

## THE STATUS OF CANADIAN ENERGY'S CO-PROCESSING TECHNOLOGIES

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Potential commercial production of synthetic liquid fuels was for many years thought to demand liquefaction of coal or upgrading of bitumen/heavy oils. By the late 1970s, however, another concept - i.e., the simultaneous co-processing of coal and heavy oil - began to receive some serious attention; and by now co-processing technology has reached a stage of development where it may appear to be the preferred upgrading procedure. This view, and the corollary that the feedstocks used for co-processing will play an increasingly important role in Canada's energy future, is supported by what is now seen as the most probable energy scenario. This scenario being:

- (a) Energy consumption, globally and in Canada, will rise by between 1 and 3 percent per year;
- (b) Crude oil prices will only very slightly increase up to 1995, but rise much more rapidly thereafter;
- (c) The steady depletion of Canadian light crude resources since the early 1970s will, over the next decade, be reflected in rapidly diminishing indigenous supplies of such oil; and
- (d) Stiffer competition in heavy oil markets, primarily from Mexico, Saudi Arabia and Venezuela, will make it important that Canada develop its own resources rather than import increasingly large volumes of crude oil.

We can also assume that the cost of heavy oil will be slightly less than conventional crude and will rise in proportion to the crude price, as well, the cost of suitable coal will not exceed \$10-13 run-of-mine/tonne and will probably only increase with inflation.

Canadian Energy Developments Inc. (CE) is therefore concentrating its efforts on developing co-processing technologies which can be shown to possess significant advantages from low feedstock costs and which, even in current market conditions, could offer acceptable rates of return. In particular, the company is working toward development of a 25,000 bbl/d (4,000 m<sup>3</sup>/d) heavy oil upgrader that would use co-processing technology.

### THE CE TECHNOLOGIES

While several agencies (such as CANMET in Canada, and EPRI, HRI, etc. in the US) are exploring a broad spectrum of coal/heavy oil co-processing as means for production of synthetic liquid hydrocarbons - Canadian Energy, in cooperation with the Alberta Office of Coal Research and Technology<sup>(1)</sup>, has focussed its attention on two specific process configurations.

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<sup>(1)</sup> A Division of the Alberta Energy, Government of Alberta

## 1. THE CCLC PROCESS

The CCLC Process consists of two stages which involves (i) a preparatory step and coal "solubilization" (or "solvolysis"), and (ii) hydrogenation of the solubilized product mix.

Depending on its API gravity, the heavy oil used in the process is fractionated by atmospheric or vacuum distillation, and the bottom stream is blended with coal to form a slurry. For the subsequent processing, coal loadings up to 45 wt %, with ash contents up to 10 wt % are used, and the first-stage coal solubilization is followed by hydrogenation at 440-460°C/14-18 MPa which consumes 2-3 wt % hydrogen.

Test runs with a feedstock comprised of 58 wt % Cold Lake vacuum bottoms<sup>(2)</sup>, 40 wt % subbituminous C coal<sup>(3)</sup> and 2 wt % "throw-away" catalyst in a continuous 2 kg/h bench scale unit have quite consistently furnished (C<sub>5</sub> to -525°C) oils that accounted for over 72 wt % of the d.a.f. feedstock.

Products available for secondary upgrading typically consisted of naphtha (25%), LGO (35%), M/HGO (14%) and a residual (+525°C) oil (8%).

The CCLC Process offers a continuous operation, high conversion, and a product slate that would require very little secondary upgrading for profitable disposition.

## 2. THE PYROSOL PROCESS

The second processing procedure under development by Canadian Energy is the PYROSOL Process which was initially conceived by West Germany's *Gesellschaft für Kohleverflüssigung mbH* (GfK) as an alternative to its more conventional high-severity coal liquefaction technology. PYROSOL seeks to generate as high or higher oil yields, but employs milder process conditions (and expends correspondingly less hydrogen) by combining a mild hydrogenation step with subsequent hydrocoking.

CE considered this approach to be another logical starting point for development of a Canadian co-processing technology, and accordingly entered into a co-operation and licence agreement with GfK.

In its present configuration and operating mode, the PYROSOL Process uses coal loadings up to 55 wt % (with up to 10 wt % ash), conducts first-stage hydrogenation at 380-420°C/8/12 MPa (with 0.8-1.5 wt % hydrogen consumption), and carries out second-stage hydrocoking at 480-520°C/8-10 MPa.

Although not yet optimized, test runs with the same feedstock as used in the CCLC Process have yielded 68 wt % oil (on d.a.f. feedstock); and product slates for secondary upgrading have been found to consist mainly of naphtha (8%), LGO (25%), M/HGO (27%) and coker oil (8%).

<sup>(2)</sup> These represent very heavy residua from oil sand bitumen processing

<sup>(3)</sup> From Manalta's Vesta Mine in Central Alberta

Advantages offered by the PYROSOL process will accrue from relatively low capital costs and easy operability, low hydrogen consumption, and an ability to process wastes in the form of coke before taking the products to secondary upgrading.

#### THE CURRENT STATUS

Canadian Energy is now working with a fully integrated, flexible 15 kg/h pilot plant which can operate in both process modes. Results from this unit are sufficiently encouraging to allow us to expect completion of the development program by 1990 and then proceed to a selection of the most suitable of the two processes for testing in a full-size demonstration plant. Commercialization may thus be possible in the early 1990s.

#### THE ECONOMICS OF CO-PROCESSING

Large-scale application of any co-processing technology obviously depends on demonstrating

- (a) that a full-scale plant can achieve a sufficient return on investment to justify the necessary capital outlay, and
- (b) that the technology is competitive with other processing options and can deliver a product that can compete against alternative fuels in the market place.

Canadian Energy has therefore initiated two feasibility studies in order to define the conditions in which a technically proven co-processing technology would have potential for commercial exploitation. One is examining the economics of stand-alone 25,000 bbl/d (4,000 m<sup>3</sup>/d) heavy oil upgrader using co-processing technology and is still in progress. But the other, which is focused on the suitability of co-processing as means for converting heavy residua to acceptable refinery feedstocks, has been completed.

In that study co-processing was assumed to be integrated with refinery operations, and five cases were explored.

The first three cases (A, B and C) envisaged a plant input of 10,000 bbl/d (1,600 m<sup>3</sup>/d) Cold Lake vacuum residua plus 1,371 tonnes/d subbituminous coal.

Case A then assumed maximum integration into the infrastructure of a refinery - i.e., the refinery is able to process the raw liquid products from co-processing without prior hydro-treating in the co-processing facility.

Case B envisaged intermediate integration - i.e., the refinery would only be capable of processing a moderately hydro-treated product from co-processing, and the co-processing facility would therefore include capacity for upgrading high-sulphur naphtha as well as for fluid catalytic cracking of heavy gas oils.

Case C considered minimum integration - with the refinery only capable of accepting a "synthetic crude" from the co-processing plant.

Case D, also based on minimum integration, envisaged a larger co-processing facility (16,000 bbl or 2,500 m<sup>3</sup>/d Cold Lake residua and 2,193 tonnes/d of run-of-mine subbituminous coal) in order to assess the impact of plant size on capital and operating costs.

And Case E examined upgrading of two situations (E-1 and E-2) in which only heavy oils were processed by conventional hydrocracking in ebullated bed and subsequent delayed coking, and compared these with C and D.

E-1 envisaged processing 10,000 bbl/d of the Cold Lake vacuum residua, while E-2 was taken to operate with 16,000 bbl/d of Cold Lake residua.

In Case C and D, the plants produced 13,000 and 21,000 bbl/d (2,070 and 3,340 m<sup>3</sup>/d), respectively, of (C<sub>5</sub> to -525°C) oil, and also furnished small amounts of C<sub>3</sub>/C<sub>4</sub>, sulphur and ammonia.

Capital costs for the upgrader units, expressed in 1987 \$Can and including all off-site facilities and utilization systems as well as project contingencies were \$310, \$385, \$416, \$539, \$410 and \$504 million for Cases A, B, C, D, E-1 and E-2 respectively.

The key data for the base case, all expressed in 1992 \$ Can., were then chosen as follows:

Plant start-up:	1992
Coal, f.o.b. Plant:	\$16.00/tonne (**)
Natural gas:	\$0.085/m <sup>3</sup> (**)
Cold Lake vacuum residua:	\$20.65/bbl (\$129.87/m <sup>3</sup> )
Value of liquid products:	Case A - \$31.55/bbl (\$197.17/m <sup>3</sup> )
	Case B - \$33.35/bbl (\$209.75/m <sup>3</sup> )
	Case C, D and E - \$35.35/bbl (\$222.33/m <sup>3</sup> )
Inflation rate to 1992:	4% per annum
Oil price forecasts:	Coles, Nikiforuk, Pennell
Equity:	100%

(\*\*) inflated to 1992

From these data, the case studies arrived to the following after-tax DCF rates of return:

Case A:	12.4%
Case B:	11.4%
Case C:	11.8%
Case D:	14.4%

For E-1 and E-2 the corresponding figures were 4.0% and 6.4% respectively.

These findings allow several important inferences. Thus:

- (a) A co-processing plant can offer an acceptable rate of return if heavy oil residua can be purchased at less than 80% of the price of crude oil, and such a plant is clearly more attractive than conventional heavy oil upgrading (cf. A, B, C and D vs. E-1 and E-2).

- (b) Minimal benefits would be gained from refinery integration if the output of the upgrader is to be a synthetic crude, and a stand-alone upgrader, which would benefit by producing some light oils from the residua, would therefore also prove economically attractive.
- (c) If the product price differentials used in the study are correct, the return on investment is not substantially affected by the extent of hydrotreating required to be conducted in the upgrader.

But perhaps the most interesting result of the study are the clear advantages which accrue to a co-processing facility from its lower feedstock costs. On a volume basis, and expressed in Canadian \$\$, feedstock and production costs per barrel of C<sub>5</sub> to -525°C oils would run to \$18.28 in co-processing and \$24.18 in conventional heavy oil upgrading (equivalent to \$114.97 and \$152.08 per m<sup>3</sup> respectively). And if the price of heavy residua were to increase by \$5.00/bbl, the cost advantage to a co-processing facility would rise by \$2.00/bbl (\$12.58 m<sup>3</sup>).

#### SUMMARY

Co-processing - i.e., simultaneous upgrading of coal and heavy oil residua - is expected to play an increasingly important role in Canada's future energy supply. Two co-processing technologies, both being developed by Canadian Energy Developments Inc., are reviewed, and six Case Studies indicating the economic potential of the process are presented. It is shown that co-processing has a significant economic advantage over conventional heavy oil upgrading, and that this advantage will increase as the cost of heavy oil increases.

Novel Dispersed-Phase Catalytic Approach to Coprocessing

by

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ABSTRACT

The Pittsburgh Energy Technology Center (PETC) is currently testing a new process concept for catalytically coprocessing a mixture of coal and petroleum-derived residual oils. The catalyst used in this process is molybdenum added directly to the reactor as an aqueous solution. Recent results are presented for product yield structure obtained in a 1-liter semibatch reactor. A discussion is also given for some recent findings obtained from coprocessing studies in a 1-liter continuous reactor system.

An important economic advantage in using this process can be gained if recovery of the dispersed catalyst from the product residue is demonstrated. A discussion is provided of an approach to catalyst recovery that does not require complicated processing steps and uses relatively inexpensive reagents. Results are presented from preliminary testing of the recovery process that indicate it is feasible to efficiently recover the catalytically active material for reuse in the process.

INTRODUCTION

The rapid consumption of conventional light petroleum reserves and the increasing need to refine lower quality petroleum feedstocks have recently prompted serious consideration of technology for coprocessing coal with petroleum residual oils or heavy bitumens. Coprocessing is attractive as a possible route for introducing the processing of coal in an evolutionary manner into existing refinery infrastructures without immediately incurring the large capital investment associated with other coal liquefaction alternatives.

Previous coprocessing experiments conducted at PETC in a noncatalytic operation (Lett and Cugini, 1986) have led to several conclusions. First,

coal is capable of enhancing demetallation of the petroleum solvent stream. The demetallation mechanism appears to be an adsorption process whereby the metals are adsorbed onto the surface of the coal remaining undissolved at the reaction conditions. Second, distillate yields in coprocessing are larger than would be predicted from linear addition of the distillate yields based on independent processing of the coal and petroleum-derived solvent. Two factors appear to be responsible for this result. First, the petroleum-derived solvent can act as a hydrogen donor solvent (although a poor one) for the coal; and second, coal enhances the conversion of the oil through the catalytic effects of the inorganics in the coal, primarily pyrite. While these are positive results obtained in the noncatalytic coprocessing approach, the liquid product yields are too low and would not appear to justify a noncatalytic approach to coprocessing.

In our preliminary catalyst-screening studies, we evaluated a single-stage approach to catalytic coprocessing. While two-stage coprocessing has merits, mainly dealing with coal's inherent ability to remove metals from the petroleum and thereby reduce second-stage catalyst aging, the use of a supported catalyst at any point increases the difficulty of ultimately recovering the expensive metals used in formulating the catalyst. A dispersed-phase catalyst would facilitate recovery of the active metals. Also, the most active materials for single-stage upgrading have been finely dispersed catalysts, either supported or unsupported. Therefore, we chose a dispersed-phase catalyst for use in single-stage coprocessing. The form chosen was a water-soluble salt, specifically ammonium molybdate. This material is readily available, and the molybdenum in a catalyst recovery process is readily recovered as ammonium molybdate.

## EXPERIMENTAL RESULTS AND DISCUSSION

### Batch Operation

Catalyst (additive) screening tests were initially conducted in 42-mL microautoclave reactors. The objective of these tests was to identify potential active catalysts for coprocessing. The catalysts (additives) tested include aqueous ammonium heptamolybdate, hydrogen sulfide, hydrogen sulfide/water, and pyrite. These catalysts were tested at typical coprocessing reaction conditions; i.e. 435°C, 1200 psig cold H<sub>2</sub> charge, a residence time of 1 hour, and a 70 wt% concentration of Maya ATB with 30 wt% Illinois #6 coal. Analyses of the major thermophysical properties of Maya ATB and Illinois No. 6 coal are presented in Tables 1 and 2.

The products from the batch tests were removed from the reactors and separated into soluble and insoluble fractions. The product yield distributions for the catalyst-screening tests are shown in Figure 1. The molybdenum catalyst was the most active catalyst tested. The use of 0.1% Mo (based on total feed slurry) as aqueous ammonium molybdate resulted in the highest heptane-soluble-oil yield and lowest pitch (THF-insolubles) yield. The use of pyrite or H<sub>2</sub>S resulted in an increase in conversion, with the pyrite being the more active of the two additives. Addition of water to the hydrogen sulfide system did not appreciably alter the product yield distribution.

The aqueous ammonium heptamolybdate catalyst precursor was also tested in a semibatch 1-liter autoclave reactor. The reaction conditions in the semibatch autoclave were similar to those in the microreactor with the exception that a flow-through gas was used. The gas rate was 4 scf of H<sub>2</sub> per hour. The feed charge consisted of 500 grams of coal/oil slurry.

The objective of these batch 1-liter tests was to determine the effect of scaling up from batch microreactor tests to semibatch operations (batch liquid, flow-through gas) on conversions and product distributions. These tests were conducted in both catalytic and noncatalytic systems. Figure 2 presents a comparison of the microreactor and 1-liter autoclave reactor product yields from coprocessing. The pitch conversion was similar in both cases. The major difference in the two systems was observed in the asphaltene (defined as heptane-insoluble/THF-soluble fraction) and oil (defined as heptane-soluble) yields. Apparently, the asphaltenes are converted to oil to a much larger extent in semibatch 1-liter reactors than in microreactors. This is observed in both catalytic and noncatalytic systems.

The work-up procedure for the semibatch system includes a distillation step. The total oil product is distilled after the heptane insolubles have been extracted. The distillation step employed a modified ASTM D1160 procedure. Figure 3 includes the results from the distillation of the heptane-soluble products for the semibatch catalytic and noncatalytic runs. The effect of the catalyst is most pronounced on the yield of distillable (C<sub>5</sub>-950°F) oil. A duplicate run for the catalytic case is also presented in Figure 5.

