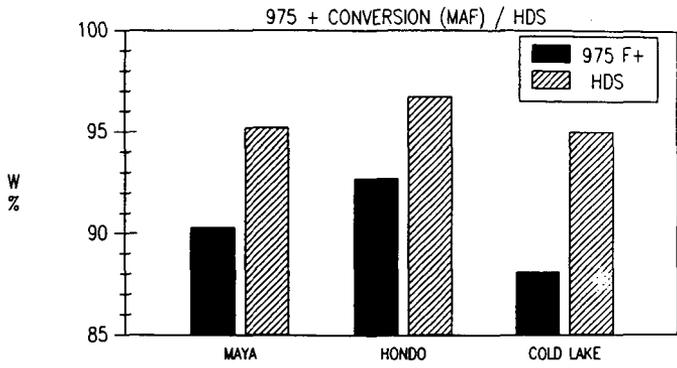


NEW MEXICO COAL PLUS HONDO

FIGURE 4



TX LIGNITE + MAYA / HONDO / COLD LAKE ^{FIGURE 5}



COUNTERFLOW REACTOR (CFR) FOR COPROCESSING OF COAL AND PETROLEUM FEEDSTOCKS

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Keywords: Coprocessing, Counterflow Reactor, Commercial Facility

ABSTRACT

CED/GfK evaluated different processes for the simultaneous upgrading of coal and heavy oil/bitumen during the past five years. The development work on the BSU (I.D. 1.2') and PDU (I.D. 3.5') scale led to a new Counterflow Reactor concept characterized by the counterflow of the liquid or slurry feed and the hydrogen recycle gas stream.

Among others, this counterflow reactor (CFR) has the following advantages over the co-current reactor:

1. Optimum internal recovery of the exothermic heat of reaction and thus less severe feed preheating;
2. No concern of solid settling as liquids and solids are removed from the bottom of the reactor;
3. Lower recycle gas rates determined by reaction kinetics only; and
4. Favorable profile of the hydrogen partial vapor pressure.

During the past years, over 10,000 hours of tests have been performed successfully with different heavy oils and heavy oil/coal slurry feeds with distillable oil yields of up to 85 wt% for heavy oil upgrading and up to 74 wt% for coprocessing. The results have been used as a basis for a technical and economical screening study for a commercial size upgrader in Canada. In the paper, results of the test work and the screening study will be presented.

INTRODUCTION

In 1984, Canadian Energy Developments Inc. (CED) had an extensive feasibility study performed to evaluate upgrading options for the vast energy resource (heavy oil and coal) of Alberta. Upgrading options considered were: heavy oil upgrading, coal liquefaction and coprocessing. At a certain price for heavy oil and at the same production capacity of synthetic crude oil, the feasibility study concluded that 1) coprocessing is economically slightly more attractive than heavy oil upgrading, 2) a heavy oil upgrading facility requires approximately 10% less capital than a coprocessing facility, and 3) coal liquefaction has the lowest return on investment and requires about 75% more capital to be built. Based on these conclusions the feasibility study recommended that for the overall development of the energy resources of Alberta, coprocessing would be the more favored option for a commercial facility.

Up until 1984, process development for coprocessing had not reached a point for commercialization. CED therefore decided to embark on a R & D program to develop its own coprocessing technology. During the past four years, CED performed extensive experimental work on both the Bench Scale Unit (BSU) and the Process Development Unit (PDU) scale and the following coprocessing technologies were evaluated:

- 1) PYROSOL Technology - i.e. hydrogenation plus coking process,
- 2) Co-Current Upflow Bubble Reactor Technology - as a one or two stage hydrogenation technology, and
- 3) Counterflow Reactor (CFR) Technology.

Based on the experimental results and the operation of the PDU for these three technologies, CED has selected the CFR technology for scale up to a commercial coprocessing facility.

COUNTERFLOW REACTOR (CFR) TECHNOLOGY

Process Description and Experimental Results

The CFR technology is a single stage hydrogenation process operating at conditions which promote coal solubilization, solubilized coal and heavy oil hydrogenation and hydrocracking in a single reactor. As the name implies, the CFR features a downward flowing coal/heavy oil slurry in contact with a counter-current make-up plus recycle hydrogen stream. CED's German partner, Gesellschaft für Kohleverflüssigung (GfK) mbH has operated a continuous PDU (8 kg/hr coal/heavy oil feed slurry) using the CFR technology for more than 10,000 hours since the second half of 1987. Individual runs lasted for up to about 700 to 800 hours.

In the CFR technology (Figure 1), the coal and heavy oil are slurried, pumped to reactor pressure and preheated to 150-250°C prior to being charged to the top of the reactor. Recycle and make-up hydrogen is preheated to 400-450°C and injected into the bottom of the reactor. The exothermic heat of reaction is used to raise the incoming feed slurry to reaction temperature. Solubilization of the coal occurs in the top portion of the reactor at a temperature of approximately 400°C, and hydrogenation/hydrocracking takes place in the main reactor zone at temperatures of 445-455°C. Reactor pressure is 18-20 MPa (2,600-2,900 psig).

Hydrogenation products are vaporized as they are formed and are withdrawn from the top of reactor, cooled, condensed and separated in a cold separator. The condensed liquid product, a full range distillate hydrocarbon product is transferred to the secondary upgrading. The hydrogen rich gas stream is scrubbed and recycled.

Unconverted heavy oil/solubilized coal and unreacted coal flow downward in the reactor, counter-current to the upward flowing hydrogen to promote solubilization of the coal and hydrogenation of the coal and heavy oil. The highest hydrogen partial vapor pressure exists at the bottom zone of the reactor where needed to promote conversion of coal and heavy oil fractions that are the most resistant to hydrogenation/hydrocracking. A slurry stream containing unconverted residuum and unreacted coal and ash is withdrawn from the bottom of the reactor, depressurized in the let-down system and charged to a vacuum flash unit.

When processing typical Cold Lake vacuum residue and Alberta subbituminous coal (Table 1) total distillable oil yields of 70-74 wt% are consistently achieved (Table 2) with a hydrogen consumption of 2.9 wt%. The distillate product (Table 3) is a full range product containing, on average, 30% naphtha, 40% middle distillate and about 30% VGO. (Typical operating conditions are shown in Table 4).

Advantages of the CFR

Most reactor technologies produce about the same total distillable oil yield and the same product distribution. The CFR, however, has significant advantages with regard to its operation and reliability which are the direct consequence of the counterflow concept used in the process.

1. No Settling Problem

Since the unconverted feed material, ash and other solid particles are allowed to settle naturally in the reactor, the settling problem associated with co-current reactors does not occur in the CFR. High superficial gas velocities typically in excess of 6 cm/sec. in co-current flow reactors are not required in the CFR as only vaporized and gaseous products leave the reactor overhead and "solids" are withdrawn at the bottom together with the liquid hydrocarbons as a slurry.

2. Low Superficial Gas Velocity

In the CFR technology, superficial gas rates are determined by reaction kinetics only and are not defined by the requirement to keep "solids" in suspension and to carry them overhead in the reactor. All PDU runs with the CFR were performed with superficial gas velocities of 0.5 to 1.9 cm/sec. Maximum duration was about 800 hours of continuous operation.

3. Low Scale-Up Risk

For a commercial size CFR the superficial gas velocities are estimated at around 3cm/sec., i.e. a commercial CFR will operate in the bubble flow regime. Since the PDU also operates in the bubble flow regime the scale up from the PDU to commercial size reactors does not pose a major problem as the reactor scale up parameters are essentially known.

4. Recovery of Exothermic Heat of Reaction

As the vaporized reaction products and hydrogen gas stream rises through the downward flowing feed slurry the exothermic heat of reaction is recovered internally within the CFR. As a result, the preheat duty for the feed slurry is reduced and lower feed preheat temperatures are possible.

5. No External Hot Separator

Because of the counterflow concept, the CFR combines the reactor and the hot separator. An external hot separator is not required to separate the slurry from the distillable oil.

6. Capital and Operating Costs

With the above "technical" advantages, the capital and operating costs for a commercial coprocessing facility will be lower when CFR technology is used as compared to co-current flow reactor technology. For example, as the CFR technology operates at lower superficial gas velocities, recycle gas rates will be reduced significantly which decreases the equipment size for the recycle gas system. Because the slurry preheating requirements are lower, operating costs are decreased as fuel consumption is decreased.

Feasibility Study for Commercial Coprocessing Facility

On behalf of CED, Kilborn Inc. performed a technical and economic feasibility study for a grass-roots commercial coprocessing facility for a suitable location in Alberta. The facility (Figure 2) was designed to process Cold Lake heavy oil and Vesta Mine subbituminous coal and to produce 4,450 cubic metres per day (28,000 BPD) of synthetic crude oil (Table 5).

Capital costs, product revenue and operating cost estimates (Table 6) were prepared and formed the basis for a financial and sensitivity analysis to evaluate the economic potential of a commercial coprocessing facility.

Total Estimated Capital Costs of \$671,100K (1989) is composed of:

Direct costs were estimated from actual cost data wherever possible. For licenced processes (secondary upgrading for example) information from potential licensors was used.

Indirect costs (home office engineering construction management, construction indirects, special winterization costs) were estimated as percent of total direct cost. Project contingency was applied at 20% of total direct costs plus home office engineering, construction management and construction indirect costs.

Other costs include allowances for initial catalyst charge, initial chemicals inventory and paid up licence and royalty fees.

Owner's costs include allowances for owner's engineering, project management, environmental application costs, permit costs, spare parts inventory and start-up costs.

Total estimated annual revenue of \$206,720K per year (1989) is based on 320 operating days per year. Unit product prices were provided by the Alberta Energy Department, Government of Alberta. It should be pointed out that about \$6.8M per year of revenue is created from 22MW excess electricity generated in the commercial facility.

Total estimated operating cost of \$129,670K per year (1989) includes the costs of feedstocks, operating and maintenance labor, maintenance parts, utilities, catalysts and chemicals, local taxes and insurance. The unit prices for the feedstocks are based on forecasts from the Alberta Energy Department. The heavy oil price excludes the cost of diluent as the diluent is recovered and returned to the heavy oil production field for use as additional diluent. Plant labor and overhead costs are based on an estimated operating supervision, maintenance and plant overhead staff of 270 personnel. In addition, a contract maintenance labor allowance has been applied for major process unit turn around equivalent to 25 maintenance personnel over the entire year or 150 personnel for two months. A pipeline tariff of \$2.00 per cubic metre of heavy oil feedstock, recovered diluent and synthetic crude oil product has been allowed to cover the construction and operating costs of heavy oil diluent and production pipelines amortized over a 20 year period.

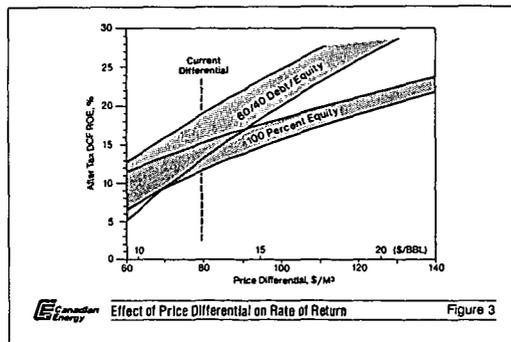
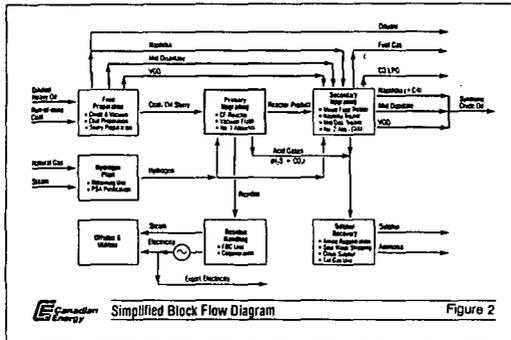
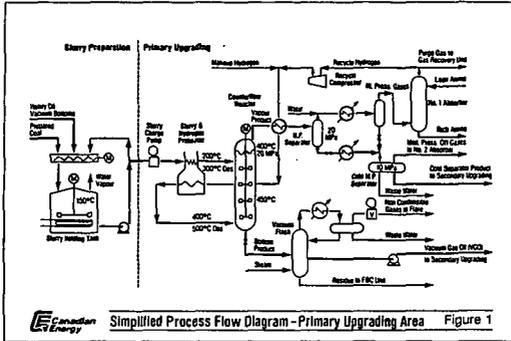
Financial and Sensitivity Analysis

A financial and sensitivity analysis was prepared on the basis of a 32 year project life including a 7 year demonstration, engineering and construction period plus a 25 year operating period. The financial analysis uses a cash flow generator model for before and after tax calculations. Cash flow simulations were used to calculate discounted cash flow return on investment/equity (DCF/ROE) for 100% equity or a given debt/equity ratio. The sensitivity analysis considered variations in the type of financing, in capital cost, in price forecasts, in the oil yield and in interest rates. The result of this sensitivity analysis is shown in Figure 3. For each of the financing options (100% equity or 60/40 debt/equity) the upper line refers to a constant percent price differential and the lower line refers to a constant dollar price differential between heavy oil and synthetic crude oil. In any case, the after tax DCF/ROE indicate that a commercial coprocessing facility is economically attractive with normal debt/equity financing methods at synthetic crude oil and bitumen price differentials that are only marginally above current differentials. Furthermore, rates of return of 20 to 22% are realized at current differentials, with project financing methods based on cost and revenue sharing and fiscal structure similar to those recently applied to major energy projects in Canada.

CONCLUSION

The Counterflow Reactor (CFR) technology for the simultaneous upgrading of coal and petroleum feedstocks has been successfully demonstrated at the PDU scale. During 10,000 operating hours, distillable oil yields and product distributions are obtained which are similar to those from a conventional co-current upflow bubble column. The counterflow regime of the CFR, however, brings advantages in operation and reliability which ultimately translates into lower capital and operating costs for a commercial facility. Superficial gas velocities which are only half or possibly one third of those in the co-current mode and the recovery of the exothermic heat of reaction inside the CFR are the main unique features of the CFR technology.

A technical and economic feasibility study suggests that a commercial coprocessing facility with the CFR technology yields attractive return on investments at present price differentials. DCF-ROE of 20-22% can be realized with proper structuring of the financial terms.



HEAVY OIL - COLD LAKE VACUUM RESIDUUM		ELEMENTAL ANALYSIS	
- DISTILLATION: IP 370°C		Wt% (DMF)	
5 Wt%	423°C	C	83.57
10 Wt%	443°C	H	10.20
15 Wt%	453°C	N	0.55
20 Wt%	460°C	S	5.30
(23.6 Wt%)		(Bv. Diff)	0.38
- DENSITY	1.026 g/ml		
- ASPHALTENES	13.63 Wt%		
- VISCOSITY 80°C	60 POISE		
120°C	2.5 POISE		
COAL - ALBERTA SUBBITUMINOUS		C	72.25
BATTLE RIVER COAL FIELD		H	5.00
WESTA COAL PINE		N	1.36
- MOISTURE	4.4 Wt%	S	0.62
- ASH	13.8 Wt% DRY BASIS		
- VOLATILES	43.9 Wt% (DMF)		
			20.77

Energy FEEDSTOCK PROPERTIES TABLE 1

FEEDS, Wt%	HEAVY OIL HYDROGENATION	COAL/HEAVY OIL COPROCESSING
Coal (DMF)	96.1	63.2
Coal (DMF)	3.9	32.7
H ₂ CONSUMPTION	1.9	2.9
PRODUCTS, Wt%	83.5	73.7
OIL YIELD 4480°C	7.6	10.2
C-C, Gas	0.4	4.0
PROD. WATER	0.4	4.0
CO ₂ (DMF)	0.4	4.0
BTOWEN 2450°C	6.4	8.4
UNCOMPACTED COAL	0.2	1.5
Wt% Conversion (+480°C)	91.5	87.0

Energy OVERALL MATERIAL BALANCE CFR-POU TABLE 2

DENSITY, KG/LITRE	HEAVY OIL HYDROGENATION	COAL/HEAVY OIL COPROCESSING
	0.898	0.894
ELEMENTAL ANALYSIS, Wt%	85.81	84.8
Carbon	11.64	11.4
Hydrogen	0.49	0.58
Nitrogen	0.18	1.72
Oxygen (Diff)	7.37	7.44
C/H		
LIQUID PRODUCT YIELD (% OF OIL YIELD)	30.0	30.0
200-240°C	50.0	40.0
>350°C	30.0	30.0
C, - 450°C	100.0	100.0

Energy HYDROGENATION PRODUCT QUALITY CFR-POU TABLE 3

Pressure, Bars	HEAVY OIL HYDROGENATION	COAL/HEAVY OIL COPROCESSING
	200.0	190.0
Temperature, °C	450.0	451.0
Top	450.0	457.0
Bottom	446.0	450.0
Hourly Space Velocity KG/HR/LITRE	0.76	0.84
Hydrogen Feed, Wt%/Kg	2.9	2.77
Superp. Gas Velocity cm/sec.	1.4	1.7
Throughput, kg/hr	7.2	8.6
Feed - Vac Resid. Wt% (DMF)	96.1	87.3
- Catalyst	None	None