#### Continuous Unit Operation

The ultimate objective was to develop a dispersed-catalyst system capable of being used in a single-stage continuous operation. Continuous catalytic coprocessing experiments were performed in a computer-controlled 1-liter bench-scale continuous unit shown in Figure 4. A mixture of 30 wt% coal ground to 200 x 0 mesh and 70 wt% Mayan atmospheric tower bottoms (ATB - 650°F+ boiling material) was injected along with an aqueous ammonium heptamolybdate stream and a hydrogen and hydrogen sulfide gas stream (the H<sub>2</sub>S insures that the molybdenum has access to adequate sulfur to be converted to its sulfide form) into a preheater and reactor combination maintained at 2500 psig. Earlier microautoclave studies demonstrated the need for a gradual heat-up of the feed slurry (Cugini and Lett, 1987). Temperature staging of the preheater and reactor was used to provide this gradual heat-up in a continuous system. The residence time in the preheat zone is approximately 20 minutes. The operating conditions used for these runs were the following:

Reactor Temperature:	435°C
Pressure:	2500 psig
Catalyst Feed Concentration (g Mo/g coal + oil)	0.003
Gas Feed Concentration (vol %):	97% H <sub>2</sub> ; 3% H <sub>2</sub> S
Space Velocity:	0.75 hr <sup>-1</sup>
Gas Feed Rate:	10 scfh

Slurry Feed Rate:

250 g/hr

The run was continuously operated for 100 hours with no operational problems. The separation scheme used to analyze product distributions was similar to that used for the semibatch 1-liter products. The product gases were sampled using gas burettes and analyzed by gas chromatography. The average material balance over the course of the 100 hours was 96.8%. Table 3 presents product distributions from a 12-hour material balance period. A high yield of distillable product is obtained with the use of catalyst in the system. The insoluble product yield is low, which indicates high conversion of coal to soluble products. The hydrogen consumption is 3.0 wt% of total feed slurry. Coupled with the yield of 80.1 wt% of C<sub>5</sub>-950°F product, the hydrogen utilization efficiency is 26.7 lb distillate per lb H<sub>2</sub>.

### Catalyst Recovery

To improve the feasibility of PETC's coprocessing scheme, it was felt that a catalyst recovery scheme should be developed. The use of an unsupported molybdenum catalyst would facilitate catalyst recovery because there would be no interferences from the support material, and the recovered form of the catalyst could readily be reused as a catalyst in the process.

The recovery scheme that is being developed is similar in concept to Exxon's recovery scheme for coal liquefaction catalysts (Francis and Veluswamy, 1983). The coprocessing residue is oxidized to separate the carbon from the catalyst-containing mineral matter and to convert the metals in the mineral matter to their oxide form. The resultant ash is extracted with an alkali solution to first solubilize the molybdenum and then solubilize the nickel and vanadium.

An experimental program has been initiated to test the feasibility of this recovery scheme. The first stage of the program was to recover molybdenum from a mixture of coal ash and added metal oxides in a ratio to represent the mixture from a calcined stream of a residue from coprocessing 30% Illinois No. 6 coal and 70% Maya ATB. The composition of this mixture is presented in Table 4. The mixture was calcined at 700°C to allow for high-temperature interactions between the metals that might occur during the calcining step. The mixture was then extracted with ammonium hydroxide at a series of pH's and temperatures. The results of three catalyst recovery tests are also presented in Table 4. These results indicate that on model systems it is possible to extract 97% of the molybdenum with little contamination by vanadium. More tests are planned to optimize the extraction method on actual coprocessing residues.

### CONCLUSIONS

The approach taken to catalytically coprocess a mixture of coal and petroleum-derived residual oil in a single-stage process has been demonstrated successfully. A high-activity unsupported catalyst has been developed that is capable of enhancing coal conversion and distillate

yields. Activation of the catalyst has been demonstrated successfully for batch and continuous operations. In a moderate-severity mode of operation, 87 weight percent of the 950°F+ organic material in the slurry feed (Maya ATB and Illinois No. 6) is converted. The hydrogen consumption is about 3 weight percent of the feed.

The catalyst precursor used in this process is ammonium heptamolybdate added directly to the reactor as an aqueous solution. Preliminary results from model compound studies for recovery of the catalyst indicate that a significant fraction of the catalyst (97 percent) can be recovered for reuse.

#### FUTURE PLANS

The results obtained to date reflect early findings of scale-up from batch to continuous operations of catalytic coprocessing in a single-stage process. The catalyst activation sequence, although successful, has not been optimized. Since the pretreatment of the catalyst played a key role in the ultimate activity of the catalyst, several interdependent investigations will be pursued: (1) the time and temperature effects of preheating in the continuous mode of operation; and (2) the effect of adding promoters to the ammonium molybdate catalyst on coprocessing performance.

A research effort will continue to develop a recovery process for the spent catalyst in the coprocessing residual products. Efforts to date indicate that recovery of catalyst from calcined residues can be performed at very high levels of recovery via an extraction process. Coprocessing residual products will be subjected to calcination and catalytic metals recovery by leaching with an ammonium hydroxide solution. The goal set for the recovery process will be greater than 97 percent recovery of the molybdenum catalyst.

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

Table 1

ILLINOIS NO. 6  
(Burning Star)

Proximate Analysis, wt%  
(as-received)

Moisture.....	4.2
Volatile Matter.....	36.9
Fixed Carbon.....	48.2
Ash.....	10.7

Ultimate Analysis, wt%  
(moisture-free)

Carbon.....	70.2
Hydrogen.....	4.8
Nitrogen.....	0.9
Sulfur.....	3.1
Oxygen (diff.).....	9.9
Ash.....	11.1

Table 2

MAYA ATB  
(650°F+)

Ultimate Analysis, wt%

Carbon.....	84.5
Hydrogen.....	10.6
Oxygen.....	0.3
Nitrogen.....	0.5
Sulfur.....	4.0
Ash.....	0.1
Ni(ppm).....	70
V (ppm).....	370
950°F-, vol%.....	30
ASTM D1160	
Heptane Insols, wt%.....	20
ASTM D3279	

Table 3

PRODUCT YIELDS AND CONVERSIONS -- (CAT-8-2)

## Yield Structure

<u>Component</u>	<u>Coal + Heavy Oil (Ash-Free) Weight Percent</u>	<u>950°F (Ash-Free) Weight Percent</u>
C <sub>1</sub> -C <sub>4</sub>	5.1*	6.9
C <sub>5</sub> -950°F	80.1	74.5
950°F+	6.9	8.7
Heptane Insolubles	3.7	4.6
Non-Hydrocarbon Gases	7.2*	9.2
Hydrogen Consumption	-3.0	-3.9

## Conversions (Ash-Free Basis)

<u>Component</u>	<u>Weight Percent</u>
950°F+	87
THF Insolubles	95
Heptane Insolubles	92

\*Estimated from tail gas sampling.

Table 4

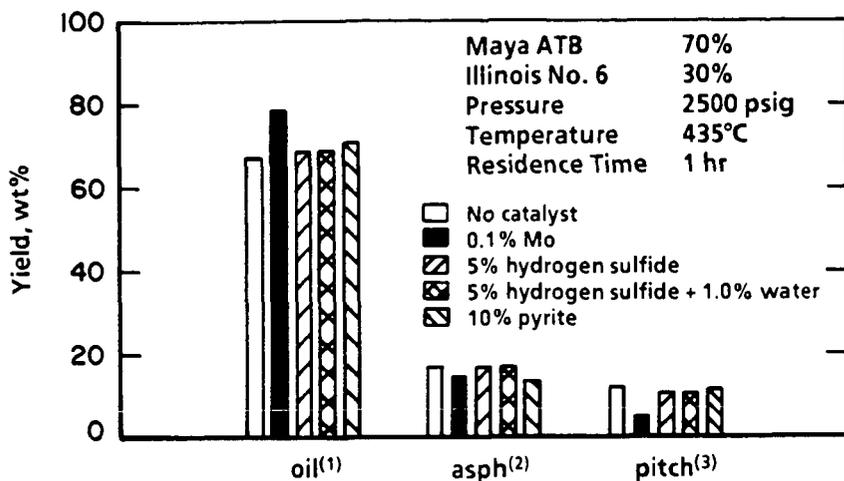
Model Compound Extractions

Model Mixture

<u>Component</u>	<u>Weight Percent</u>
Coal Ash	92.8
V <sub>2</sub> O <sub>5</sub>	2.8
NiO	0.1
MoO <sub>3</sub>	4.3

Molybdenum Recovery

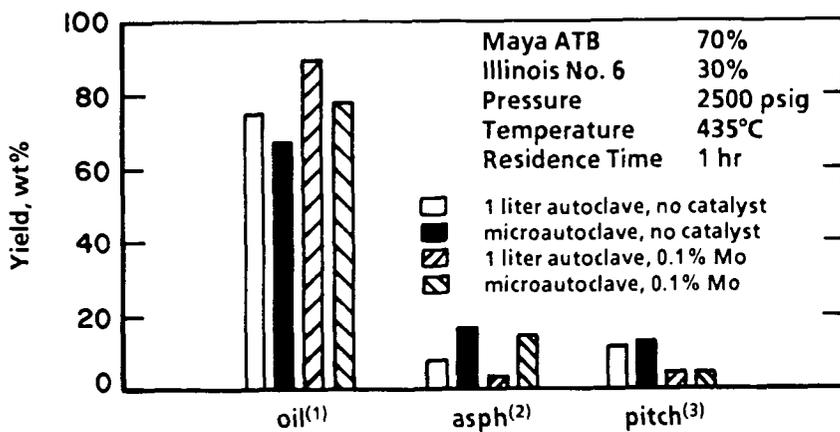
<u>Test</u>	<u>Wt% Mo Recovered As Molybdate</u>	<u>Wt% of V Recovered with Molybdate</u>
1	75	2
2	95	5
3	97	22



- (1) heptane solubles
- (2) heptane insoluble/THF soluble
- (3) THF insolubles

Figure 1.

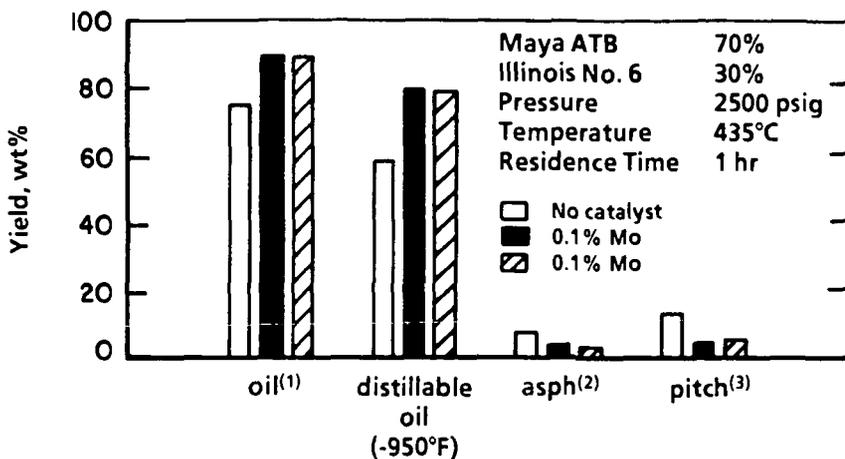
MICROAUTOCLAVE PRODUCT YIELDS



- (1) heptane solubles  
 (2) heptane insoluble/THF soluble  
 (3) THF insolubles

Figure 2.

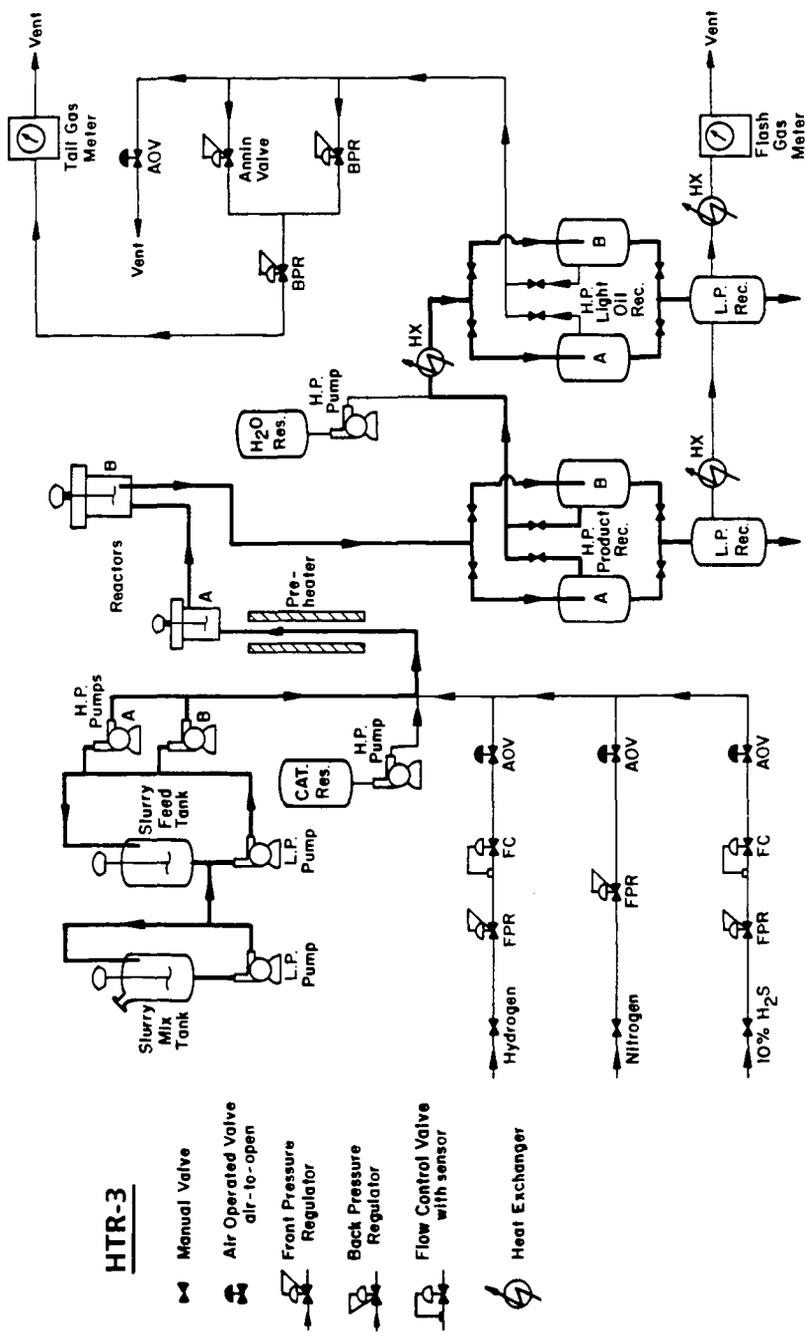
COMPARISON OF MICRO- AND 1 LITER-AUTOCCLAVE REACTOR SYSTEMS



- (1) heptane solubles
- (2) heptane insoluble/THF soluble
- (3) THF insolubles

Figure 3.

BATCH 1 LITER AUTOCLAVE YIELDS



**HTR-3**

-  Manual Valve
-  Air Operated Valve air-to-open
-  Front Pressure Regulator
-  Back Pressure Regulator
-  Flow Control Valve with sensor
-  Heat Exchanger

Figure 4. Schematic of Bench-Scale Continuous Coprocessing Unit

## THE BEHAVIOUR OF HIGHVALE AND VESTA COALS UNDER CO-PROCESSING CONDITIONS

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### INTRODUCTION

Co-processing involves the conversion of relatively low-cost coal and heavy oil in the presence of hydrogen to synthetic crudes that can be further upgraded into premium liquid fuels. This alternative coal conversion concept eliminates or significantly reduces the need for solvent recycle and hence offers greater potential for improving economic performance over current direct coal liquefaction technologies.

Alberta is endowed with large reserves of subbituminous coals, bitumen and heavy oils. The combined processing of these feedstocks is attractive for the Alberta scenario. Alberta Research Council has been active in developing the co-processing technology (1,2). Due to the high oxygen and mineral matter contents in Alberta subbituminous coals plus the high sulfur and metal contents in bitumens, special considerations are necessary when processing these feedstocks, for example, removal of oxygen to avoid excessive hydrogen consumption; removal of mineral matter to reduce deactivation of expensive catalysts; or use of less efficient, low-cost disposable catalysts. Alberta Research Council developed a two-stage process which involves a first-stage coal solubilization in bitumen or heavy oil using a mixture of carbon monoxide and steam in the presence of an alkali metal catalyst, followed by a catalytic hydrogenation second-stage (3).

This paper is focused on the use of disposable iron oxide catalysts in co-processing two Alberta subbituminous coal and bitumen feed pairs. Effects of reaction severity, pressure and coal concentration will be discussed.

### EXPERIMENTAL

#### Process Unit

Co-processing experiments were carried out in a two-stage, continuous flow reactor system with a nominal capacity of 2 Kg/h of slurry feed. The reactor system consists of two stirred tanks of one and two litres in volume connected in series. Products were collected over a material balance period of eight hours under steady state conditions. For all experiments reported in this paper, the material balances were within  $100 \pm 3\%$ . For comparative purposes, all data were normalized to give 100% recovery by adjusting the weight of the slurry product. Details of the process unit are available elsewhere (4).

Slurry products were distilled according to a modified ASTM D-1160 procedure, followed by extraction using pyridine in a soxhlet apparatus.

#### Feedstocks

The co-processing characteristics of two feed pairs, Highvale (subbituminous B) / Athabasca bitumen and Vesta (subbituminous C) / Cold Lake bitumen, were evaluated. The two coal samples were obtained from the Alberta Research Council's sample bank.