Energy TYPICAL OPERATING CONDITIONS CFR-POU TABLE 4

Feedstocks	
● Heavy Oil (Diluted)	5000 m ³ /d
● Heavy Oil (Diluent Free)	3500 m ³ /d
● Coal	2200 t/d
● Natural Gas	972 000 Nm ³ /d
Products	
● Synthetic Crude Oil	4450 m ³ /d
● Electricity	22 MW
● Propane	200 m ³ /d
● Sulphur	138 t/d
● Ammonia	30 t/d
● Diluent (Recycled)	1500 m ³ /d

 **Feedstock and Product Quantities** Table 5

Direct Costs	413,800
Indirect Costs	214,300
Other Costs	14,000
Owner's Costs	29,000
Total Estimated Capital Cost	671,100

 **Capital Cost, \$K(1989)** Table 6

Feedstocks			
● Heavy Oil	3500 m ³ /d	\$63,90/m ³	60,370
● Coal	2200 t/d	\$15,00/t	10,860
● Natural Gas	970 000 Nm ³ /d	\$ 0,05/Nm ³	15,550
Other Operating Costs			
Pipeline Tariffs			36,180
Total Estimated Operating Cost*			7,010
			129,670

 **Annual Operating Cost** Table 6 cont

Feedstocks			
Syncrude	4450 m ³ /d	\$133,65/m ³	190,320
Electricity	22 MW	\$ 0,04/KWH	6,760
Propane	200 m ³ /d	\$ 55,00/m ³	3,520
Sulphur	138 t/d	\$ 95,00/t	4,200
Ammonia	30 t/d	\$200,00/t	1,920
Total Estimated Revenue*			206,720

 **Annual Product Revenue** Table 6 cont

*Based on 320 operating days per year

*Based on 320 operating days per year

COAL/RESID COPROCESSING OVER EQUILIBRIUM HYDROTREATING CATALYST

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ABSTRACT

Resid and a 10% coal/resid mixture were hydroprocessed in a flow unit at 760-790°F over an equilibrium commercial hydrotreating catalyst. Coal addition resulted in improvements in both hydrodemetalization activity and Ramsicarbon conversion; however, hydrodesulfurization activity remained the same. The addition of 10% decanted oil to the coal/resid feed considerably improved coal conversion.

INTRODUCTION

Extensive information on coal/petroleum resid coprocessing is available in the open literature, both for experiments in batch units and in continuous bench scale units. Oelert (1) provides a review of the background technology and discusses research and development in various coprocessing schemes. Many of these coprocessing studies claim synergisms, or benefits relative to resid hydroprocessing or coal liquefaction. Among these synergisms are:

- a) Improved unit operability due to the formation of less solids or coke (2). This benefit may also allow unit operation at higher temperatures than those possible with just resid hydroprocessing.
- b) Enhanced metals removal (3-6), which has been attributed to the preferential deposition of the metals on the coal solids instead of on the catalyst (7). This benefit may allow the processing of resids with high metal contents (8).
- c) Improved heteroatom removal (4,5,9) (i.e., sulfur, nitrogen and oxygen).
- d) Increased distillate yields (4,9,10).
- e) Reduction of overall hydrogen requirement (relative to coal liquefaction) with the use of higher H-content resid.

The goal of the current work is to verify and quantify synergisms for the coprocessing of coal and resid over commercial equilibrium hydrotreating catalyst in a continuous bench scale flow unit. The specific objectives are (a) to evaluate the effects of process variables, such as temperature and solvent addition, on coal/resid conversion and product properties, and (b) to determine the impact (if any) of coprocessing on catalyst activity maintenance and catalyst life.

EXPERIMENTAL

Feed Properties

Hydroprocessing experiments were performed on a resid and a blend of this resid with Illinois No. 6 coal, with or without decanted oil. The properties of the above feeds are shown in Table 1.

Reaction Conditions

The hydroprocessing experiments were conducted in an upflow high-pressure unit which contains two 1-liter Autoclave reactors in series. Catalyst baskets, each filled with 60 cc of equilibrium hydrotreating catalyst, were placed in

both reactors. To prevent elutriation, the catalyst was covered with 10 cc of 3 mm glass balls and 1/4 inch of glass wool. Table II gives the experimental conditions for the following four tests:

Test No. 1	Hydroprocessing of Resid
Test No. 2	Coprocessing of 10% Coal + 90% Resid
Test No. 3	Hydroprocessing of 10% DCO + 90% Resid
Test No. 4	Coprocessing of 10% Coal + 9% DCO + 81% Resid

Product Analysis

Products from the hydroprocessing runs were analyzed for tetrahydrofuran (THF) and hexane insolubles. Samples were also subjected to Shell hot filtration tests (SHFT) to determine "solids" concentration. In this test, the sample is filtered through Whatman 50 paper at about 200°F; if the sample does not filter after one hour, 10-20 psi nitrogen is applied. The solids are then washed with hexane (four 50 ml washes for 10 g sample) before final filtration; the recovered solids are termed the SHFT solids. The resulting SHFT filtrate was then analyzed for elemental composition (C, H, N, S, O), metals (Ni, V) and Ramscarbon contents (Tables III and IV). Product gas samples from selected runs were also analyzed by gas chromatography to determine the total material balance closure, which averaged 93% due to plugging problems.

RESULTS AND DISCUSSION

Resid and Coal/Resid Coprocessing Without DCO (Tests No. 1 and No. 2)

Coal addition considerably improved the hydrodemetalization (HDM, calculated as shown in the appendix) of resid at 760-790°F (Figure 1). The HDM benefit from coal addition became smaller at higher temperatures.

The Ramscarbon conversion (HDC, calculated as shown in the appendix) also increased with coal addition, as shown in Figure 2. It is possible that adsorption of asphaltenes (or Ramscarbon to some degree) by unconverted coal resulted in this apparent increase in Ramscarbon conversion. As with HDM, the HDC benefit with coal addition became smaller at higher temperatures.

The hydrodesulfurization (HDS, calculated as shown in the appendix) was not affected by coal addition, as shown in Figure 3. Nitrogen and oxygen removal were low due to the high space velocity and low hydrogenation activity of the equilibrium catalyst.

The THF insolubles (See Table III) were used to estimate coal conversion (see appendix). Within experimental error, the coal conversion remained relatively constant from 760 to 780°F at a minimum of 46-48% to a maximum of 60-62% (see Table V). These conversions were lower than those obtained in the liquefaction of Illinois No. 6 (with coal liquids as solvent) under comparable coal liquefaction conditions (11). The lower coal conversion during coal/resid coprocessing may be due to the poor solvent quality of the petroleum resid.

Resid and Coal/Resid Coprocessing With DCO (Tests No. 3 and No. 4)

Initially a mixture of 90% resid and 10% decanted oil was hydroprocessed for about 120 hours. Then 10% coal was added to the feed and the coal/resid/DCO mixture was hydrotreated for 180 hours. At the end of this run, the coal was removed and the (resid+DCO) was processed for 120 hours to check the baseline. Figures 4-6 show HDM, HDC, and HDS of liquid products as a function of the time on stream. As in the coprocessing without decanted oil, the addition of coal resulted in increases in HDM and HDC (Figures 4 and 5); HDS was only

slightly improved (Figure 6). Regression lines (the solid lines in Figures 4-6) indicated that the equilibrium catalyst was undergoing further deactivation. The addition of coal did not affect this deactivation rate. Catalyst activity for HDM drastically decreased two days after coal was removed from the feed. We do not have an explanation for this unusual observation.

The addition of DCO improved coal conversion, as seen in Table VI. For hydroprocessing at 780°F, coal conversion increased from a minimum of 46% (maximum of 60%) without DCO to a minimum of 66% (maximum of 80%) with DCO addition to the coal/resid mixture.

CONCLUSIONS

The addition of decanted oil to a coal/resid mixture resulted in improved coal conversion. When 10% Illinois No. 6 coal was coprocessed with resid, both metals and Ramsarbon removal from resid were increased, with or without decanted oil. Increases in apparent resid Ramsarbon removal with coal present can be due to heavy molecule adsorption by unconverted coal. Sulfur removal, however, was not affected by coal addition.

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Table I. Hydroprocessing Feed Properties

Feed No.	Composition, % MAF		ZSHFT Solids	ZTHF	ZSHFT Insol	% C	% H	% N	% S	% O	% Rams-carbon	ppm		
	Resid	Coal										DCO	NI	V
1	100	0	0	N.D. ¹	1.6	84.65	10.35	0.45	4.70	0.40	17.7	54	215	21
2	0	0	100	N.D.	N.D.	90.75	7.22	0.17	1.68	1.48	9.4	0	0	0
3	0	100	0	91.06 ²	N.D.	77.31 ³	5.13 ³	1.43 ³	3.93 ³	12.20 ³	N.D.	15	32	15,300
4	90	0	10	N.D.	1.43	85.26	10.04	0.42	4.40	0.51	16.9	49	194	19
5	90	10	0	9.11 ⁴	11.4	83.92	9.83	0.55	4.62	1.58	25.0	50	197	1549
6	81	10	9	9.11 ⁴	11.3	84.47	9.55	0.52	4.35	1.68	20.3	45	177	1547

1 N.D. = not determined

2 98.0% MF coal

3 Wt% MAF (coal contained 1.14 wt% ash and 7.1 wt% moisture)

4 9.8% MF coal

Table II. Hydroprocessing Conditions

	1st Stage Reactor		2nd Stage Reactor		Reactor Train	
		206		206		206
Average Feed Rate, g/hr		206		206		206
Equilibrium Catalyst						
Catalyst Volume, cc		60		60		120
Catalyst Weight, g		65		65		130
WHSV, 1/hr		7.4		7.4		3.7
(based on fresh catalyst)						
WHSV, 1/hr		3.2		3.2		1.6
(based on equil. catalyst)						
Effective Reactor Volume*, cc		282		282		564
Residence Time, hr		1.37		1.37		2.74
LHSV, 1/hr		3.4		3.4		1.7
Pressure, psig		2500		2500		2500
Hydrogen Flow Rate						
SCFH		10		10		10
SCFB		7700		7700		7700
Agitator Speed, rpm		1650		1000		

*Effective reactor volume calculated assuming 10% gas holdup and 0.2 cc/g spent catalyst pore volume, i.e.,

Effective Volume = Total Liquid Volume Outside Catalyst Pores x (1-gas holdup fraction) + Catalyst Pore Volume

= 300 (1 - 0.1) + 60 (0.2) = 282

TABLE III: Analysis of Products from Resid and Coal Resid Hydroprocessing

Test No.	Feed Comp ¹ %Coal % DCO	Temp (°F)	Time (hr)	%THF Insol.	% SHFT Solids	% C	% H	% N	% S	% O	% Rams-carbon	ppm Ni	ppm V	ppm Fe
1	0	780	63	0.14 ²	5.60	85.86	11.14	0.41	2.31	1.06	10.6	14	53	2
1	0	770	136	0.33 ²	3.67	85.63	10.90	0.44	2.57	1.06	12.5	22	78	2
1	0	760	155	0.21 ²	4.07 ⁴	85.63	10.77	0.47	2.83	1.29	13.4	29	105	2
1	0	790	179	0.17 ²	5.47	86.07	11.26	0.37	1.97	1.10	9.3	8	31	2
2	10	780	255	4.44 ³	13.96 ⁵	85.65	10.67	0.49	2.54	1.48	13.0	15	38	2
2	10	770	283	2.92	17.05	85.42	10.69	0.48	2.71	N.D.	13.8	19	53	2
2	10	770	297	5.93	N.D.	85.10	10.43	0.51	3.05	1.41	14.9	24	74	2
2	10	760	309	5.13	N.D.	85.31	10.68	0.46	2.95	1.63	13.0	20	62	2
2	10	760	325	3.76	14.87	85.04	10.61	0.48	3.06	1.09	14.4	24	74	2

¹ %Coal + %DCO + %Resid = 100%

² Average THF insolubles for entire time on stream at the given temperature.

³ Average of THF insolubles at 255 and 270 hours.

⁴ SHFT solids at 165 hours.

⁵ SHFT solids at 270 hours.

N.D. = not determined.

TABLE IV. Analysis of Products from Resid and Coal/Resid Hydroprocessing with Decanted Oil¹

Test No.	Feed Comp ² % Coal % DCO	Temp. Time (°F) (hr)	%THF		%SHFT Solids	%Hexane Insol.		%C	%H	%N	%S	Filtered Product Quality		ppm V	ppm Fe
			Insol.			Insol.						% Rams-carbon	ppm Ni		
3	0	10	780	38	N.D.	2.39	4.93	86.18	10.67	0.45	2.37	12.5	24	73	2
3	0	10	780	62	N.D.	2.45	6.85	86.07	10.68	0.42	2.22	11.4	21	64	2
3	0	10	780	73	0.62	2.24	9.75	85.84	10.71	0.42	2.32	11.4	21	65	2
3	0	10	780	84	N.D.	2.42	9.85	85.34	10.67	0.40	2.39	11.6	23	74	2
3	0	10	780	106	0.50	2.04	9.41	86.46	10.70	0.42	2.38	11.5	22	70	2
4	10	9	780	128	N.D.	6.90	N.D.	86.35	10.56	0.45	2.18	12.0	15	42	2
4	10	9	780	152	3.77	10.61	N.D.	86.33	10.47	0.42	2.35	11.9	15	34	1
4	10	9	780	175	3.36	8.58	14.11	85.99	10.33	0.43	2.42	12.0	17	35	1
4	10	9	780	196	N.D.	10.21	14.92	86.16	10.45	0.49	2.57	13.2	18	42	1
4	10	9	780	216	2.57	10.08	15.43	86.18	10.35	0.43	2.49	12.6	20	44	1
4	10	9	780	239	N.D.	9.72	14.71	86.13	10.43	0.46	2.54	13.7	22	44	15
4	10	9	780	263	3.29	9.49	14.15	85.48	10.43	0.40	2.45	12.8	16	34	1
4	10	9	780	287	N.D.	11.00	15.72	86.03	10.36	0.41	2.65	13.6	22	48	1
3	0	10	780	310	N.D.	3.19	N.D.	85.89	10.39	0.44	3.08	13.3	27	83	1
3	0	10	780	333	N.D.	2.45	N.D.	86.06	10.55	0.42	2.89	13.0	24	74	0
3	0	10	780	357	0.59	2.03	11.51	85.96	10.52	0.43	3.07	13.4	34	126	2
3	0	10	780	381	N.D.	1.89	11.40	86.02	10.45	0.42	3.09	13.3	35	126	2
3	0	10	780	405	0.60	2.08	11.29	86.00	10.30	0.41	3.13	13.5	35	127	2
3	0	10	780	429	N.D.	1.74	N.D.	85.74	10.34	0.41	3.11	13.4	34	127	2

¹ No oxygen analyses were performed for this set of runs.

² %Coal + %DCO + %Resid = 100%

Table V. Conversion of THF Insolubles

Temperature, °F	%THF Insolubles in Product		% Coal Conversion	
	Resid	Resid + Coal	Minimum	Maximum
760	0.2	4.4	47	61
770	0.3	4.4	48	62
780	0.1	4.4	46	60

*THF insolubles in coal/resid feed = 9.1%
 Ash in coal/resid feed = 1.1%

TABLE VI. Hydroprocessing at 780°F

Test	Feed	Time (hr)	% HDM			% SHFT Solids	% Coal Conversion	
			%HDM	%HDC	%HDS		Minimum	Maximum
1	Resid	63	77	44	54	6	--	--
2	Resid+Coal	255	82	56	53	14	46	60
3	Resid+DCO	62	66	35	51	2	--	--
4	Resid+DCO+Coal	263	80	44	50	9	66	80

FIGURE 1.
COAL/RESID COPROCESSING - HYDRODEMETALLIZATION

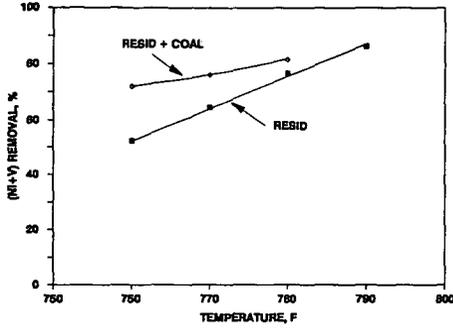


FIGURE 2.
COAL/RESID COPROCESSING - RAMSCARBON CONVERSION

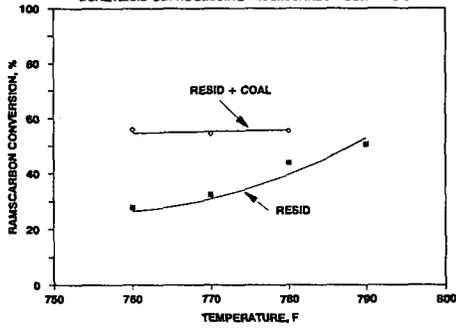


FIGURE 3.
COAL/RESID COPROCESSING - HYDRODESULFURIZATION

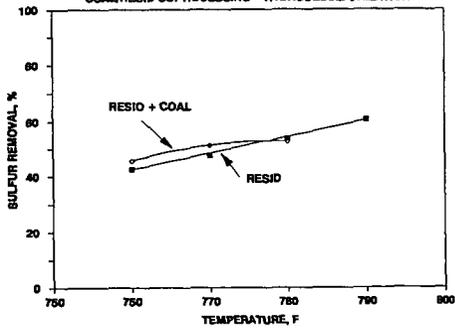


FIGURE 4.