The Athabasca bitumen sample was a Suncor coker feed (IBP 222°C) while the Cold Lake sample was an atmospheric distillation residuum obtained from the Imperial Oil Strathcona Refinery, Edmonton. Analyses of the coals and bitumen samples are given in Tables 1 and 2, respectively.

### Reaction Severity

Previous batch autoclave experiments (5) indicated that iron oxides can be used as effective catalysts to solubilize Alberta coals in petroleum derived solvents at temperatures up to 470°C under a hydrogen atmosphere of about 21 MPa. In order to avoid excessive coking, the continuous flow CSTR experiments were carried out at temperatures below 470°C.

Reaction temperature and space time in both reactors were varied to determine the impact of reaction severity on product yields and qualities. As a first approximation, a simplistic approach was taken by defining a reaction severity index which combined the effects of the temperature (T) and nominal residence time (N. RTime) in a reactor.

$$\text{Reaction Severity (SV)} = [ (\text{N. RTime}) * \text{EXP}(-E/RT) ]_{1\text{st reactor}} \\ + [ (\text{N. RTime}) * \text{EXP}(-E/RT) ]_{2\text{nd reactor}}$$

The activation energy (E) for both stages was assumed to be  $1.26 \times 10^5$  joules/g-mole (30 Kcal/g-mole). A reference severity index of unity was arbitrarily defined at the condition of 400°C for 60 min.

Figure 1 compares co-processing results obtained at various degrees of reaction severity ( $2 < \text{SV} < 5$ ) for the Vesta/Cold Lake pair with moisture-and-ash-free (maf) coal loadings between 27 and 30 wt%. The simplistic, reaction severity index approach gives good correlation with product yields when expressed in terms of maf feed basis. Yields of carbon oxides and hydrogen sulfides are relatively constant over the whole range of conditions studied. Also, as the reaction severity increases the hydrocarbon gas yield increases proportionately, while the pyridine insoluble organic matter (IOM) decreases. Even at the highest reaction severity conditions tested, there was no sign of excessive coke formation, as reflected by the steady decrease in the amount of IOM in the residual solids. These IOM values correspond to coal conversions (measured by pyridine extraction) between 93-99 wt% maf coal, which were found to be in agreement with coal liquefaction results obtained under similar process conditions (7).

With increasing severity distillable oils (IBP-500°C) are formed at the expense of pyridine extractable materials. Using the two-stage CSTR system, a maximum yield of 62 wt% maf feed was obtained at the highest severity tested. Distillable oil yields of as high as 75% maf feed were observed using a tubular reactor system (6).

Comparing product yields from co-processing of the two feed pairs (refer to Figure 1 and 2), the Highvale/Athabasca pair seems to produce more carbon oxides, hydrocarbon gases and IOM, but less distillable oils. These differences which become more pronounced at higher reaction severity conditions, cannot be correlated to the elemental and petrographic analyses as given in Table 1. Although Vesta and Highvale coals have a similar vitrinite content, Vesta coal contains a higher percentage of inertinite and thus is expected to be less reactive. However, conversions of Highvale coal (82-85 wt%) were in fact 10-14 wt% lower than Vesta coal. A similar result was also obtained under the direct coal liquefaction mode (7). On the other hand, the difference in carbon oxides yield from co-processing contradicts previous results obtained for these coals under liquefaction mode (7).

Figures 1 and 2 reveal similar yields of non-distillable, pyridine extractable material for both feed pairs. However, detailed compound class analysis (3) suggests

that most of the residual oils occurred in the form of hydrocarbons, resins and asphaltenes with less than 30 wt% as preasphaltenes. The higher preasphaltene content in products from the Highvale/Athabasca pair further confirmed the lower reactivity of this feed pair.

### Pressure

Effect of system pressure was studied over a narrow range of 14.2 to 20.7 MPa at two different reaction severities. The low pressure experiments were carried out at a slightly lower maf coal loading of 27 wt%, while the high pressure data were collected using 30 wt% of coal. Considering the slight difference in coal loading, there are no significant effects on product distribution due to the lower operating pressure, as indicated in table 3. However, low pressure operating conditions, which may create long term operating problems, warrant further investigation in a large scale pilot unit.

### Coal Concentration

Bitumen is considered a poorer solvent than coal-derived liquids for coal solubilization. In once-through mode operation, the ability of bitumen to solubilize coals may deteriorate as the coal concentration increases. As illustrated in Figure 4, produce yields from co-processing of Highvale/Athabasca under relatively mild severity conditions increase steadily as the coal concentration increases from 0 to 35 wt%. The bitumen-only case gives 58 wt% (feed bitumen basis) of distillable oils. The incremental oil yield at a coal loading of 35 wt% is about 18 wt% on a bitumen feed basis. Translating back to maf coal basis, this is equivalent to 33 wt%, which is 10-15 wt% higher than the typical values when anthracene oil was used as a solvent, under similar process conditions. The higher incremental oil yield provides additional incentive for co-processing of coals and bitumen.

### CONCLUSION

Co-processing of Alberta Subbituminous coals and bitumen in a two-stage, once-through mode is technically feasible. These results indicate that synergistic effects occur when the Highvale and Vesta coals are processed with Athabasca and Cold Lake bitumen, respectively. Decreasing the system pressure from 20.7 to 14.2 MPa has no significant effect on product distribution. Despite the over simplification of the two-stage CSTR model, good correlations are obtained between product yields and the reaction severity index.

### ACKNOWLEDGEMENT

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Table 1. Typical Properties of Highvale and Vesta Coals

	Highvale	Vesta
ASTM Rank	Subbit. B	Subbit. C
<u>Proximate Analysis (wt%)</u>		
Capacity Moisture	19.6	24.7
Moisture Free Ash	11.4	12.4
Volatile Matter (maf)	39.6	41.9
Fixed Carbon (maf)	60.4	58.1
<u>Elemental Analysis (wt%)</u>		
Carbon	75.0	74.4
Hydrogen	4.3	5.0
Nitrogen	1.1	1.5
Sulfur	0.2	0.6
Oxygen	19.3	18.5
H/C	0.69	0.81
<u>Petrographic Composition (vol%)</u>		
Vitrinite	75.0	73.0
Liptinite	2.1	0.3
Semi-fusinite	22.2	8.9
Inertinite	1.1	17.0

Table 2. Typical Analysis of Feed Oils

	Athabasca Coker Feed	Cold Lake Atm. Bottom
<u>Elemental Analysis (maf)</u>	wt%	wt%
Carbon	82.9	83.2
Hydrogen	10.3	10.3
Nitrogen	0.5	0.9
Sulfur	5.3	5.3
Oxygen (by diff.)	1.1	0.3
H/C	1.49	1.49
<u>Distillation and Extraction</u>		
Moisture	-	0.01
IBP-500°C	29.5	29.2
Residual Oils	69.9	70.7
Residual Solids	0.6	0.05
<u>Compound Class Analysis</u>		
Hydrogen & Resin	79.8	70.5
Asphaltene	18.9	27.2
Preasphaltene	1.3	2.3

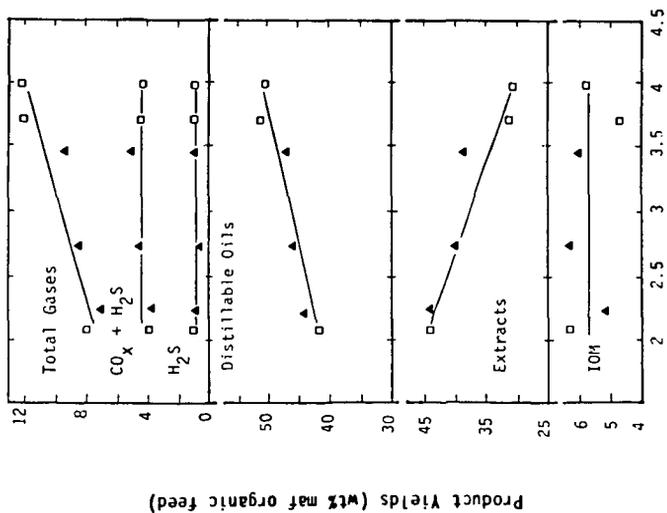
Table 3. Effect of Pressure on Co-processing of Vesta/Cold Lake Atmospheric Bottom Using Iron Oxide as Catalysts

	High Severity		Low Severity	
	Case A	Case B	Case C	Case D
Pressure (MPa)	20.7	14.3	20.7	14.2
Temperature (°C)	431/431	431/430	420/419	418/416
Severity Index	3.52	3.90	2.65	2.56
<u>Product Distribution (maf wt% feed)</u>				
C1 - C5	4.53	5.20	3.15	4.08
IBP-200°C	11.14	14.32	7.23	10.43
200-375°C	10.93	16.58	8.54	10.40
375-500°C	31.86	28.76	31.27	29.11
500°C+	36.56	33.81	44.10	42.90
IOM	1.33	1.73	1.76	2.61
H <sub>2</sub> consumed	1.86	2.85	1.65	2.42

Figure 2

Co-processing of Highvale Coal and Athabasca Bitumen (Suncor Coker Feed)

(using dispersed iron oxide as catalyst)

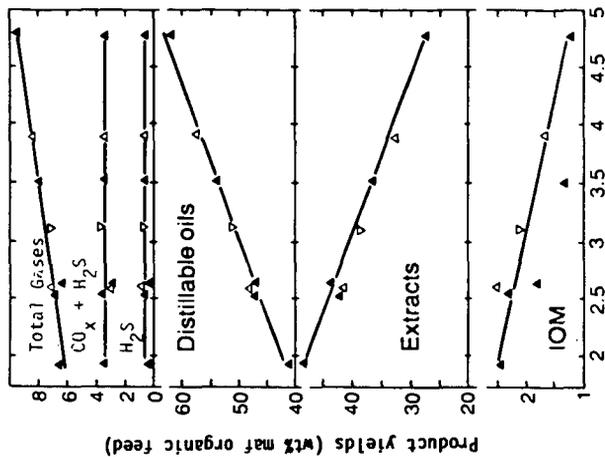


Coal concentration: □, 30%; ▲, 35% (maf)  
Reaction Severity Index

Figure 1

Co-processing of Vesta Coal and Cold Lake Atmospheric Bottom

(using dispersed iron oxide as catalyst - bench unit)



Reaction severity index  
Pressure (MPa): ▲, 14.3; ▼, 17.0; △, 20.7

Figure 4

Effects of Coal Concentration  
 - low severity (Highvale Coal/  
 Athabasca bitumen, iron oxide  
 as catalyst)

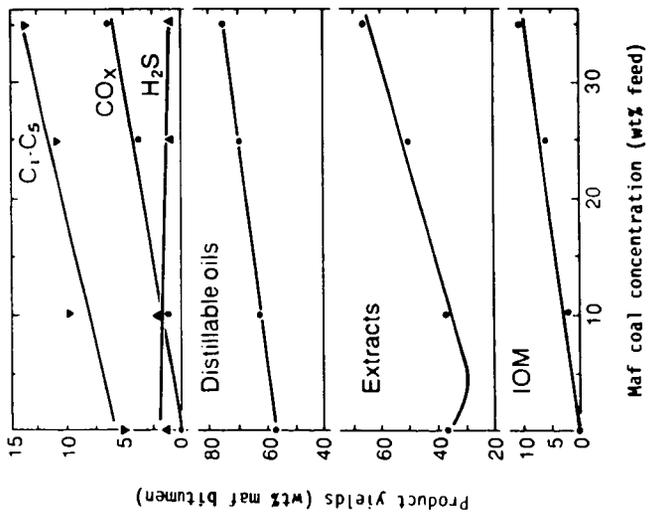
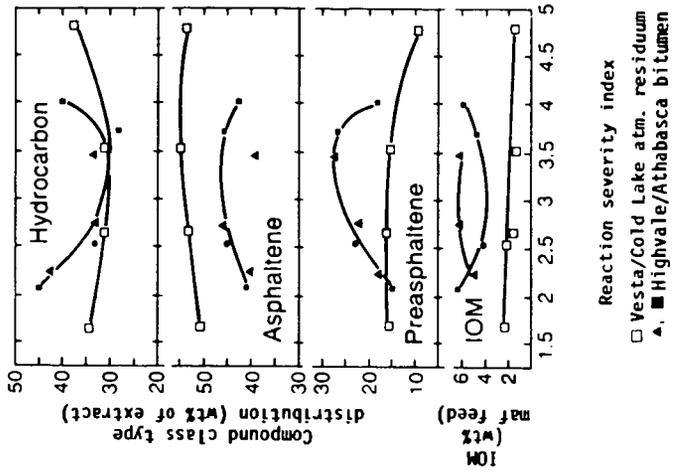


Figure 3  
 Compound Class Type Distribution  
 of Co-processing Product



## COPROCESSING - THE HYDROGENATION OF LIGNITE TOGETHER WITH RESIDUAL OILS

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### 1 ABSTRACT

The current overflow on the crude oil market must not obscure the fact that world oil resources are limited. Instead, it must be our goal to develop practicable concepts for the conversion of fossil raw materials and optimize their economic viability. The joint development programme of the Rheinische Braunkohlenwerke AG and the Union Rheinische Braunkohlen Kraftstoff AG for the catalytic hydrogenation of fossil raw materials in the liquid phase aims at this goal.

In a continuously operating process development unit extensive investigations have been carried out focussing on:

- conversion of lignite,
- development of catalysts based on lignite coke,
- conversion of heavy residual oils,
- conversion of mixtures of lignite and residual oils (coprocessing).

In this paper the results of these investigations are discussed.

A comparison of lignite liquefaction and coprocessing elucidates the advantage of coprocessing. Thanks to a change in the process route and a yield-improving synergistic effect, coal liquefaction via coprocessing will reach economic viability earlier than the liquefaction of coal alone.

### 2 RESEARCH AND DEVELOPMENT PROJECTS TO CONVERT FOSSIL RAW MATERIALS

In view of the future situation in the crude oil market where oil less in quantity and quality will be available it is necessary to develop practicable concepts for the conversion of fossil fuels.

In the field of refining, e.g., there are several processes permitting the conversion of heavy residual oils or even extra-heavy crude oils into lower-boiling products. Some of these processes have for quite some time been applied on an industrial scale; they include coking, deasphaltization, and H-oil processes. Limiting factors in respect of process application are the quality of feed oils (content of heavy metals) and/or the quality of by-products (petrol coke).

The process suitable for use in a much wider field of application is the conversion of fossil fuels in liquid-phase hydrogenation; it is based on coal liquefaction according to Bergius-Pier, a process which can look back on many years of application. In our group, e.g., it was used from 1941 to 1964 to process lignite and heavy oil on a commercial scale.

The development programme on which the Rheinische Braunkohlenwerke AG (Rheinbraun) and the Union Rheinische Braunkohlen Kraftstoff AG (Union Kraftstoff) have been cooperating since 1978 and which deals with the hydrogenation of fossil fuels to make high-grade liquid hydrocarbons centres around the following:

- hydroliquefaction of lignite,
- hydroliquefaction of residual oils,
- hydroliquefaction of mixtures of lignite and residual oils (coprocessing),
- development of suitable catalysts based on lignite coke.

In its first stage, i.e. on a process-development scale, we implement the development programme with the aim of

- further developing and optimizing the processes applied from 1941 to 1964,
- determining process data,
- finding out whether hydrogenation of fossil fuels will be economically viable.

Major fields of these projects were and are financially supported by the Federal Ministry of Research and Technology.

In the following, this paper will deal not only with the results obtained in the investigations of coprocessing; in order to facilitate understanding of this subject, it will also discuss the results which are achieved in the investigations of lignite liquefaction, hydrogenation of residual oils, and development of catalysts.

### 3 FUNDAMENTAL PROCESS DIFFERENCES IN THE CASE OF HYDROGENATION OF COAL, MIXTURES AND RESIDUAL OILS

Between coal liquefaction, on the one hand, and hydrogenation of mixtures and residual oils, on the other hand, there is a major difference in process engineering (Figure 1). Today, conversion of residues and coprocessing are generally operated in a "once-through mode"; contrary to this, coal liquefaction calls for cycling of the slurry oil, and the operating mode preferably used to hydrogenate residual oils in the commercial-scale plants until 1964 was recycling of the cold separator heavy oil and parts of the hot separator sludge. Since recycling is no longer required, coprocessing - contrary to coal hydrogenation - permits a major simplification of the process route. In coprocessing, the mineral oil-derived residual oil acts as slurry oil which is converted into lower-boiling products without any cycling being required.

Due to today's advanced refining technique it is advisable not to recycle the heavy oil produced during hydrogenation, but to hydrocrack it and produce naphtha and gas oil for use in the motor fuel sector or feedstocks for use in petrochemistry.

The liquid-phase process benefits from the "once-through mode"; here, the reaction zone is not filled with cycled heavy oil and, hence, permits full charge with heavy oil.

### 4 TEST INSTALLATION

#### SET-UP AND OPERATION OF THE PROCESS DEVELOPMENT UNIT

Figure 2 shows the set-up of the test plant for lignite hydroliquefaction.