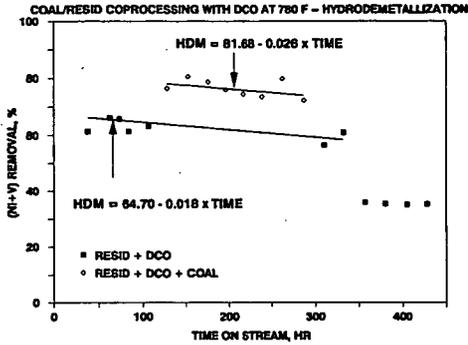


FIGURE 5.

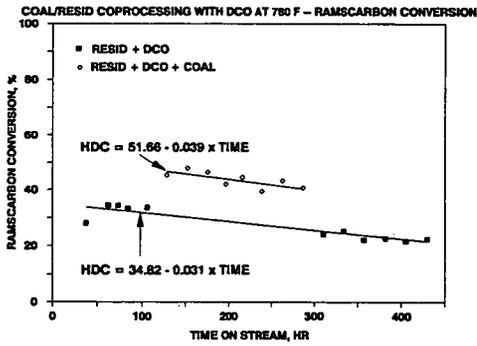
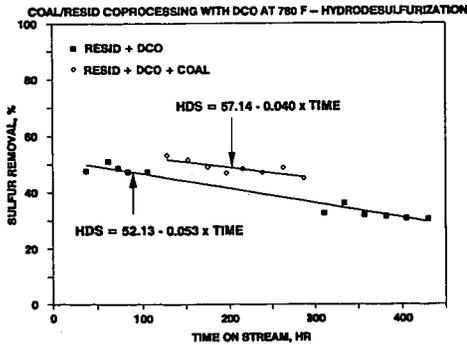


FIGURE 6.



APPENDIX

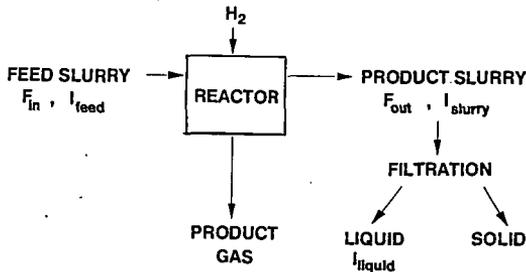
Conversion Calculations

Figure A-1 shows the block diagram for the reactor system, along with the feed and product streams, and their analysis. The analytical results reported in Tables III and IV were used to calculate the following levels of conversion or removal in the liquid product (assuming no product loss on filtration):

$$\% \text{ Conversion or Removal of Component I (HDI):} \\ \{ [F_{in}I_{feed} - F_{out}(1 - \text{SHFT solids fraction})I_{liquid}] / [F_{in}I_{feed}] \} \times 100$$

where for hydrodemetallization (HDM), I = ppm (Ni+V); for Ramscarbon conversion (HDC), I = % Ramscarbon; and for hydrodesulfurization (HDS), I = % Sulfur. F_{out}/F_{in} represents the material balance which may be calculated based on the total material (0.93), or based on a forced carbon balance (0.99). In Figures 1-6, $F_{out}/F_{in} = 0.99$ is used; the use of $F_{out}/F_{in} = 0.93$ gives values that are at most 10% higher.

Figure A-1.
Material Balance Block Diagram for Flow Unit



Coal conversion was estimated by conversion to THF solubles. It was assumed that the coal-derived THF insolubles (THF) is given by the difference between the THFI in the coprocessing product and the THFI in the resid hydroprocessing product (weighted by its fraction in the coprocessing feed), i.e.,

Coal Conversion to THF Solubles:

$$1 - \{ (\text{THFI-Ash})_{\text{coproc product}} - 0.9\text{THFI}_{\text{resid run}} \} / (\text{THFI-Ash})_{\text{coproc feed}}$$

The ash deposition on the catalyst could not be evaluated because the catalyst was severely coked and could not be recovered for analysis. Two approaches were used to estimate the ash levels in the coprocessing product. In the first, it was assumed that all of the ash deposited in the catalyst so that $\text{Ash}_{\text{coproc product}} = 0$; the calculated coal conversion is then a minimum. In the second, it was assumed that no ash deposited in the catalyst so that $\text{Ash}_{\text{coproc product}} = \text{Ash}_{\text{coproc feed}} = 1.14\%$; the calculated conversion is then the maximum possible.

MATHEMATICAL MODELLING OF COPROCESSING KINETICS

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Keywords: Heavy Oil/Coal Upgrading, Modelling, Optimization

INTRODUCTION

CANMET has played a major role in heavy oil/coal coprocessing since the late 1970's. CANMET has conducted studies on determining characteristics of the products and residues from the coprocessing of heavy oil and coal, development of high performance catalysts for the coprocessing of heavy oils and coal, and demonstrating the feasibility of coprocessing Canadian feedstocks. An ongoing experimental program using a continuous bench-scale reactor system has generated a significant amount of scientific and engineering information on process performance and operation. These data were previously reviewed and analyzed for reaction engineering models (1). As a continuation of that study, CANMET and Lobbe undertook a program on computer simulation of coprocessing with special emphasis on studying the effects of coal and additives on the yield and selectivity of coprocessing products, and development of a Coprocessing Simulator as a tool for further work (2).

EXPERIMENTAL

The experiments were conducted in a continuous-flow unit. A detailed description of the unit is given elsewhere (3). Forestburg subbituminous coal from Alberta and Cold Lake + 454°C cut vacuum bottoms were used in the experiments. The coal was ground to -200 mesh and slurried with heavy oil at concentrations of 5 to 30 percent, daf slurry basis. A disposable iron sulphide catalyst was added in amounts from 0.5 to 1.0 percent (w/w Fe on daf slurry). Methods used for catalyst preparation were described previously by Fouda and Kelly (4).

The coprocessing runs were conducted over a temperature range of 400 to 450°C, nominal slurry space velocity 0.5 to 1.5 kg/l/hr, reactor pressure 2000 to 3000 psig, and run duration of 80 to 120 minutes each. The coprocessing workup procedures and product analysis are depicted in Figure 1. The relationships between pitch and distillate yields, and product selectivity are shown in Figures 2 and 3.

MODELLING COPROCESSING KINETICS

Previous publications and reports (1) (2) (5) have shown that despite the limitations of lumping procedures (grouping of the product components) in describing kinetics of complex reaction mixtures like heavy oil/coal, the lumping approach can provide a good approximation of the behavior of various product groups in coprocessing. The performed analyses showed that the characteristics of the model components in Figure 4 are independent of the severity of coprocessing and, therefore, they can be used as a definition of pseudo-components in kinetic analysis. Typical predictive capabilities for low and high severity runs of the developed kinetic models (1) (2) are shown in Table 1. The differences between Model A and Model B pertain to the difference in kinetic rate constants only and not the model structure. This was due to the fact that rate constants for formation of Naphtha and other lighter components were weak functions of temperature and required small adjustments for coprocessing experiments conducted over a wide temperature range as shown in Table 1.

In the current work, a simulator capable of optimizing coprocessing parameters was developed. The simulator included lumped kinetic models for coprocessing reactants and product, coke formation models and hydrogen consumption models as a function of feed composition, additive concentration and reactor operating parameters. Selected examples of product yield simulation over a range of temperatures, for three space velocities, are depicted in Figures 5 to 8. The data shows strong interdependence of temperature and space velocity, over the range studied, and the presence of localized maxima and minima product yield and selectivity, over the reactor operating parameters studied.