This plant is also used to carry out tests on conversion of heavy residual oils and coprocessing.

The plant is designed for fully continuous operation.

The feedstock is predried powdered lignite with a residual water content of up to 12% wt and a maximum grain size of 1 mm and/or oil with an initial atmospheric boiling point of  $> 510^{\circ}\text{C}$ .

The reaction pressure of hydrogenation ranged between 150 and 300 bar.

The reactor has a volume of approx. 8 l. Two reactors with an inner diameter of 4.5 cm each are connected in series. The pumps are designed for an hourly

throughput of coal slurry or oils of up to 16 l/hr.

The average availability of the plant was 60% for hydrogenation on the basis of coal while it rose to more than 80% for hydrogenation with residual oil.

## 5 LIGNITE HYDROLIQUEFACTION

### 5.1 RESULTS OBTAINED DURING TESTS IN THE PROCESS DEVELOPMENT UNIT

Within the scope of the lignite hydroliquefaction projects we performed, from 1978 to 1983, extensive development work in that process development unit.

In the following, the major results are summarized.

#### Yields as a function of temperature and gas throughput

In the temperature range under investigation, the oil yields as a function of temperature rise from 41 to 48 parts by weight. The residue portion decreases from 28 to 18 parts by weight, and the amount of hydrocarbon gases produced rises from 13 to 26 parts by weight, each related to 100 parts by weight at a coal throughput, maf, of 0.5 to 0.6 kg/l x hr.

Through an increase in the cycle gas amount of 30% the oil yield rises to approx. 53 parts by weight in the temperature range under investigation, while only some 12 parts by weight (Figure 3) will be obtained as residue.

It has not yet been possible to make definite statements about whether an increase in the amount of cycle gas will also produce higher yields in commercial-scale reactors with different fluid dynamics conditions.

#### Yield as a function of pressure

The tests in the process development unit have shown that at a pressure of 220 bar and with the same linear flow velocity as at 300 bar - for this, the volume of cycle gas was reduced from 18 to 14 m<sup>3</sup>/hr - the oil yield decreases by 3 parts by weight as a result of the lower pressure. The portion of residue increases by the same amount. In the temperature range under investigation, the hydrocarbon gases correspond to the comparative values at 300 bar.

At a pressure of 150 bar and with the same cycle gas velocity as at 300 bar (9 m<sup>3</sup>/hr) the process development unit yields an amount of oil which is about 10 parts by weight lower.

#### Recycling of supercritical fluid (SCF) extract

Thanks to the high extract yields, the supercritical fluid extraction technique produced considerably higher oil amounts and lower portions of residue than would be obtained, if conventional vacuum distillation of the sludge were employed under the same conditions. Figure 4 shows a comparison of the yields.

A final judgement on this technique can only be given when the test results to be obtained in a pilot plant will be on hand.

#### Sludge recycling

A crucial problem in hydroliquefaction is the formation of CaCO<sub>3</sub> containing sediments which give rise to coking.

Since part of the hot separator sludge (approx. 20% of the slurry oil) was recycled into the reaction zone, we were able to prevent cokings and deposits in the reactors of the process development unit; this was due to an improved fluid dynamics resulting from a better "carrying capacity" of the reaction mixture which in turn was caused by a rise in density.

The yields correspond to comparative figures obtained without sludge recycling.

## 5.2 PROCESS CONCEPT

The process concept of lignite hydroliquefaction consists of the following steps:

- coal drying and slurring,
- hydrogenation in the liquid phase at pressures between 200 and 300 bar,
- partial cycling of sludge from the hot separator to the slurry oil,
- separation of the remaining hot separator product by way of distillation or supercritical fluid extraction into a solids-free oil for slurring and a residue for hydrogen production,
- use of H<sub>2</sub>S as co-catalyst, and
- coal-oil refining.

The question of whether this process concept can be implemented on a commercial scale has to be cleared up in two development stages, i.e. first in a pilot plant, and then in a demonstration plant where its industrial-scale feasibility and its economic viability are to be verified.

The results we obtained during operation of the process development unit formed a basis for the basic engineering and authority permittance required for a lignite hydrogenation pilot plant. In mid-1983, the competent authority granted the building and operating licences for a plant designed for an hourly coal throughput of up to 25 t (t - tonne) and to be located on the grounds of the Union Kraftstoff.

Due to economic considerations construction of this pilot plant has been postponed because the current price of gasoline produced by lignite hydrogenation is still about two times as high as that of petroleum-derived gasoline.

## 6 HYDROLIQUEFACTION OF RESIDUAL OILS

Within the scope of the project dealing with residual oil hydrogenation we carried out investigations in the process development unit with the aim of:

- clearing up the mode of action of liquid-phase catalysts and developing a suitable catalyst on the basis of lignite products, and
- determining yields and product qualities when different residual oils are used.

### 6.1 DEVELOPMENT OF CATALYSTS

From 1948 to 1964 when the commercial-scale liquid-phase plant worked with atmospheric distillation and cracking residues, entrained dust from lignite gasification was used as a base material for developing catalysts. With the addition of ferrous salts this material constituted an efficient and low-priced disposable catalyst.

Since today such or similar products from lignite gasification are either no longer available or occur in such small quantities that are insufficient to meet commercial-scale requirements, tests were made to develop a suitable

and low-priced substitution product which is likewise derived from lignite products.

The result we obtained in the extensive research work on catalyst development showed that the following materials are particularly suitable:

- entrained dust from High-Temperature Winkler gasification,
- powdered coke from the rotary-hearth furnace process (rotary-hearth furnace coke),
- steam-activated rotary-hearth furnace coke.

For economical reasons, rotary-hearth furnace coke is preferably used (Figure 5).

The previous tests have shown that the catalysts influence not only the yield structure, but also the performance of the hydrogenation plant. A troublefree long-time performance without any temperature inhomogeneity and coke deposits in the reactors was only obtained when a lignite coke-derived catalyst was added.

Thanks to the successful research work described above we can now provide sufficient quantities of highly suitable and low-priced catalysts for coprocessing and liquid-phase hydrogenation of residual oils.

#### Mode of action of liquid-phase catalysts

The lignite-based solid matter which is added as catalyst to the liquid-phase process passes slowly through the reactors and is subsequently discharged from the hot separator.

Investigations of this solid matter have shown that due to its surface properties the catalyst used serves as an adsorbent for asphaltenes and carries them out of the reaction zone, thus preventing coking and coke deposits there. We discovered that in this way up to 1% wt of the residual oil fed was discharged along with the catalyst from the process cycle. As electron-microscopical analyses have shown, major part of the catalyst surface is preserved in this process.

Figure 6 compares the X-ray fluorescence analysis of the solid matter isolated from the hot separator sludge with that of powdered coke.

For powdered coke, only the components of lignite ash are indicated. In the electron-microscopical analysis of the solid matter leaving the hot separator, the heavy metals, nickel and vanadium, occur in addition. This is an indication that apart from asphaltenes the liquid-phase catalyst also adsorbs the heavy metal components in the residual oil. Taking-up of the transition metals with hydrocracking activities allows the catalyst to step up its catalytic activity in the liquid phase.

From the catalytic properties of the coke alone, after having been "activated" in the liquid phase and with account taken of the capturing effect on asphaltenes, we can derive the following model representation of the catalyst's mode of action:

- the catalyst on the basis of lignite coke has a hydrocracking effect because of its surface properties and its mineral composition;
- due to the absorption of nickel and vanadium the catalyst on the basis of lignite coke reaches its maximum catalytic activity in the liquid phase;
- due to its surface properties the catalyst on the basis of lignite coke acts as an adsorbent on potential coke precursors and carries them out of the reaction zone; thus, it prevents coking and coke deposits there, and

- under the reaction conditions of liquid-phase hydrogenation the catalyst on the basis of lignite coke has a similar fluid-dynamics behaviour to that of the residual oil; it is discharged in an "once-through mode".

## 6.2 RESULTS OBTAINED WITH DIFFERENT RESIDUAL OILS

The chemical and physical properties of heavy residual oils strongly vary depending on their crude oil origin. Thus, different yields and product qualities are obtained depending on what feedstock is used in liquid-phase hydrogenation of heavy residual oils. Against this background, we conducted an investigation with the object of determining yields and product qualities for a variety of residual oils with most different chemical compositions and, in addition, defining optimum reaction conditions and operating modes in the process development unit.

Figure 7 classifies the different residual oils by their heavy metal contents and the prevailing type of hydrocarbons they contain.

Of the crude oil types classified in Figure 7, we investigated vacuum and visbreaking residues in the process development unit. In doing so, we focussed our activities on the investigation of asphaltene-rich residues since these matters would chiefly be processed in an industrial-scale plant.

The results we obtained in this extensive investigation can be summarized as follows:

- depending on the residual oil used the conversion rates obtained ranged between 70% and 95%;
- under optimized reaction conditions, the oil yields were between 60 and 85% wt; the residue decreased to amounts between 5 and 23% wt; depending on the feedstock, the yield of hydrocarbon gases was 5 to 15% wt;
- under the same reaction conditions, vacuum residues produced higher oil yields than corresponding visbreaking residues; since it was possible to convert visbreaking residues under more severe reaction conditions than vacuum residues, we obtained comparable yield distributions from both products;
- residual oils rich in asphaltene and heavy metals showed a smaller tendency towards coking in the reactors than naphthene- and paraffin-rich residual oils with lower heavy metal contents.

## 7 COPROCESSING RESULTS

Within the scope of the coprocessing investigations, it was examined whether mixtures of dry lignite and residual oils can be processed under liquid-phase conditions as well.

The tests in the process development unit demonstrated the technical feasibility of coprocessing; in this case, approx. 30% of the vacuum residue was replaced by dry lignite; but almost the same yield distribution was obtained.

Under optimal conditions, coprocessing yielded conversion rates of about 90%. In the temperature range under study and with different reactor throughputs, we obtained oil yields of approx. 80% wt and portions of hydrogenation residue and hydrocarbon gases amounting to approx. 10% each.

In addition it was found that in the case of coprocessing and, in particular, with small reactor throughputs the absolute values of oil yields obtained from the mixture were higher than the comparative amounts in residual oil hydrogenation. It is an unexpected result since with approx. 48% wt the oil yields in conventional lignite liquefaction are much lower than those obtained in residual oil conversion. So, if the oil yields from coprocessing

were calculated theoretically, the resulting values would be always lower than those in residual oil hydrogenation. This result is shown in Figure 8.

The bar graph shows yields which were obtained under equal reaction conditions in residual oil hydrogenation, coprocessing and lignite liquefaction. In the case of coprocessing, we specified not only the figure of the yield distribution determined experimentally in the process development unit, but also the result obtained theoretically.

Figure 8 shows that under the given reaction conditions the oil yield of coprocessing determined experimentally is not only much higher than suggested by the theoretical calculation on the basis of the result obtained in separate hydrogenation of residual oils and coal; in absolute figures, it is even comparable to the oil yield in residual oil conversion.

Due to the oil yields which in practical operation are higher than expected in theory we obtain a desired reduction in the quantities of hydrogenation residue and gaseous hydrocarbons. Since these gases are unwanted products which are formed by using expensive hydrogen, it can be considered another advantage of coprocessing. The synergistic behaviour was observed over the entire temperature range and with varying reactor throughputs, and it was verified under all reaction conditions. The synergism was all the more pronounced, the smaller the reactor throughput was. This effect may be due to the heavy metal contents in the residual oil. The heavy metals can be expected to have a catalytic effect on lignite liquefaction as well. It is also conceivable that lignite or its ash will catalytically act on residual oil hydrogenation.

In the course of our work on coprocessing we determined not only the yield distribution and the quality of the products; furthermore, we critically examined the operating performance of the plant, especially in respect of coke deposits.

During coprocessing no coke deposits were observed in the reactors. Neither did we detect the formation of calcium carbonate-containing sediments known from lignite liquefaction. Obviously, the residual oil which can carry the solids particles away prevents the formation of deposits in the reaction zone which have always given rise to coking. During the above investigations of lignite liquefaction a similar effect was produced by partial recycling of the hot separator sludge.

As already mentioned, coprocessing compared with coal liquefaction alone has the considerable advantage of making slurry oil cycling superfluous. In coprocessing, the residual oil acts as slurry oil that, on its part, is converted into lower-boiling products. In the case of lignite liquefaction, the portion of cycle oil amounts to some 1.5 t per tonne of dry lignite fed. As an "inert flow" this portion takes up a major part of the reactor volume which in the case of coprocessing can be utilized for further conversion.

This permits higher specific conversion rates relative to the reaction volume. Therefore, coprocessing is expected to reach its commercial viability earlier than coal liquefaction.

Figure 9 shows in quantitative terms how the reaction volume is utilized for lignite liquefaction, hydrogenation of residual oil and coprocessing. The mass flows specified for feed and oil yield are quantities related to the same reaction volume, and thus specific quantities. Two results are given for coprocessing. On the one hand, it is the yield distribution obtained in the process development unit, and, on the other hand, the result achieved by way of theoretical calculation. The oil yield which in practical operation is higher than expected in theory can be attributed to a synergistic cooperation

of the components of lignite and residual oils. For the sake of comparison, Figure 9 shows the data of a "two-liquid-phase mode" obtained in two separate plants of the same size for coal liquefaction and residual oil hydrogenation.

The comparison of the relative specific oil yields shown in Figure 9 illustrates the considerable advantage of coprocessing over coal liquefaction alone. In coprocessing, the specific oil yield determined experimentally is 3.5 times higher than in coal liquefaction. In a theoretical calculation, a value of 3.2 is obtained.

When compared with the "two-liquid-phase mode", coprocessing has some advantages as well. For example, the relative oil yield is 3.2 (theoretical) and 3.5 (practical) as against 2.3 in the case of the "two-liquid-phase mode".

Apart from the advantages of coprocessing mentioned before account must be taken of the fact that the quality of the oils produced is slightly inferior to that from residual oil conversion alone. Depending on the boiling range and conversion rate, the oils still contain oxygen of up to about 2% wt. Due to the oxygen content of lignite and the increased formation of gaseous hydrocarbons during lignite liquefaction it is quite understandable that the chemical H<sub>2</sub> consumption in coprocessing is somewhat higher than for residual oil hydrogenation.

In order to corroborate the findings gained so far the coprocessing tests on a process-development scale will be continued within the scope of a follow-up project financially supported by the Federal Ministry of Research and Technology.

## 8 OUTLOOK

Hydrogenation of residual oil and coprocessing have the advantage of producing an oil yield in a liquid-phase plant of the same size which is about three times higher than in the case of coal hydrogenation alone. This is due to the fact that cycling of slurry oil is no longer required. Almost the entire feedstock can be processed into usable products.

If we compare plant sizes and process steps required for liquid-phase hydrogenation of residual oils from mineral oil processing and those for mixtures of dry lignite and residual oils with hydrogenation of lignite alone, the result will be as follows:

- processing of mixtures of dry lignite and residual oils calls for additional process stages, viz. slurring and waste water treatment;
- due to a throughput which is about three times higher in coprocessing than in lignite hydrogenation alone, coprocessing permits the use of downstream conversion steps with comparable dimensions to those required for downstream conversion of residual oils;
- thus, coprocessing will call for lower specific capital expenditure than hydrogenation of lignite alone.

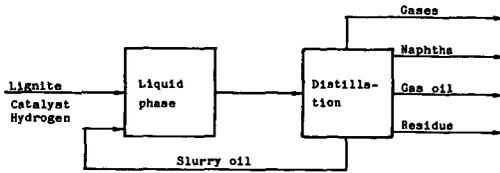
Figure 10 gives a qualitative comparison of the product costs arising in lignite hydrogenation, coprocessing and residual oil hydrogenation as a function of the costs arising for the feedstock.

Figure 10 shows that residual oil hydrogenation will reach the threshold of profitability earlier than coprocessing, while hydrogenation of lignite alone which might become a potentially important market for coal in future, will probably take much longer to reach profitability.

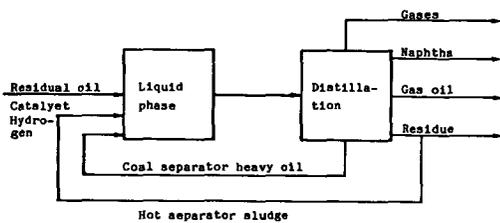
In addition, Figure 10 shows that with the relatively expensive residual oil and the relatively low-priced coal coprocessing will involve lower product costs than residual oil hydrogenation.

This expected graduation in time is reflected in the development programme on hydrogenation of fossil raw materials, which has been pursued by Rheinbraun and Union Kraftstoff. As a first step, a liquid-phase hydrogenation plant is planned for residual oil. In a second step, this plant can be extended to permit coprocessing. Coprocessing will allow important experience to be gained which is necessary to take the subsequent third step towards hydrogenation of lignite alone, without requiring great expenditure on a separate pilot or demonstration phase for lignite liquefaction.

I. FUNDAMENTAL PROCESS DIFFERENCES



II. OLD LIQUID PHASE



III. NEW LIQUID PHASE

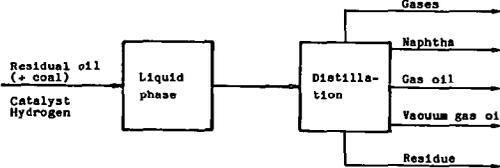


Fig. 1: FUNDAMENTAL PROCESS DIFFERENCES

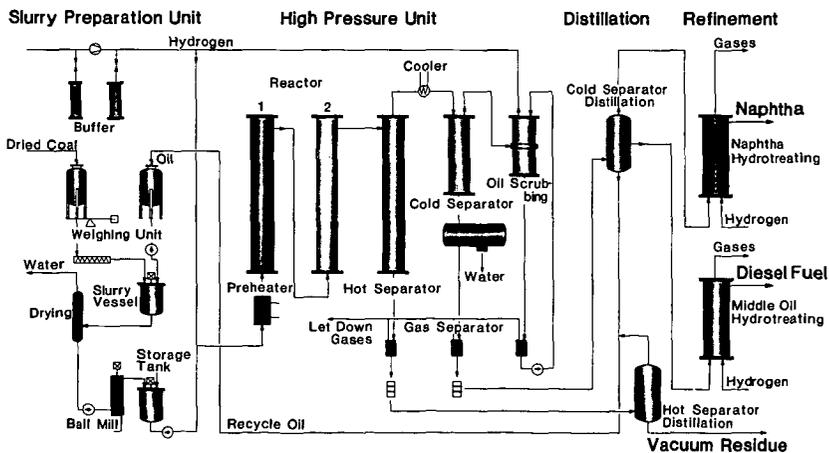


Fig. 2: FLOW SHEET OF THE HVB - TEST PLANT

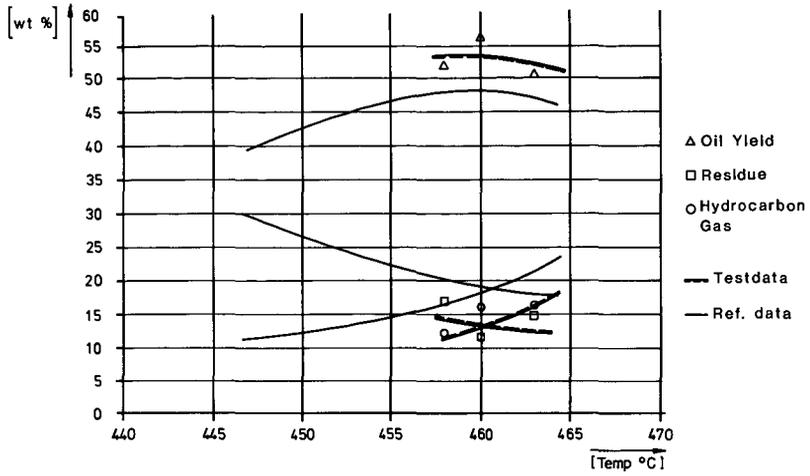


Fig. 3: YIELD AS A FUNCTION OF TEMPERATURE AND GAS INJECTION RATE

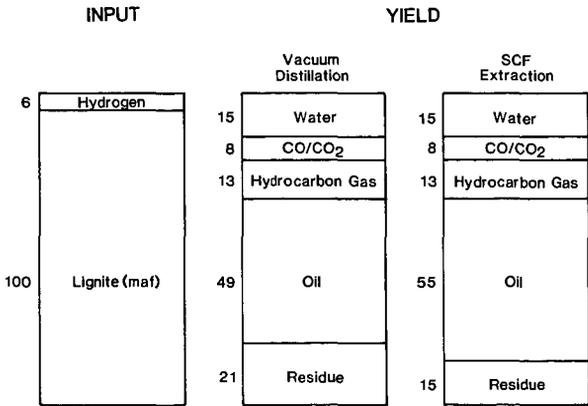


Fig. 4: COMPARISON OF PRODUCT DISTRIBUTION

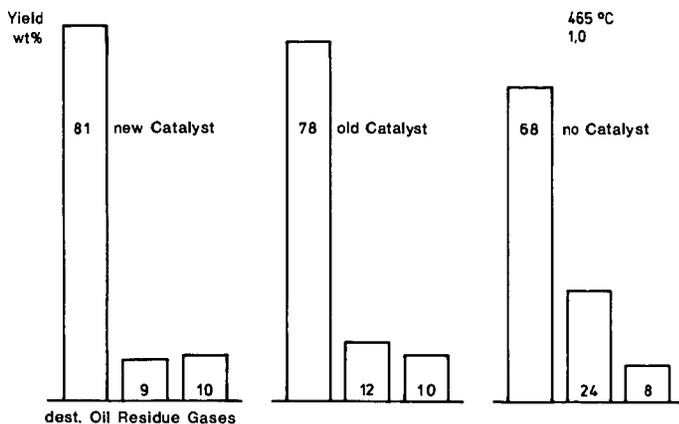
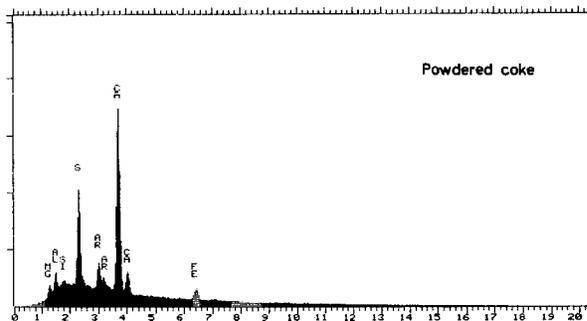
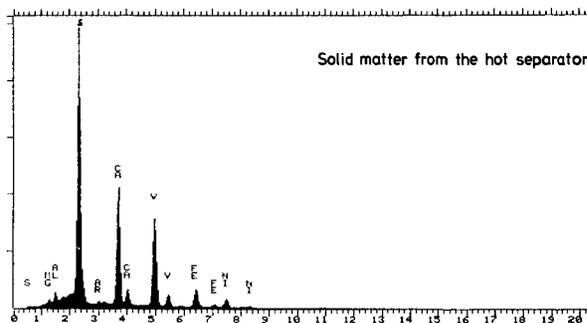


Fig. 5: YIELD STRUCTURE AS A RESULT OF RESIDUAL OIL CONVERSION IN THE PRESENCE OF DIFFERENT CATALYSTS



X-ray fluorescence analysis of powdered coke



X-ray fluorescence analysis of the solid matter from the hot separator

Fig. 6: X-RAY FLUORESCENCE ANALYSIS

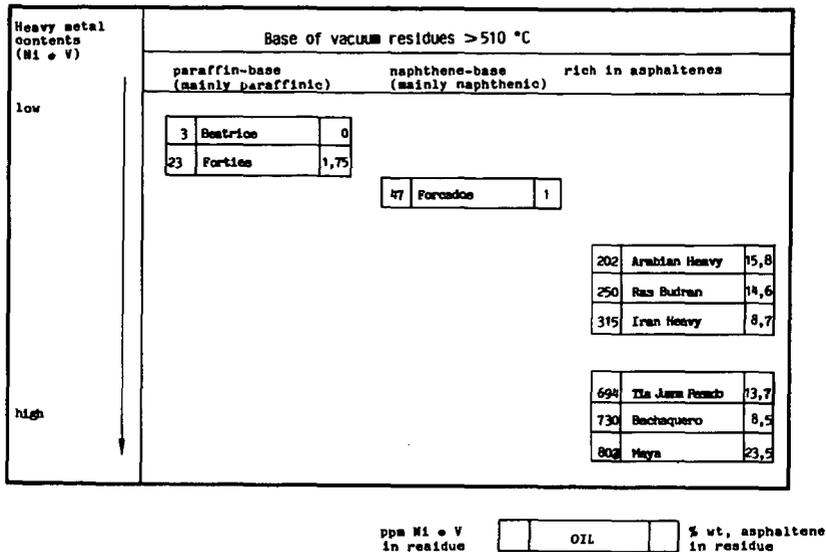


Fig.7: CHARACTERIZATION OF RESIDUAL OILS

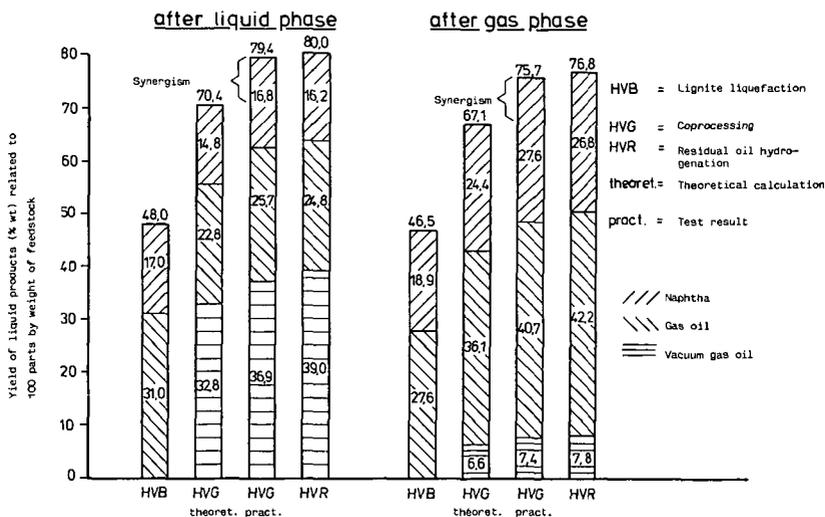


Fig. 8: OIL YIELDS IN HYDROGENATION OF RESIDUAL OILS, LIGNITE AND MIXTURES OF BOTH

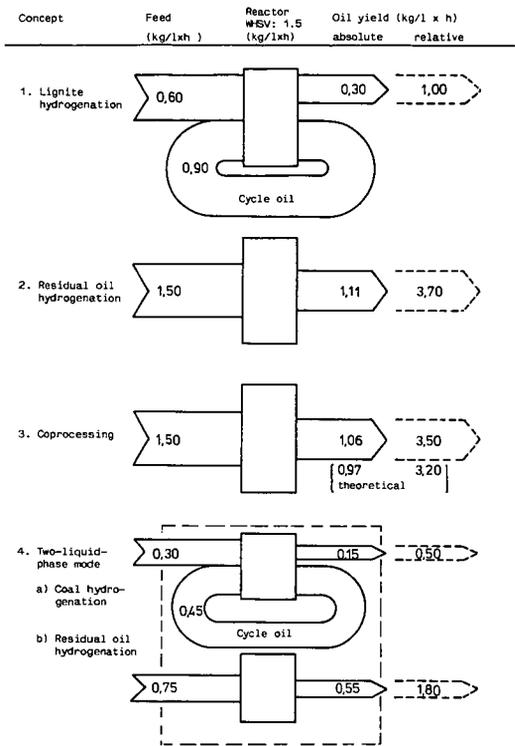


Fig.9 : PROCESS CONCEPTS

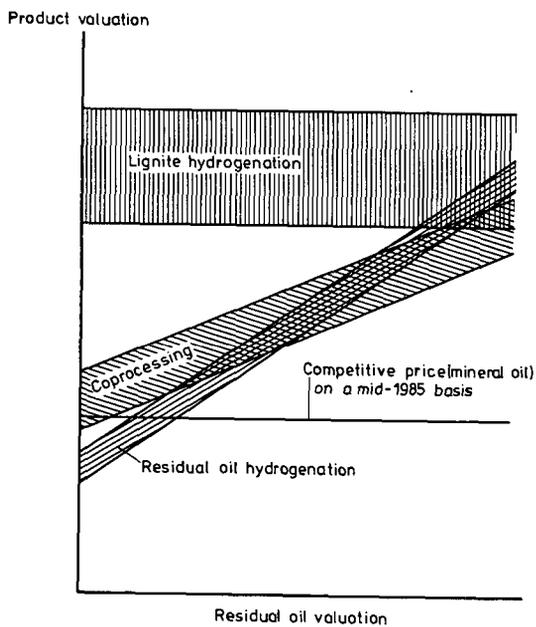


Fig.10 : PRODUCT COSTS AS A FUNKTION OF FEEDSTOCK COSTS (QUALITATIVE)

THE NEW COPROCESSING PILOT PLANT AT  
CANMET'S ENERGY RESEARCH LABORATORIES

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## I. INTRODUCTION

Canada's large deposits of heavy oil and coal and their proximity warrants the development of coprocessing technology. Coprocessing involves treating a slurry of coal in heavy oil, bitumen or resid with high pressure hydrogen with or without other reducing gas between 400°C and 500°C. Under these conditions coal liquefies and the coal-derived liquids together with the heavy oil hydrocrack to lighter materials.

The advantages of coprocessing over coal liquefaction have been known for some time and bench-scale research in coprocessing has been underway at CANMET since about 1980. (1,2,3). The bench-scale experiments have indicated a considerable economic potential for the simultaneous processing of coal and bitumen. To develop this process to a stage where it can be evaluated with confidence for further scale-up to demonstration size, the construction of a half-tonne per day pilot plant was initiated.

Whereas the bench-scale facilities are being used to investigate the effect of the process variables on the product yields and quality in short experimental runs, the large pilot plant will be used to solve problems that normally result from long experimental runs lasting up to 60 days. Further, the pilot plant will be able to generate more accurately yield data that is not normally possible with smaller bench scale units, and will enable the production of the much larger quantities of products needed for the detailed assessments required for commercialization.

This paper describes the coprocessing pilot plant which is now being commissioned at CANMET's Energy Research Laboratories.

## II. PROCESS DESCRIPTION

### (a) Design Basis

- Nominal space velocity of 1.0 reactor volumes/h (1.0 LHSV)
- Feed slurry concentrations of coal from 5 to 50 wt %
- Hydrogen recycle rate of 200 L/h at 15°C (13.9 MPa)
- Pressure capability to 21 MPa (≈3000 psi)
- Reactor temperature to 500°C.

### (b) Description of Flow Diagram

The coal from producers will be ground and dried in a new coal preparation unit. This facility handles coal up to 0.63 cm (1/4 in.) in size and up to 60% moisture to produce up to 227 kg/h of dry coal (maximum 10% moisture) at a maximum particle size of 74  $\mu$ m (-200 mesh). The dried coal is put in 45 gallon drums with plastic liners and sealed to exclude moisture. The ground coal is then mixed with heated heavy oil in tanks. After mixing with the recycled gas stream containing the desired concentration of hydrogen, the hot feed slurry is pumped through a preheating section into the reactor which will be maintained at the desired reaction temperature by electrical heaters (Fig.1). The temperature profile in the reactor is measured and controlled by external heaters. Provision has been made for introduction of other process monitors such as pressure transducers and densitometers.

The effluent from the reactor is fed to a high temperature high pressure separator from which a heavy oil product (containing any undissolved coal) is withdrawn. The overhead are then fed to a low temperature-high pressure separator from which a light oil is collected. The gas is then fed to the scrubbing section which removes gaseous hydrocarbons, as well as gaseous nitrogen and sulphur compounds. This scrubbed H<sub>2</sub> stream is then recycled after addition of fresh make-up hydrogen to the recycle gas and then mixed with slurry entering the preheater. Off-gas streams from the product let-down systems will be measured and analyzed.

The feed and the two liquid product streams are weighed continuously, then samples of the product are distilled and analyzed. Considering the flowrates used and the accuracy in measurement, a good mass balance can be expected.

## III. PILOT PLANT - ASSEMBLY OF SUB-SYSTEMS

### (a) Slurry Preparation Section

The slurry preparation system consists of two tanks, two slurry recirculation pumps and two recirculation loops 4 and 50 m long respectively. The internal pipe size in these loops is 3.81 cm. Since the slurry viscosity is very dependent on temperature, the piping and tanks are equipped with heaters. The length of the larger loop was determined according to the location of the slurry preparation area, i.e., some distance from the main processing area. The high pressure reciprocating feed pump in the process area is fed by part of the recirculating slurry at one end of the large loop. The shorter loop is used for circulating slurry in the other tank when it is not in use, or when the slurry is being prepared from coal and heavy oil. Figure 2 shows a photograph of the slurry area.

Sizing of lines and the power required for recirculating the slurry were estimated for the linear velocity required to prevent settling of coal particles based on Spell's equation (4). The system was designed so that either recirculation pump could be used with either tank in the event of failure during operation. This flexibility along with other characteristics of the long loop make it ideal for the study of mixing phenomena, or in the absence of other data, a means for determining slurry viscosity from known flow and pressure drops.

During slurry preparation, the coal and heavy oil contacting will be done by: (a) an agitator within the tank, (b) recycle flows through the 4 m loop or (c) the use of an eductor within the short loop.