Interesting features of coprocessing results are presented in Figure 9, depicting simulation of distillate yield over a range of coal concentration, with and without adjustment of the process model for relative volatility of coprocessing feed and product components. It is shown that the extent of product/feed flashing (adjusted ϕ constants) affects the residence time distribution (RTD) of the heavy components and results in apparent synergistic effects between heavy oil and coal. These effects are particularly strong at low coal concentration and low process severity.

An interesting effect was also shown by optimization studies using derived coke formation and hydrogen consumption models for coprocessing. Table 2 gives optimized results for two different constraints (limits) on coke formation. The data show relatively similar product slate composition despite significant differences (by an order of about 20) in the amount of coke being formed.

SUMMARY

Detailed modelling of the coprocessing of heavy oil bottoms and subbituminous coal, and an evaluation of the effects of coal and additive concentration on product yields and selectivity were completed for the CANMET process. Also, a computer simulation package was developed for simulating and optimizing heavy oil and coal coprocessing kinetics, refining kinetic models and assisting reaction engineering studies for various feedstocks.

Simulation studies revealed: 1) the synergistic effects between heavy oil and coal could be explained, in part, by simulating variant mean residence time distribution (RTD) for the feed and product components; 2) the maximum in the yield of preasphaltenes was shown to shift to lower temperature with increasing residence time; and 3) the extent of product/feed flashing strongly affected the RTD of the heavy components with the RTD effects being most pronounced at low coal concentration and low process severity.

Optimization studies showed that hydrogen consumption was not the key optimization variable at the process conditions studied, i.e., at relatively high heavy gas/oil yield. Also, the studies showed that coke formation and its sensitivity to temperature made optimization of the product slate difficult, i.e., coke formation was a monotonic function of the initial coal and additive concentration, while temperature acted like a threshold variable above which coke was formed rapidly.

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Table 1. COPROCESSING PRODUCT YIELD FOR MODEL A AND MODEL B RATE CONSTANTS

	<u>MODEL A</u>	<u>MODEL B</u>	<u>EXPERIMENT</u>
LOW SEVERITY RUN			
THFI	15.7	15.2	14.7
Preasphaltenes	5.1	5.0	1.8
Asphaltenes	14.1	15.3	13.7
Oil	40.1	39.7	37.9
HGO 1&2	13.6	15.2	13.7
LGO	7.3	7.7	6.3
Naphtha	3.5	1.7	4.0
C ₁ -C ₄	0.3	0.3	---
HIGH SEVERITY RUN			
THFI	2.5	1.3	4.3
Preasphaltenes	5.2	2.7	1.8
Asphaltenes	8.3	8.7	1.5
Oil	6.8	5.6	6.7
HGO 1&2	22.4	31.3	32.6
LGO	18.3	26.1	25.7
Naphtha	28.0	18.1	15.3
C ₁ -C ₄	8.6	6.1	6.4

Table 2. OPTIMIZATION RESULTS FOR FORESTBURG AND COLD LAKE FEED

	<u>SPECIFIED CONCENTRATIONS FOR COKE</u>	
	<u>< 2%</u>	<u>< 5%</u>
Product Slate Optimized		
THFI	0.9	0.8
PA	2.9	2.8
A	6.5	6.3
O	4.0	3.8
HGO	28.4	28.3
LGO	25.5	25.1
NAPHTHA	24.9	25.7
C ₁ -C ₄	6.9	7.1
Hydrogen Consumption	3.52	3.59
Estimated Coke	0.19	3.55

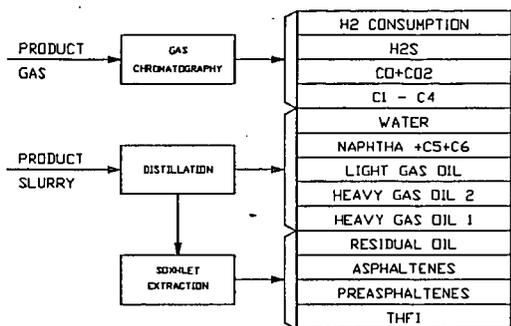


Figure 1. SUMMARY OF PRODUCT ANALYSES

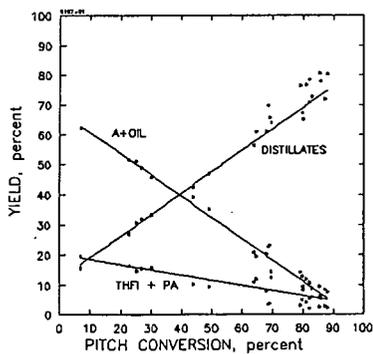


Figure 2. SELECTIVITY OF COPROCESSING PRODUCTS

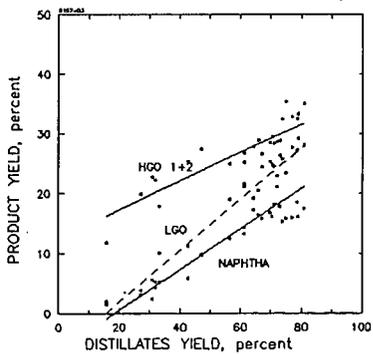


Figure 3. SELECTIVITY OF DISTILLATE FRACTIONS

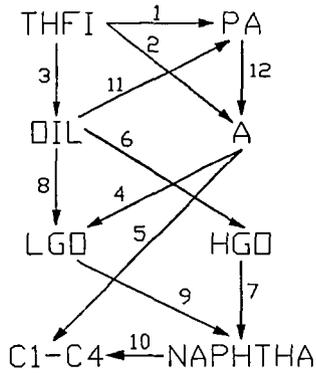


Figure 4. CANMET COPROCESSING MODEL INCORPORATING ADDUCT FORMATION

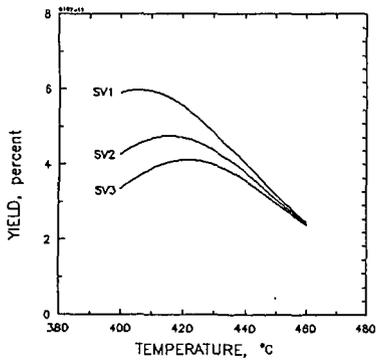


Figure 5. EFFECT OF TEMPERATURE ON PREASPHALTENES YIELD AT THREE SPACE VELOCITIES

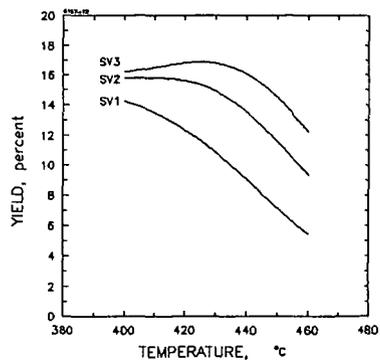


Figure 6. EFFECT OF TEMPERATURE ON ASPHALTENES YIELD AT THREE SPACE VELOCITIES

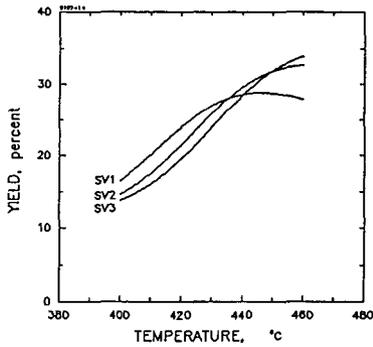


Figure 7. EFFECT OF TEMPERATURE ON HEAVY GAS OIL (1&2) YIELD AT THREE SPACE VELOCITIES

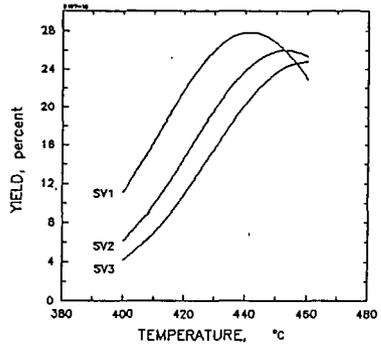


Figure 8. EFFECT OF TEMPERATURE ON LIGHT GAS OIL YIELD AT THREE SPACE VELOCITIES

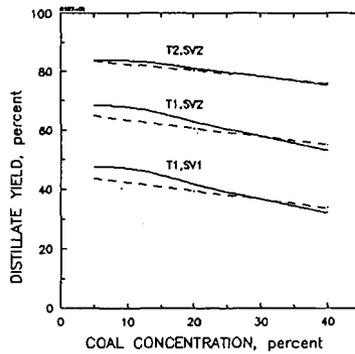


Figure 9. SIMULATED EFFECT OF COAL CONCENTRATION ON TOTAL DISTILLATE YIELD (solid lines for adjusted ϕ constants)

HYDROTREATING AND PRODUCTION OF TRANSPORTATION FUEL FROM COPROCESSED DISTILLATES

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Keywords: Coprocessing, hydrotreating, isotope

INTRODUCTION

Production of refinery feedstocks and transportation fuels from coprocessing liquids were the objectives of this study. Coal-heavy oil coprocessed products are significantly different from conventional petroleum. In most coprocessing schemes, the first stage coprocessed products contain high concentrations of nitrogen and sulfur, directly inherited from the feed coal and the feed heavy oil. Nitrogen and sulfur must be removed from these first stage products by further catalytic hydrotreating to produce a synthetic crude to be marketed directly to existing refineries for further upgrading. The investigation of nitrogen and sulfur removal focused on producing refinery acceptable products with reference to existing refinery specifications.