In the coal liquefaction literature interesting rheological behaviour is described where the temperature - viscosity relationship indicates the presence of a gel at certain temperatures (5). Since similar rheological characteristics may be encountered with coal/heavy oil slurries the preheater section has numerous temperature and pressure sensors for monitoring the rheology and flow control (6).

#### (b) Reactors

The pilot plant has two tubular reactors. One has a 18-L capacity, is 7.62 cm in diameter and is 3.937 m long. The other has a 10-L capacity, is 5.08 cm in diameter and is 4.876 m long. Also there is a 10-L continuous stirred tank reactor (CSTR).

The reactors and separators were designed to accommodate instruments for studying fluid dynamics and for changing reactor geometry. Reactor configuration can be altered to study residence time distributions under various conditions.

The maximum L/D ratio for the tubular reactors is 96. The ratio can be reduced by using one of many holes in the wall as the outlet. The reactors can be connected in various ways for different experiments including multi-step processes. Combinations of CSTR and tubular reactors with various L/D ratios will enable the study of the effect of the degree of mixing on the coprocessing reaction for a wide range of Peclet numbers. Such data are often required to develop or verify scale-up models (7).

The hydrodynamic phenomena of slurry bubble columns at high temperatures and pressures are not well understood. Consequently our experience derived from the use of gamma-ray interrogation techniques during CANMET's development of hydrocracking processes will be applied to coprocessing (8). Figure 3 shows the gamma-ray scanner which will be modified slightly for this new system.

The many thermocouples and sampling systems in the three reactors have resulted in complex instrumentation. This complexity is illustrated in the piping and instrument diagram shown in Fig. 4. The sampling system involves metering control valves and this is seen in the photograph in Figure 5.

#### (c) Product Separation

It is necessary to separate the products in the reactor effluent. The design of the hot and cold separators was based on experience obtained from hydrocracking of vacuum tower bottoms or bitumen. Although no difficulty is anticipated in the discharge of undissolved coal solids, the efficient removal of solids from reactor effluent is likely to warrant further study. Extra vessels or solids separation equipment can easily be connected to the bottom of the high temperature separator.

The gases from the cold separator initially will be scrubbed by a water and oil scrubber. These scrubbers were designed for investigation of mass transfer. Effective gas clean-up will be required if coprocessing plants are built. Eventually absorbant liquids other than water and oil will be studied.

(d) Gamma-Ray Densitometer

Techniques have been successfully developed for the study of hydrodynamic phenomena in hydrocracking reactors using gamma-ray densitometry. The techniques measure the spatial and temporal void fractions, flow regimes, and bubble size distributions in the reactor (6). These techniques which were developed in our laboratories, contribute to the development, scale-up and successful operation of a large scale Canadian hydrocracking process. The application of gamma-ray densitometry in solid sedimentation is being developed. All of these techniques will be incorporated in the new coprocessing pilot plant. The dotted vertical line in Fig. 4 represents the track for the gamma-ray densitometer.

**IV. COMPUTERIZED PROCESS MONITORING SYSTEM**

The plan is to have the pilot plant controlled by dedicated controllers. All plant data are collected and stored by a computerized data acquisition and process monitoring system. Field sensors such as thermocouples and pressure gauges are wired to remote processing units (RPU) which perform analogue to digital conversion and translate the sensor output to engineering units. The signals from the RPU are then sent to a plant computer which can display data in various formats including mimics, historical trends and alarm indication. All points are scanned every 10 seconds on average. The plant computer sends all data every minute to the central computer that keeps all the information on a hard disk. Minute and hourly averages are stored for up to 60 days and written every hour to tape. The data stored by the central computer can be recalled for trends, plots and reports. The central system handles data from three separate pilot plants. As a precaution, 60 of the most important points are also recorded on multichannel strip chart recorders. Those points recorded by the computer are shown in Fig. 4 by a circle within a square.

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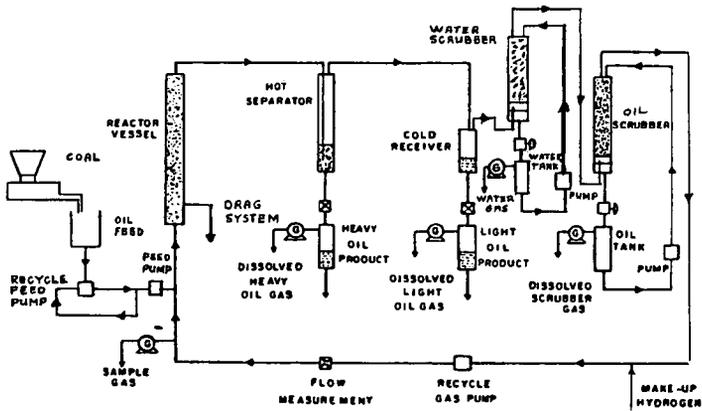


FIGURE 1. SCHEMATIC FLOW SHEET OF COPROCESSING PILOT PLANT

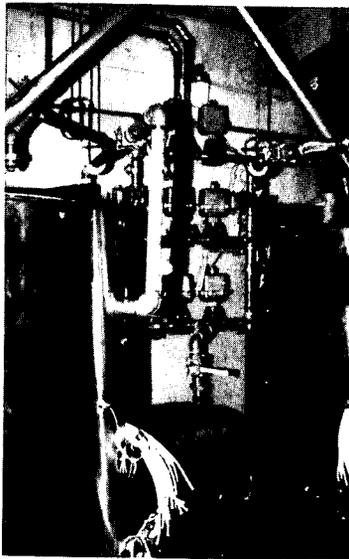


FIGURE 2. PHOTOGRAPH OF SLURRY PREPARATION AREA

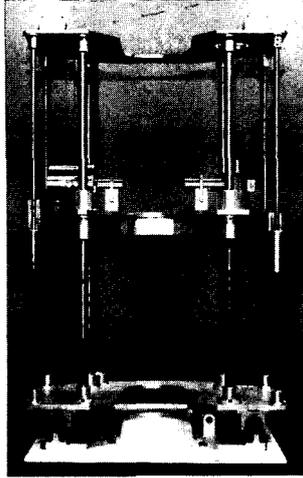


FIGURE 3. GAMMA-RAY SCANNER

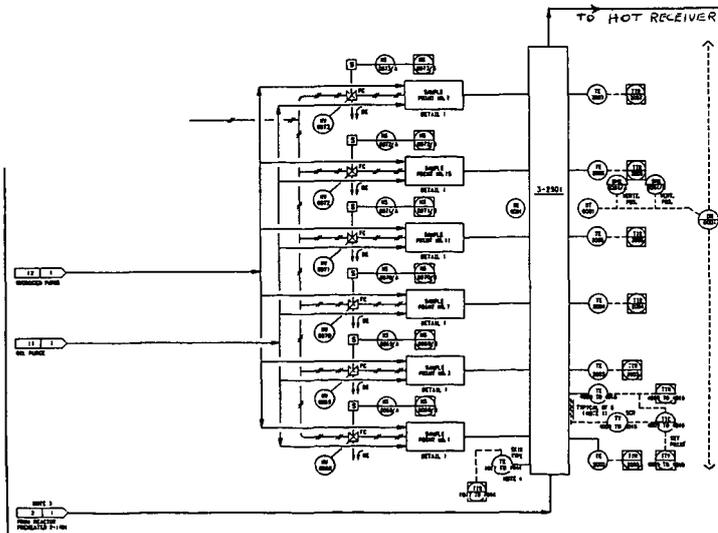


FIGURE 4. PARTIAL P&ID OF TUBULAR REACTOR



FIGURE 5. PHOTOGRAPH OF TUBULAR REACTOR

**BENEFICIATION OF LIGNITE BY OIL AGGLOMERATION  
AS AN INTEGRAL PART OF COPROCESSING**

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**Abstract**

The low cost of Canadian low-rank coals makes them prime feedstocks for coprocessing with bitumens and heavy oils. Depending on the coal concentration in the feed slurry, the high ash level in some of these coals can cause operational problems as well as reduce the overall process efficiency and the net liquid product yield. To reduce the ash content in the feed slurry, oil agglomeration can be used for coal beneficiation (deashing) as an integral part of coprocessing technology. However, an optimum integrated approach requires the use of undiluted bitumen or heavy oil feedstocks as a bridging liquid. Also, low-rank coals as well as oxidized higher rank coals often possess a relatively hydrophilic surface. This makes the application of oil agglomeration extremely difficult.

A novel method of beneficiating low-rank coals for coprocessing by oil agglomeration using a part of the feed bitumen for coprocessing has been conceived and developed. This method overcomes the hydrophilic surface problem of low-rank coals and allows the use of undiluted coprocessing feed oils as viscous as vacuum bottoms.

Experimental results on the beneficiation of a Canadian lignite with vacuum bottoms are presented. The efficiency of the process was evaluated in terms of combustibles recovery and ash rejection. The agglomeration of Willowbunch lignite (ash content from 20 to 22 wt % on a mf basis) with Interprovincial Pipe Line (IPPL conventional crude) vacuum bottoms resulted in 51 to 97 wt % combustibles recovery and a corresponding 77 to 42 wt % ash rejection. The effects of vacuum bottoms concentration, operating temperature, and processing time on the beneficiation performance are discussed.

**Introduction**

Low-rank coals that are often recovered by surface mining are inexpensive and good feedstocks for coal-oil coprocessing. Unfortunately, Canadian low-rank coals are often characterized by their high ash content. For instance, the ash content of Canadian lignites is between 15 and 30%. Most of the low-rank coal deposits in the USA, Australia and other countries also have high ash contents. When such a coal is subjected to coprocessing with heavy oil or bitumen, the high ash content can reduce the net liquid product yields and the overall efficiency of the plant. Also, the handling of process residues with high solids contents may cause operational problems.

An effective route to overcome the high ash problem in the feed coal is coal beneficiation, i.e., deashing of the coal to a certain degree prior to coprocessing. The choice of an appropriate beneficiation process depends on coal rank, composition, surface properties, dissemination of mineral matter, and the end use of the cleaned coal.

Coal beneficiation based on gravity separation of carbonaceous and mineral particles is the most widely used commercial method. However, the efficiency of this technique depends on coal washability, i.e., percentage of mineral matter which can be separated by gravity from various size fractions of coal. For low-rank coals in which mineral particles are often found in a very fine state, beneficiation based on gravity separation may be ineffective.

Selective oil agglomeration, alone or in combination with other methods, may be appropriate for the beneficiation of low rank coals. This technique involves the addition of oil to an aqueous suspension of coal and ash particles. The oil preferentially wets the carbonaceous constituents and causes adhesion of the coal particles by capillary interfacial forces (1). The carbonaceous constituents are agglomerated by oil and recovered from the suspension whereas the ash remains in suspension and is rejected. The oil agglomeration method is based on differences in the surface properties between organic and inorganic matter, the first usually being hydrophobic and the latter hydrophilic. For successful oil agglomeration of coal, the carbonaceous constituents must be less hydrophilic than the ash. As coals decrease in rank from bituminous to subbituminous and to lignite their surface properties become more hydrophilic. This is the major reason that oil agglomeration becomes more difficult for low rank coals (1-3).

The application of selective oil agglomeration to fine coal beneficiation may be especially advantageous if it can be used as an integral part of coprocessing. In coprocessing, coal is ground and mixed with heavy oil to prepare the feed slurry. Normally the feed slurry contains oil and coal at approximately a 2 to 1 ratio. Thus a portion of the heavy oil or bitumen for coprocessing could be utilized for the selective oil agglomeration beneficiation of the feed coal prior to the preparation of the feed slurry (Figure 1). Clean coal particles in the form of agglomerates would then be sent to coal-oil slurry preparation. This integrated process configuration does not result in any additional cost for coal grinding and bridging oil. Also, the overall efficiency and economics of coprocessing will improve by reducing the need for dilution of high ash content residues to permit easier downstream handling.

This paper presents experimental results on a method for lignite beneficiation using vacuum bottoms only as an agglomerating oil. It was shown that at elevated temperatures the vacuum bottoms performed well as a bridging liquid and a hard-to-agglomerate lignite was successfully agglomerated and beneficiated.

## EXPERIMENTAL

All beneficiation experiments were carried out using Willowbunch lignite ground to less than 208  $\mu\text{m}$  (less than 65 Tyler mesh size). A nominal 500 mL of an aqueous solution containing coal surface conditioner and surfactant was prepared to make approximately a 10% coal suspension. The coal suspension was heated in a closed high pressure mixer to a predetermined temperature and a measured quantity of melted vacuum bottoms was injected into the aqueous solution. High shear mixing (4800-5000 rpm) for 5-20 min was used to create microagglomerates followed by low shear mixing (2000-2300 rpm) for 4-10 min to allow for agglomerates growth. Upon completion of an experiment, the vessel contents were discharged into a vessel filled with water at atmospheric pressure. The agglomerates were then separated over a 100 mesh sieve while the tailings were collected in a dish under the sieve. Residues in the vessel were collected by rinsing with water, then Varsol.

Moisture and ash analyses of lignite samples were carried out prior to oil agglomeration tests in accordance with ASTM procedures. Moisture, ash and oil analyses of agglomerates and tailings were performed at the completion of each run. For the determination of the moisture content of agglomerates, a 2-3 g sample of air-dried agglomerates was weighed, then dried in an oven at  $107 \pm 3$   $^{\circ}\text{C}$  to a constant weight. For the determination of the ash content of agglomerates, a 2-3 g sample of air-dried agglomerates was weighed, then heated in a closed crucible in a furnace to  $750^{\circ}\text{C}$  and kept at this temperature until no further weight change was recorded.

To determine the ash content of agglomerated lignite on a moisture-oil-free basis, the oil had to be removed from the agglomerates prior to ashing. Since bitumens used for agglomeration of the lignite have high boiling temperatures, they were removed by solvent extraction using toluene. A 3-4 g sample of dried agglomerates was placed in a predried Soxhlet extractor thimble. Upon completion of the extraction, the thimble was dried in a vacuum oven at  $90^{\circ}\text{C}$  to remove any toluene residues. The moisture-oil free lignite sample was then weighed and ashed.

Ash rejection and combustibles recovery were calculated as follows:

$$\text{Ash rejection (wt \%)} = B / (A+B+C) \times 100 \quad 1)$$

where A, B, and C denote ash in agglomerates, in tailings, and in residues in the agglomeration vessel respectively (all on a moisture-oil-free basis).

$$\text{Combustibles recovery (wt \%)} = (E+F) / (D+E+F) \times 100 \quad 2)$$

where D, E, and F denote combustibles in tailings, in agglomerates, and in residues in the agglomeration vessel respectively (all on a moisture-ash-free basis).

Tables 1 and 2 give typical ultimate and proximate analyses of Willowbunch (Saskatchewan) lignite and the properties of IPPL vacuum bottoms respectively.

## RESULTS AND DISCUSSION

Figure 2 summarizes the effect of vacuum bottoms concentration on the ash rejection and combustibles recovery. The vacuum bottoms concentration was varied from 20 to 64% based on moisture free lignite. When small amounts of vacuum bottoms are used, little agglomeration occurs and the largest part of the ash remains in the tailings. The results in Figure 2 were obtained at 150°C in high and low shear mixing stages. The duration of the high shear mixing was kept at 20 min and that for the low shear mixing was varied between 4 and 10 min.

As the vacuum bottoms concentration is increased from 20 to 40%, combustibles recovery increases from 50 to 93%. However, further increase in vacuum bottoms concentration shows no significant enhancement in combustibles recovery. Ash rejection decreases monotonously with increasing vacuum bottoms concentration.

These results can be explained as follows: When the amount of vacuum bottoms is insufficient for the effective agglomeration of lignite particles in the suspension, the agglomeration is simply incomplete and a large fraction of the lignite particles passes through the 100 mesh sieve with the tailings suspension. As the vacuum bottoms concentration is raised, more vacuum bottoms droplets become available for collision and eventual agglomeration of lignite particles; thus the combustibles recovery further increases. However, at higher combustibles recovery, ash rejection is reduced since there is ash associated with incremental lignite recovery. In addition, an excessive amount of vacuum bottoms in the aqueous suspension results in the formation of emulsion-like agglomerates which contained most of the lignite particles bridged together, as well as a substantial amount of entrapped ash particles. As a result, combustibles recovery is marginally higher but there is an attendant decline in ash rejection.

Figure 3 shows the effect of operating temperature at 40% vacuum bottoms concentration. At 130°C and 140°C, the combustibles recovery was as high as 97.6 to 98.1% at an ash rejection of between 52.5 and 53.1%. The tailings and washings had a clear appearance with very light colored ash settling at the bottom of the tailings collection pan. When the temperature was increased to between 150-160°C, the combustibles recovery slightly decreased to between 94.0 and 95.7% whereas the ash rejection remained essentially constant. This may be explained by the increased viscosity of vacuum bottoms droplets in the suspension. The vacuum bottoms are more viscous at the lower temperature, and when the vacuum bottoms droplets collide, they tend to aggregate resulting in higher combustibles recovery. Because the concentration of suspension is in the order of 10 to 15%, the overall viscosity of the suspension will not change appreciably by the increased vacuum bottoms viscosity. Therefore, it is more advantageous to operate with a vessel temperature as low as practical to promote high combustibles recovery without sacrificing ash rejection. It should be noted, however, that when the temperature of the vacuum bottoms is too low, it becomes impossible to create the fine oil droplets that are needed for oil agglomeration.

Figure 4 shows the effect of processing time used for the high shear mixing. This series of runs was conducted at 150°C and 40% vacuum bottoms concentration. It is seen that high shear mixing for 5-7 min achieved high combustibles recovery and sufficient ash rejection. A further increase of high shear mixing time resulted in a slight decrease of combustibles recovery. This may reflect the fact that some of the microagglomerates were destroyed during prolonged high shear mixing. It was observed that after 3 to 5 min of high shear mixing, the vessel contents had gradually changed from black to gray and then to white. After 7 to 9 min of high shear mixing, a darkening of the vessel contents was observed. Also the appearance of the tailings obtained after 7 min of high shear mixing was clear with mostly white ash settled to the bottom of the tailings collection pan whereas a darkening of the settled particles was observed for the prolonged runs at 9 to 20 min. At 300 min of high shear mixing the combustibles recovery was down to 49.4% and ash rejection increased to 66% indicating unsatisfactory agglomeration. It can therefore be concluded that the present process requires only a very short processing time, and an excessively long mixing time has detrimental effects on the overall agglomeration performance.

#### CONCLUSIONS

An oil agglomeration technique using vacuum bottoms only as a bridging liquid was developed for low-rank coal beneficiation. It was shown that at elevated temperatures the vacuum bottoms performed well as a bridging liquid and a hard-to-agglomerate lignite was successfully agglomerated and beneficiated. In this work a processing time of 5 to 10 min was sufficient to achieve greater than 90% combustibles recovery and more than 55% ash rejection. The present process is ideally suited for ash reduction in coprocessing feed because it can use a part of the coprocessing feed oil for agglomeration before preparation of the slurry feed to the reactor.

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Table 1 Ultimate and Proximate Analyses of Willowbunch lignite

<u>Ultimate analysis (wt %)</u>	
Carbon	52.1
Hydrogen	4.0
Sulphur	0.9
Nitrogen	0.5
Ash	21.5
Oxygen (by difference)	21.0
<u>Proximate analysis (wt % mf)</u>	
Volatile	39.6
Fixed carbon	38.5
Ash	21.0
Sulphur	0.9

Table 2 Properties of IPPL vacuum bottoms

<u>General</u>	
Minus 525°C fraction (wt %)	0
Plus 525°C fraction (wt %)	100
Aromaticity	30
Toluene insolubles (wt %)	0.92
Viscosity (cSt) at 100°C	906
110	514
130	184
<u>Elemental analysis (wt %)</u>	
Carbon	86.4
Hydrogen	10.4
Nitrogen	0.43
Sulphur	1.71
Oxygen	0.56

Figure 1

Flowsheet: Oil Agglomeration Beneficiation Integrated with Coprocessing

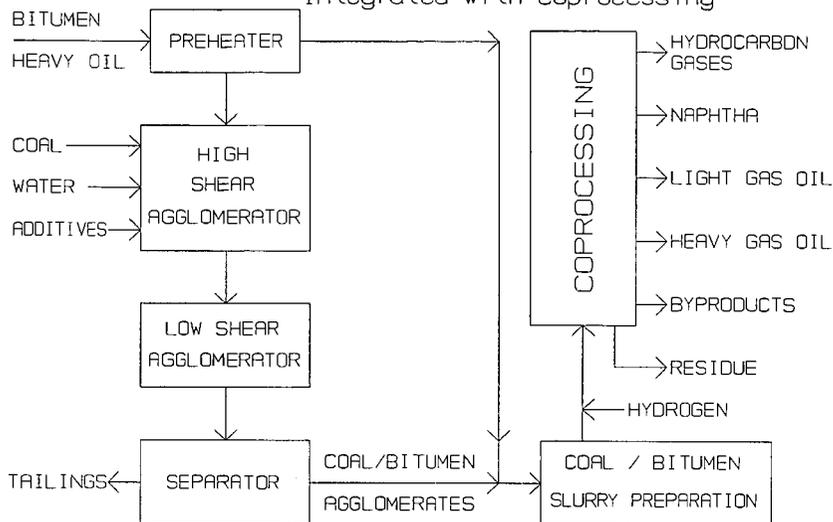


Figure 2

Effect of Vacuum Bottoms Usage

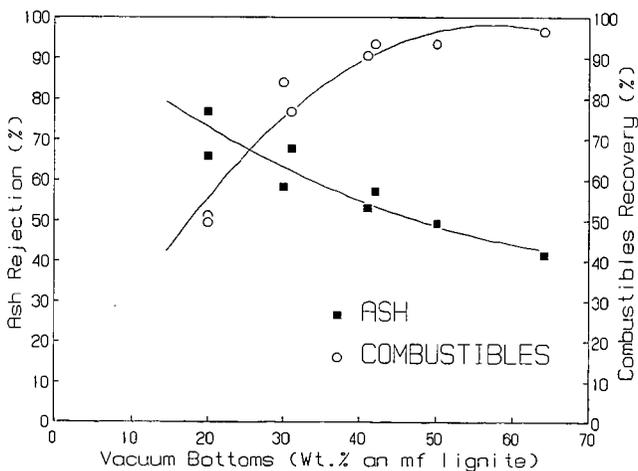


Figure 3  
Effect of Operating Temperature

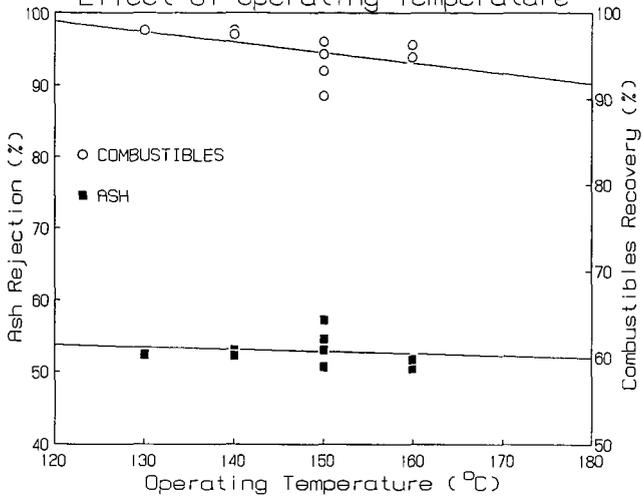
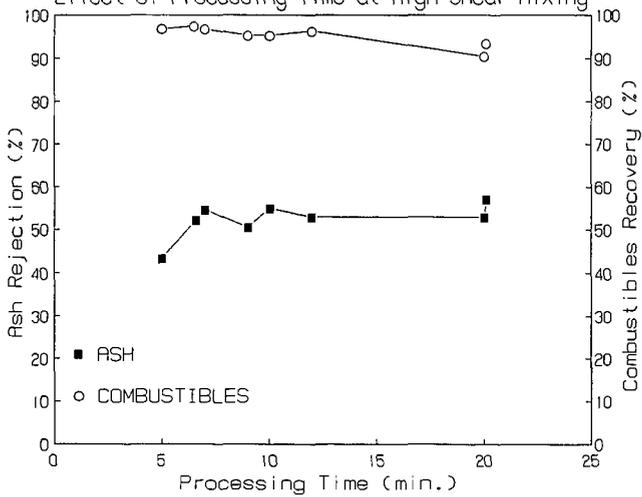


Figure 4  
Effect of Processing Time at High Shear Mixing



## THE CHEMICAL ORIGIN OF SYNERGY IN LIQUEFACTION AND COPROCESSING

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### INTRODUCTION

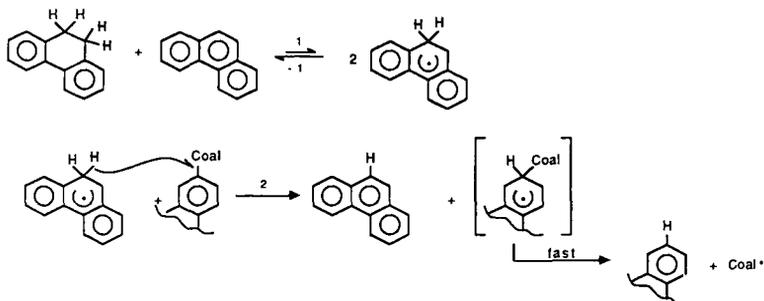
The question of possible synergistic effects for coal liquefaction has been raised recently in the context of coprocessing and also in that of straight donor-solvent liquefaction. Synergy is generally defined to occur when the effect of a combination of components exceeds the sum of the effects of the individual components. The existence of such synergism is more difficult to demonstrate in the coprocessing context, because liquefaction of coal alone, that is, in the absence of any other component (e.g., residual oil), is not viable in process terms, and therefore one of the boundary conditions is not available. Synergism can be much more readily assessed in the context of straight liquefaction, where there is always a liquefaction medium, which can be made up of a number of components. This paper specifically addresses liquefaction data, but the conclusions drawn are all equally applicable to coprocessing.

Recently there have been several reports of coal liquefaction illustrating the interactive effect of various components (1-3). We have used these results in conjunction with an improved mechanistic model for coal liquefaction to help shed some light on the chemical origin of such interactive effects. First, it should be noted that the traditional liquefaction mechanism, which ties liquefaction effectiveness to the efficiency with which donor components scavenge fragment radicals formed in the spontaneous thermal scission of the coal structure, cannot easily accommodate interactive effects. On the other hand, such effects would actually be anticipated for mechanisms that are not unimolecular in solvent components, but, in general terms, involve reaction of one component with another to form an intermediate, which then reacts with the coal component. Specifically, we show that the various H-transfer processes that we have hypothesized as leading to bond cleavage by "solvent-mediated hydrogenolysis" clearly fall in the second category of reaction type. As previously discussed by us (4,5), most of these processes require both a hydrogen "donor" species\* and an "acceptor" species in order to form the active H-transfer intermediate,

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\*In the discussion that follows, we use the word "donor" specifically to mean a hydrocarbon, whether aliphatic, alkyl-aromatic, or hydroaromatic, that can contribute a hydrogen atom to a radical or other acceptor. We make this distinction because some of these substances, such as fluorene, are good hydrogen-atom donors in this sense but are not good donor solvents.

a cyclohexadienyl "carrier" radical, which can transfer hydrogen to engender cleavage of even strong bonds.



In the following paragraphs, we summarize two of the more recent and more striking examples of synergism. One of these uses only nonhydroaromatic donors and the other hydroaromatic donors. We then discuss, in qualitative terms, how a coal-liquefaction picture that includes strong bond hydrogenolysis mediated by solvent carrier radicals can easily accommodate the liquefaction results. The case involving hydroaromatic solvents is more amenable to mechanistic modeling, and for this case we will compare cleavage rates predicted by the model with the actual liquefaction results. Finally, we extend the mechanistic insight gained in rationalizing the positive interaction among solvent components in coal liquefaction to account for the interactive effects reported for coprocessing.

#### EXAMPLES OF REPORTED SYNERGY

##### 1. Improvement of Hydroaromatic Solvents by Addition of Non-Donor Aromatic Components

Cassidy and coworkers have very recently published results using a hot-charged, time-sampled autoclave that show substantial increases in oil yield resulting from the replacement of half of the tetralin in the solvent with various aromatics (1). Figure 1 shows the oil yields as a function of time that were obtained when three different PCAH were added to the solvent. Pyrene is clearly the most effective additive, increasing the oil yields by some 30 percentage points at very short as well as longer reaction times. Anthracene and phenanthrene are somewhat less effective, in that order. These changes are remarkable, particularly since the PCAH replaced half of the tetralin, such that the donor content was actually lowered from 50 to 25%! The authors recognized this and evidently took particular pains to assure themselves that the results were reproducible.

These results are parallel to, but more striking than, earlier results of Derbyshire et al., who reported that conversion of an Illinois No. 6 coal

(to THF-solubles) in 70% pyrene, 30% tetralin was better than conversion in pure tetralin, at two different hydrogen pressures (2).

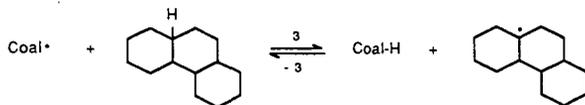
## 2. Aromatic Components Make Accessible Pathways for Bond Cleavage via Solvent-Mediated Hydrogenolysis

The results of Clarke et al. provide a dramatic illustration of the importance of H-acceptor solvent components (3). These workers report that whereas conversion (to quinoline-solubles) of an 84% carbon coal in various perhydro-PCAH was quite poor, it improved slightly when naphthalene was added, and improved quite markedly when PCAH such as phenanthrene or pyrene were added. These results are depicted in Figure 2. The conversion levels achieved with the 3- or 4-ring PCAH (good acceptors) are almost as high as that achieved with octahydrophenanthrene, which is known to be an excellent solvent. The authors also note that only in the presence of the 3- or 4-ring PCAH is there any significant dehydrogenation of the perhydroaromatics. However, in the absence of the PCAH, the perhydroaromatics were observed to undergo cis-trans isomerization, indicating the formation of bridgehead radicals.

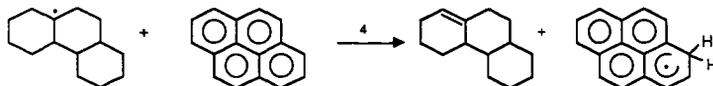
### RATIONALIZATION IN TERMS OF SOLVENT-MEDIATED HYDROGENOLYSIS

The above results are entirely consistent with (and so far as we know cannot be rationalized without) the mechanistic picture of coal liquefaction that includes solvent-mediated hydrogenolysis of strong bonds by radical hydrogen-transfer (RHT): formation of H-atom "carrier" species from PCAH, followed by H-transfer from these carrier species to ipso- positions on aromatic clusters within the coal structure that bear linkages to other clusters, resulting in hydrogenolysis of these linkages.

Any thermally produced coal radicals can, at a modest rate, abstract aliphatic hydrogens from perhydrophenanthrene or other perhydroaromatics.



In the absence of any PCAH molecules, which can act as H-acceptors, the cycloalkyl radicals will recapture a hydrogen (reaction -3) or undergo a  $\beta$ -scission of a C-C bond to produce an olefin and a another alkyl radical.  $\beta$ -Scission of a C-H bond leading to free H-atoms, which could engage in further bond cleavages, is estimated to be about 6 orders of magnitude too slow to compete effectively with either of these reactions (6-8). On the other hand, transfer of a hydrogen to a PCAH molecule from the cycloalkyl radicals is comparable to the hydrogen recapture (reaction -3) or the  $\beta$ -scission of a C-C bond.



Transfer of a hydrogen to a PCAH molecule produces a cyclic olefin and a cyclohexadienyl radical. These cyclohexadienyl radicals can result in hydrogenolysis of other bonds in the coal structure by RHT (reaction 2). Furthermore, the cyclic olefin has much weakened allylic C-H bonds and the removal of one of these hydrogens ultimately leads to the formation of hydroaromatic structures. Thus, the PCAH molecules can channel the hydrogens available in the perhydroaromatic molecules into useful cleavage reactions.

The above scenario has been borne out more rigorously with the help of a mechanistic numerical model for the case of Cassidy et al. For modeling purposes, we used the cleavage of dinaphthylmethane as a surrogate for those structures in coal that cannot cleave by simple thermolysis under the conditions of reaction, and whose cleavage has to be mediated by the solvent. We modeled the cleavage of dinaphthylmethane with the donor hydroaromatics alone and for cases in which a portion of the hydroaromatic replaced by a non-donor species such as pyrene or anthracene.

Figure 3 shows the computed rates of cleavage resulting from H-transfer (to the ipso position of a naphthalene-X structure) by RHT and free H-additions, as well as the total cleavage rate for a 10:1 dihydrophenanthrene:phenanthrene mixture. Also shown (dark bars) are the rates computed for the case where 10% of the dihydrophenanthrene has been replaced by anthracene. The replacement results in a contribution from a step labeled RHT', that is, H-transfer from the anthracene-derived carrier radical. It also results in a substantial increase in the concentration of, and therefore transfer from, the hydroanthryl radical, and in an increase in the free H-atom contribution, such that the overall increase in cleavage rate is 120%. Examination of the various reactions producing and consuming the hydrophenanthryl radical shows that the increase is mainly due to the rapid formation of  $AnH^{\cdot}$ , owing to the very good H-acceptor nature of anthracene. The increased  $AnH^{\cdot}$  concentration then results in an increased production of  $PhenH^{\cdot}$  through reaction of  $AnH^{\cdot}$  with  $PhenH_2$ . The increase in computed cleavage rate is larger or smaller as the system is poorer or richer, respectively, in "native" acceptor (e.g., phenanthrene). In other words, systems that are "over-hydrogenated," or poorest in acceptors, appear to benefit most from the addition of a good acceptor.