An initial study of transportation fuels from coprocessing liquids resulted in production of one gasoline and two diesel products from distillate and gas oil fractions. They were engine tested to evaluate octane and cetane number and other properties which were then compared to the Canadian Standard Specifications.

The isotopic analysis of $^{13}\text{C}/^{12}\text{C}$ ratio provides information for quantifying amounts of coal derived matter incorporated into product slates. In the coprocessing of coal and heavy oil, both components of feed are upgraded simultaneously. Quantitative assessment of coal transformation into product fractions would give kinetic and engineering data for efficient development of coprocessing schemes. Using isotopic mass balance techniques, coal incorporation into the first stage coprocessed products (experimental feeds) and secondary upgraded products were calculated.

Consequently, this study consisted of (a) investigation of nitrogen and sulfur removal from coprocessed liquids, (b) preliminary production of transportation fuels, and (c) quantitative assessment of coal derived material incorporated into both first stage and secondary upgraded products.

EXPERIMENTAL

Feedstock. Coprocessed slurry was obtained from a process development unit operated by Canadian Energy Developments Inc. (CED). Feed to the unit consisted of an Alberta subbituminous coal (Vesta) and an iron based catalyst

slurried with Cold Lake vacuum bottoms. This slurry was then processed at temperature above 400°C and pressure above 17 MPa. The coprocessed slurry was separated by distillation into naphtha (below 177°C), distillate (178 to 343°C) and gas oil (344 to 508°C) fractions. Table 1 gives the analyses of starting feeds and nitrogen and sulfur concentration of distillables compared to refinery specifications. These fractions were secondary upgraded separately; the ratio of hydrogen flow to feed (vol./vol. ratio) was 1000 unless otherwise provided.

Catalysts. Three commercial catalysts were used: a Ni/Mo for hydrotreating, a different Ni/Mo for hydrocracking and platinum catalyst for reforming. Following presulfidation of the catalyst, and prior to hydrotreating/hydrocracking experiments, the catalysts were conditioned for a minimum 30 hours using a bitumen derived distillate feed. The platinum catalyst was used as received.

Hydrotreating. A continuous flow trickle bed reactor system was used, having a volume of 100 ml. For hydrotreating experiments of the naphtha fraction, a two level factorial experimental design was used. The two levels of three variables were selected as follows: 390 and 420°C, 8.3 and 12.4 MPa, 1.0 and 3.0 h⁻¹. For the distillate and gas oil fractions, a Box-Behnken statistical experimental design approach was used to study the simultaneous effect of varying reaction temperature (400 to 440°C), pressure (6.9 to 11.0 MPa) and WHSV (1.0 to 4.0 h⁻¹)²

Preliminary Production of Transportation Fuels. For gasoline production, the feed naphtha was hydrotreated at 420°, 12.4 MPa, WHSV of 3.0 h⁻¹ followed by reforming at 500°C, 3.5 MPa, 1.0 h⁻¹ and H₂/feed (vol./vol.) of 300. Two diesel products were obtained. One diesel product was produced by hydrotreating of the first stage distillate fraction at 440°C, 6.9 MPa and 2.5 h⁻¹. The other was obtained from the gas oil fraction by hydrotreating at the same conditions used for the distillate followed by further hydrocracking of the hydrotreated gas oil (which was separated by distillation) at 420°, 6.9 MPa and 1.0 h⁻¹

Distribution Of Coal In Product Slates. In order to quantify the amounts of coal derived matter incorporated into product fractions, an isotopic analysis of 13C/12C ratio was carried out. The procedure is described elsewhere³.

RESULTS AND DISCUSSION

(a) Nitrogen and Sulfur Removal From First Stage Coprocessed Products.

Naphtha. Table 2 summarizes the results of hydrotreating of the naphtha fractions and whether the resulting products met refinery specifications (Table 1). Even though the experimental conditions were varied for a two level statistical analysis, the small differences between concentrations of heteroatoms in the products of different experiments did not allow a meaningful analysis of the effect of hydrotreating conditions on nitrogen and sulfur removal. Product specifications for nitrogen were met under all operating conditions; however, those for sulfur were not.

Distillate. The experimental results of the three level test matrix for hydrotreating of the distillate fraction were fit using a quadratic fraction.

Figure 1 illustrates calculated response surfaces of change in concentration of nitrogen in the total liquid product against both reactor temperature and WHSV for hydrotreating of the distillate fraction. These figures show the relative order of effects on nitrogen removal for this range of conditions to be: WHSV > temperature > pressure. Also, some interaction of the three parameters was noted; decreasing WHSV at 400°C dramatically decreased nitrogen content of products but had a lesser effect at 440°C. For all of the conditions studied, the nitrogen concentration of products was below 200 ppm, meeting the specifications of nitrogen content. In terms of sulfur removal, the pressure required to produce acceptable refinery feeds was 6.9 MPa, the lowest in the entire experiments studied. Figure 2 shows the relationship between sulfur concentration in the products and hydrotreatment temperature with varying WHSV at a pressure of 6.9 MPa. This figure illustrates the sensitivity of sulfur content to reaction temperature, especially above 410°C. Decreasing WHSV from 4.0 to 3.0 h⁻¹ also reduced sulfur content but further reduction had little effect.

Gas Oil. Figure 3 gives the response surfaces of nitrogen content in products of hydrotreating of the gas oil. Increasing temperature, decreasing WHSV and increasing pressure maximized nitrogen removal. Little interaction of three parameters was observed. The effect of pressure on sulfur removal from the gas oil was negligible. Figure 4 gives contours of sulfur concentration in products with varying WHSV at 6.9 MPa. It provides a range of operating temperature and WHSV that would be available to produce refinery acceptable feeds at 6.9 MPa. Also, using the estimated values from these curves, the activation energy with respect to sulfur removal was calculated using a first order model giving an activation energy of 56.3 kJ/mole.

(b) Preliminary Study of Transportation Fuel Production From Coprocessed Liquids.

In order to maximize the yield of value-added product such as diesel, the conversion of gas oil to distillate should be high. The response surface in Figure 5 shows the yield of distillate from gas oil hydrotreating. The relative order of parameter effects on the yield was temperature > WHSV with pressure having negligible effect. Generally, increasing temperature improved distillate yield. At high temperatures, decreasing WHSV increased distillate yield, while at low temperature, the change in yield from a change in WHSV was negligible.

Selected fractions from the products of secondary upgrading were further processed and tested for their properties as transportation fuels. Table 3 shows the results of an overall mass balance in the secondary upgrading experiments of first stage coprocessed liquids. The difference of 2.0% between amounts of feed and those of upgraded products represents amounts of gaseous products and some experimental errors involved.

Gasoline Product. The hydrotreated naphtha and the naphtha obtained from the product of hydrotreated distillate were combined and then reformed for engine testing as a gasoline product. This product had an octane number of 76.6, slightly less than the Canadian Specification minimum of 83.6 (January, Alberta). Either blending or different reforming conditions would be required to produce an unleaded gasoline product to meet the specifications.

Diesel Product. Table 4 gives the properties of diesel fractions obtained from two different sources compared to the Canadian specifications. One diesel was from hydrotreating of distillate fraction of first stage, and the other from hydrocracking of hydrotreated gas oil fraction. Key measures of diesel quality are cetane number and sulfur concentration. The results of engine testing of the first diesel product (produced from the distillate fraction) gave a cetane number of 40.9, slightly exceeding the minimum specification of 40. Sulfur concentration of this diesel was 349 ppm, much less than the 0.5% maximum specification, indicating that this diesel can be sold to market directly. The second diesel product (produced from the gas oil fraction) had a low cetane number of 28.6; however, the sulfur concentration was again well below the specification. In order to increase the cetane number of the second diesel product, more hydrogen must be added into this fraction, suggesting that further process options must be investigated. Most of the other diesel specification parameters can be adjusted by addition of fuel improvers.

(c) Distribution of Coal Incorporated Into Product Slates

Using a combination of isotopic analysis, elemental analysis of carbon and yield data of the feeds and the hydrotreated products, the concentration of coal derived carbon in each product fraction can be calculated. Figure 6 gives the distribution of coal derived carbon incorporated into the first stage coprocessed products. Figures 7 and 8 illustrate those of the hydrotreated products, indicating that the majority of coal derived carbon existed in the heavier fractions. However, significant amounts of coal derived carbon existed in the distillable products. After hydrotreating, the combined results gave the following concentrations of coal derived carbon in the product fractions: 20.3% in naphtha, 9.2% in distillate and 15.8 % in gas oil.

CONCLUSIONS

The following was concluded from this study:

1. Synthetic crude refinery feedstock specifications for nitrogen and sulfur content could be met for the distillate and gas oil fractions of coal-bitumen coprocessing.
2. The relative effectiveness on nitrogen removal during hydrotreating was $WHSV - \text{temperature} > \text{pressure}$.
3. On sulfur removal during hydrotreating, temperature had the greatest impact and pressure had a negligible effect.
4. Hydrotreating of distillate fraction directly produced a diesel which met several of the Canadian specifications.
5. Hydrotreatment followed by hydrocracking of gas oil produced a diesel fraction which did not meet the cetane number specification.
6. Coal derived carbon concentrations in the naphtha, distillate and gas oil product fractions after secondary upgrading were 20.3, 9.2 and 15.8 % respectively.

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Table 1 ELEMENTAL ANALYSES OF FEEOSTOCKS AND REFINERY SPECIFICATIONS

Starting material as received(%)				
	C	H	N	S
Vesta Coal	49.7	3.2	0.94	0.36
Cold Lake V.B.	83.1	9.9	0.75	5.77

Heteroatom concentrations of feeds and refinery specifications(ppm)				
	Feeds		Specifications	
	N	S	N	S
Naphtha(<177 C)	770	5200	10	15
Distillate(178-343 C)	3120	17500	200	1000
Gas Oil(>3444 C)	5200	24500	<2100	-
Total Blend				<3100

Table 2 HDN AND HDS: Hydrotreating of Naphtha from CED #1

Process Temperature °C		390	420
Pressure (MPa)	WHSV (hr ⁻¹)	0	0
		0	0
8.3	1.0 N	0	0
	S	0	0
3.0	N	0	0
	S	0	0
12.4	1.0 N	0	0
	S	0	0
3.0	N	0	0
	S	0	0

0: meets refinery specifications
*: does not meet

Table 3

MASS BALANCE
(Based on slurry without water and gas)

% Feed	% Product		
	Naphtha (gasoline)	Distillate (diesel)	GO
Naphtha 4.9	4.9 **		
Distillate 14.7			
	Hydrotreating 1.7	12.3 **	
Gas Oil 24.4			
	Hydrotreating 1.2	1.8	(20.7*)
	*Hydrocracking (0.4)	(1.3)	(15.4)
(Subtotal)	8.2	10.4**	15.4
Total 44.0		42.0	

** Engine Tested

Table 4

PROPERTIES OF DISTILLATES COMPARED TO DIESEL SPECIFICATIONS

Property	Type of Diesel A	From Distillate	From Gas Oil
Ignition Quality	40	40.9	28.6
Cetane Number			
Sulfur, % Mass Max.	0.5	0.035	0.019
Flash Point °C, Min.	40	46.0	77.5
Cloud Point °C, Max.	-34	-27	-22
Pour Point °C, Max.	-39	-30	-15
Kinematic Viscosity at 40°C, cSt, Min.	1.3	2.01	3.05
	Max.	4.1	
Distillation:			
90% Recovered °C, Max.	315	314.5	323
Total Acid Number Max.	0.10	0.009	0.01

Figure 1 HYDROTREATING OF DISTILLATE FROM COPROCESSING PRODUCTS:
NITROGEN CONCENTRATION IN PRODUCTS

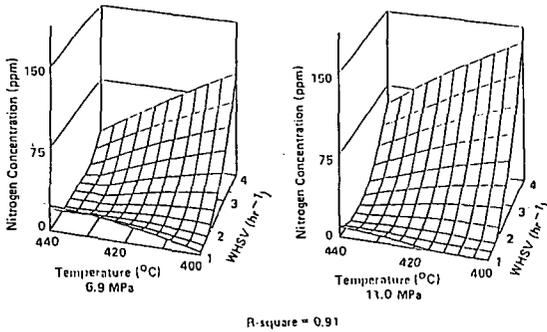


Figure 3 HYDROTREATING OF GAS OIL FROM COPROCESSING PRODUCTS:
NITROGEN CONCENTRATION IN PRODUCTS

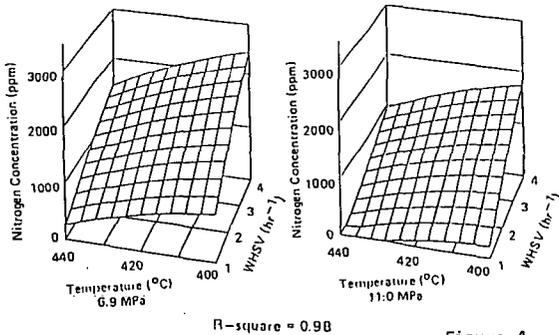


Figure 2 HYDROTREATING OF DISTILLATE FROM COPROCESSING PRODUCTS:
EFFECTS OF WHSV AND TEMPERATURE AT 6.9 MPa ON SULFUR REMOVAL

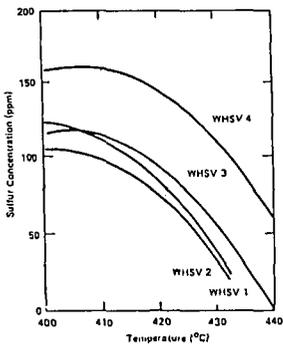


Figure 4 HYDROTREATING OF GAS OIL FROM COPROCESSING PRODUCTS:
EFFECTS OF WHSV AND PROCESS TEMPERATURE AT 6.9 MPa
ON SULFUR REMOVAL

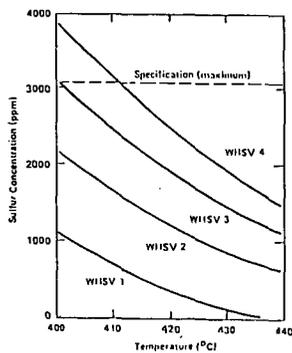


Figure 5
DISTILLATE YIELD PRODUCED FROM GAS OIL OF COPROCESSING PRODUCTS BY HYDROTREATING

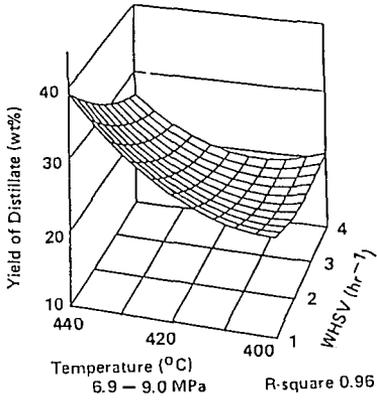


Figure 6
First Stage Coprocessing: Distribution of Coal Derived Carbon by Isotopic Analysis

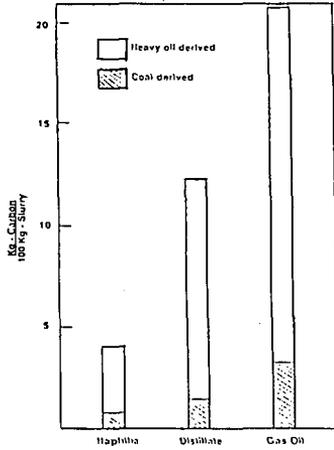


Figure 7
Secondary Upgrading of Distillate from Coprocessing: Distribution of Coal Derived Carbon by Isotopic Analysis

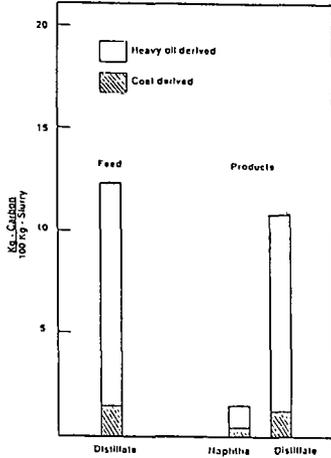


Figure 8
Secondary Upgrading of Gas Oil from Coprocessing: Distribution of Coal Derived Carbon by Isotopic Analysis