The increased production of  $PhenH^{\cdot}$  is in part analogous to the reduction of anthracene by dihydrophenanthrene, which was reported by Billmers and Stein to be catalyzed by the addition of small amounts of dihydroanthracene (9). In both cases a large pool of  $AnH^{\cdot}$  radicals produces additional  $PhenH^{\cdot}$  by abstraction of H from  $PhenH_2$ . In the case described by Stein, this pool of  $AnH^{\cdot}$  radicals arises because of the very good H-donor quality of the added  $AnH_2$ . In the present case, the radical pool increases because of the very good acceptor quality of anthracene itself.

## KEY HYDROGEN-TRANSFER REACTIONS IN COPROCESSING

In coprocessing of coals and heavy oils, we have a situation where the heavy oils have a relatively large amount of aliphatic hydrogen that is potentially useful for cleavage of coal structures. We suggest that the PCAH in the coal interact with the aliphatic hydrocarbons in a way very similar to the one we have described the case of coal conversion results in PCAH and perhydro-PCAH reported by Clarke et al. (3), making it possible to utilize the hydrogen from aliphatic compounds. In addition, because petroleum resids contain some amount of polycyclic aromatics (typically as long-chain alkyl aromatics), the benzylic hydrogens on their side chains provide a source of relatively weakly bonded hydrogens that can, along with the coal radicals, serve as initiating sources. Similarly, to the extent that the  $\beta$ -scission breakup of the alkyl chains produces some amount of olefins (even in the presence of  $H_2$ ), the allylic hydrogens on these olefins will be easily transferred. These aspects of coprocessing chemistry are currently being explored by Bockrath and coworkers using pure hydrocarbons as models for the resids (10). The results of their studies can be expected to provide tests for some of the speculations made here.

### SUMMARY

Analysis of synergistic effects of solvent components in coal liquefaction studies indicates that the key chemical features of coprocessing component interaction are:

- (1) Coal radicals generate aliphatic radicals from the resid;
- (2) The aliphatic radicals can undergo  $\beta$ -scission of C-C bonds to convert the resid, or can transfer a hydrogen to the PCAH to form carrier species capable of engendering hydrogenolysis;
- (3) In the presence of gaseous hydrogen, radical abstraction from  $H_2$  adds a propagation step that facilitates the utilization of  $H_2$  for hydrogenolysis.

These reactions allow the hydrogen in the aliphatic resid components, which are known to be poor liquefaction solvent components, to be made available for coal conversion.

Acknowledgment: We gratefully acknowledge the support of the U.S. Department of Energy (PETC), Contract No. DE-FG22-86PC90908.

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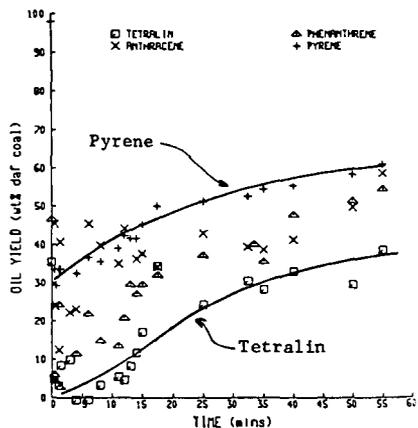


Figure 1: Impact of PCAH addition on liquefaction of Illinois No. 6 coal in tetralin. (Figure from Cassidy et al., Ref. 1)

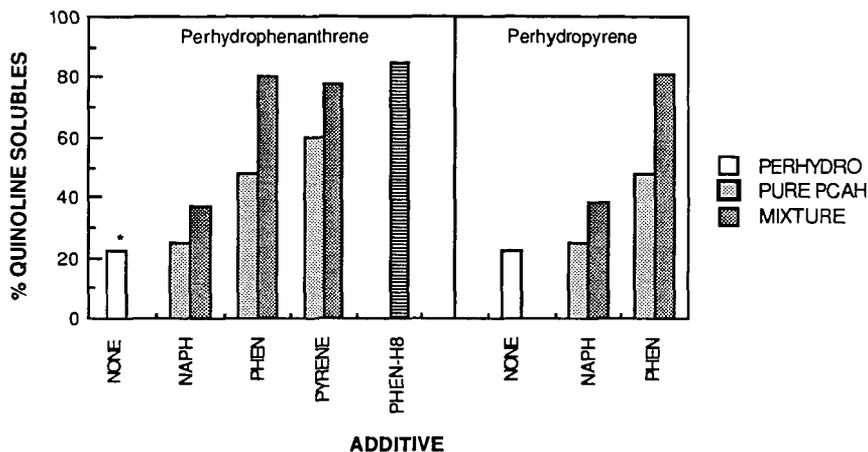


Figure 2. Impact of added PCAH on coal liquefaction in perhydroaromatics. Conversion in 1:1 mixture of perhydroaromatic and aromatic compared with conversion in either pure component. \* Upper limit. (Data from Clarke et al., Ref. 3)

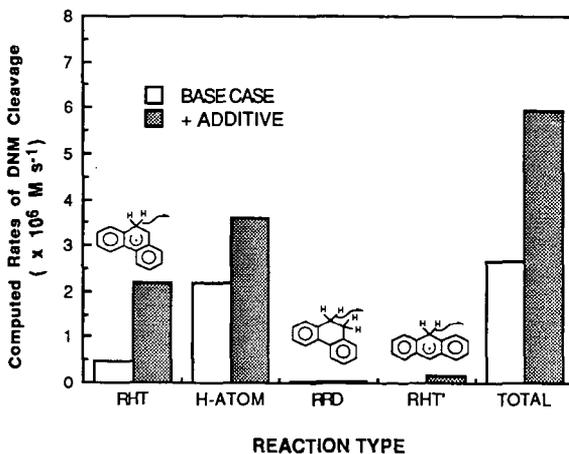


Figure 3: Computed impact of partial replacement of donor with a good acceptor. Base case: PhenH<sub>2</sub>/Phen = 10/1; additive is 0.3 M anthracene, replacing an equal amount of dihydrophenanthrene.

EVALUATION OF THE INTERACTIVE CHEMISTRY OF COAL-PETROLEUM SYSTEMS  
USING MODEL AND ACTUAL REACTANTS

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The coprocessing of coal with petroleum residuum simultaneously liquefies coal and upgrades petroleum residuum into higher value products. However, coal and petroleum residuum manifest very different chemical properties with coal being more aromatic with a H/C ratio of 0.6 - 0.8 and petroleum residuum more aliphatic with a H/C ratio of 1.4 to 1.6. Although a number of studies have demonstrated the feasibility of coprocessing on the basis of product selectivity and metals reduction (1-8), the interactive chemistry involved between the coal and petroleum materials during coprocessing has not yet been determined.

In this study, the interactive chemistry between coal and petroleum molecules has been examined: first by using model compound types representative of coal and residuum and then by combining the model systems with Illinois No. 6 coal and Maya topped long residuum (TLR). The model systems, composed of naphthalene (NAPH) representing aromatics, 1,4-dimethylcyclohexane (DMC) representing saturated compounds, phenol (PN) representing phenolics, benzothophene (BZT) representing sulfur compounds, and quinoline (QN) representing nitrogen compounds, were reacted thermally and catalytically using a Shell 324 NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst. The model systems were reacted individually and then combined together to ascertain the effect of the different components on the thermal and catalytic reactions of the different model systems. Illinois No. 6 coal and Maya TLR were each, respectively, added to the model compound systems and reacted thermally and catalytically.

#### Experimental

Model Reactions. The model systems, NAPH, DMC, PN, BZT and QN, were reacted as 2 wt% reactant in hexadecane at 350°C with 1250 psi H<sub>2</sub> (cold) for 30 minutes and agitated at 850 rpm. The reactor used was a 12.3 cc stainless steel vertical tubing bomb with a Nupro fine metering valve for gas introduction. For the catalytic reactions, 0.25 g of presulfided 1/32" Shell 324 NiMo/Al<sub>2</sub>O<sub>3</sub> extrudates were used. The reaction systems were built in the following manner: NAPH; NAPH and DMC; NAPH, DMC and PN; NAPH, DMC and BZT; and NAPH, DMC and QN. A Varian Model 3700 FID gas chromatograph equipped with a 30 m DB-5 fused silica column was used for analyzing the products from model systems reactions. Para-xylene was used as an internal standard. Product identification was achieved by spiking with authentic compounds and by GC/MS analysis. Gases produced during the reaction were analyzed for hydrogen using a Varian 3700 TCD chromatograph.

Coal and Residuum Reactions. Illinois No. 6 coal (-15 mesh) and Maya TLR were each added individually at 10 wt% to the model compound systems and were reacted under the thermal and catalytic conditions described above. Typical analyses of Illinois No. 6 coal and Maya TLR are detailed elsewhere (5). When residuum was reacted with the model systems, insoluble matter (IM) was produced during the reaction. The IM was recovered by precipitating it from the product mixture by centrifuging and decanting the liquid product mixture. The IM produced during thermal residuum - model systems reactions averaged 8% while that produced during catalytic reactions averaged 5%.

## Results and Discussion

In this investigation, each model system produced a number of products from the catalytic reactions. In order to summarize and compare the data, several terms have been defined. These terms are: percent hydrogenation, percent deoxygenation, percent desulfurization, percent denitrogenation, and percent hydrogenolysis. Percent hydrogenation is the number of moles of hydrogen required to produce the observed product distribution from a given reactant as a percentage of the moles of hydrogen required to obtain the most hydrogenated product. Percent deoxygenation is the summation of the mole percents of components not containing oxygen. Percent desulfurization is the summation of the mole percents of the components not containing sulfur. Percent denitrogenation is the summation of the mole percent of the components not containing nitrogen. Percent hydrogenolysis is the mole percents of the components which have undergone cleavage of the carbon-heteroatom bond.

Naphthalene Hydrogenation. NAPH hydrogenation may be represented as a sequential and reversible reaction of NAPH hydrogenating to tetralin followed by hydrogenation to decalin. Thermal reactions of NAPH individually and in combination with other model systems showed no NAPH hydrogenation. Neither the addition of coal nor residuum affected the thermal hydrogenation of NAPH.

Significant hydrogenation of NAPH occurred under catalytic conditions as shown in Table 1. The addition of DMC had no influence on NAPH hydrogenation; however, the addition of the heteroatomic species, PN, BZT, and QN, reduced NAPH hydrogenation with QN giving the most substantial reduction. The addition of Maya TLR and coal to NAPH each produced a substantial reduction in NAPH hydrogenation with residuum being more detrimental than coal under these process conditions. It should be noted that at 350°C not all of the coal was converted to soluble products, thereby reducing its influence on NAPH hydrogenation. Addition of DMC and the heteroatomic species to either the NAPH/Maya TLR or NAPH/coal systems further reduced the hydrogenation of NAPH with the order of influence being QN > BZT > PN > DMC. In terms of being most detrimental to NAPH hydrogenation, the order of model components ranked as QN > BZT > PN > DMC and of coal and residuum ranked as Maya TLR > Coal.

Table 1  
Effect of Different Systems on the Catalytic  
Hydrotreatment of Naphthalene

<u>Systems</u>	<u>Hydrogenation, %</u>
Naphthalene	94.7
Naphthalene/DMC	94.8
Naphthalene/DMC/Phenol	89.0
Naphthalene/DMC/Benzothiophene	75.9
Naphthalene/DMC/Quinoline	32.5
Naphthalene/Coal	57.8
Naphthalene/Resid	39.4
Naphthalene/DMC/Coal	57.0
Naphthalene/DMC/Resid	36.1
Naphthalene/DMC/Phenol/Coal	54.3
Naphthalene/DMC/Phenol/Resid	36.4
Naphthalene/DMC/Benzothiophene/Coal	50.6
Naphthalene/DMC/Benzothiophene/Resid	32.1
Naphthalene/DMC/Quinoline/Coal	17.9
Naphthalene/DMC/Quinoline/Resid	16.3

Phenol Hydrodeoxygenation. PN undergoes deoxygenation to form benzene and further hydrogenation to cyclohexane under hydrogenation conditions. The benzene - cyclohexane reaction is reversible (9). Under thermal conditions, no conversion of phenol was observed. Under catalytic conditions, PN underwent complete hydrogenation and deoxygenation as shown in Table 2. Neither the addition of NAPH and DMC nor coal had any effect on the hydrogenation or deoxygenation of PN. However, the addition of Maya TLR reduced both PN hydrogenation and deoxygenation. The addition of NAPH and DMC to the PN/Maya TLR system moderated the detrimental effect of the residuum.

Table 2  
Effect of Different Systems on the  
Catalytic Hydrotreatment of Phenol

Systems	Hydrogenation, %	Deoxygenation, %
Phenol	100	100
Phenol/DMC/Naphthalene	100	100
Phenol/Coal	100	100
Phenol/Resid	82.0	82.0
Phenol/DMC/Naphthalene/Coal	100	100
Phenol/DMC/Naphthalene/Resid	88.9	88.9

Benzothiophene Hydrodesulfurization. BZT undergoes hydrogenation to 2,3-dihydrobenzothiophene followed by hydrogenolysis to o-ethylphenol, then hydrogenolysis to ethylbenzene and, finally, hydrogenation to ethylcyclohexane (10). No reaction was observed with BZT under thermal reaction conditions. Under catalytic conditions, two products, ethylbenzene and ethylcyclohexane, were formed in agreement with the literature (9). For the individual BZT catalytic reaction as presented in Table 3, complete desulfurization and ~71% hydrogenation occurred. The addition of the hydrocarbons, NAPH and DMC, as well as coal and Maya TLR reduced the hydrogenation of BZT. In contrast, the residuum only reduced the desulfurization and hydrogenolysis of BZT. The addition of NAPH and DMC to the BZT/Maya TLR system moderated the effect of the residuum by increasing the percent hydrogenation by 3% and both desulfurization and hydrogenolysis to 100%.

Table 3  
Effect of Different Systems on the  
Catalytic Hydrotreatment of Benzothiophene

Systems	Hydrogenation, %	Desulfurization, %	Hydrogenolysis, %
Benzothiophene	71.2	100	100
Benzothiophene/ DMC/Naphthalene	66.3	100	100
Benzothiophene/ Coal	56.3	100	100
Benzothiophene/ Resid	48.6	96.2	96.2
Benzothiophene/ DMC/Naphthalene/ Coal	55.4	100	100
Benzothiophene/ DMC/Naphthalene/ Resid	51.6	100	100

Quinoline Hydrodenitrogenation. The hydrodenitrogenation of quinoline follows a complicated pathway (11) as shown in Figure 1. In thermal reactions at 350°C, 13% THQ was produced. Neither hydrogenolysis nor denitrogenation was observed. Introduction of NAPH and DMC decreased QN conversion and reduced the amount of THQ produced by half. The addition of coal to the thermal QN reaction blocked conversion of QN to THQ. The addition of NAPH and DMC to the QN/coal system had no effect. The thermal reaction of Maya TLR with QN also prevented any hydrogenation of QN; the addition of NAPH and DMC to the Maya TLR/QN system had no effect.

In the catalytic QN reaction as shown in Table 4, substantial hydrogenation, 79.4%, denitrogenation, 48.9%, and hydrogenolysis, 50.6%, occurred. The addition of NAPH and DMC to QN increased both denitrogenation, 54.6%, and hydrogenolysis, 56.6%. Both the addition of coal and residuum to QN substantially reduced hydrogenation, denitrogenation and hydrogenolysis. The addition of NAPH and DMC to the QN/coal moderated slightly the effect of coal on denitrogenation and hydrogenolysis. The addition of NAPH and DMC to the QN/resid system increased all three reactions, hydrogenation, denitrogenation and hydrogenolysis, more substantively than the QN/coal system.

Table 4  
Effect of Different Systems on the Catalytic  
Hydrotreatment of Quinoline

<u>Systems</u>	<u>Hydrogenation, %</u>	<u>Denitrogenation, %</u>	<u>Hydrogenolysis, %</u>
Quinoline	79.4	48.9	50.6
Quinoline/DMC/ Naphthalene	79.9	54.6	56.6
Quinoline/Coal	61.0	35.1	39.3
Quinoline/Resid	60.6	34.7	42.5
Quinoline/DMC/ Naphthalene/Coal	61.1	36.6	41.0
Quinoline/DMC/ Naphthalene/Resid	62.8	38.0	47.0

#### Summary

Thermal hydrogenation reactions at 350°C as performed in this work did not lead to the hydrogenation of any of the model systems except for QN. Combinations of the model systems did not result in thermal chemical reactions among the species except in the case of QN where the addition of hydrocarbons reduced the amount of hydrogenation while coal and residuum totally eliminated it.

In the catalytic reactions, no effect on the hydrogenation of NAPH was observed by the presence of DMC. However, the addition of NAPH and DMC to the reaction systems containing Maya TLR/PN, Maya TLR/BZT, and Maya TLR/QN showed a promoting effect on heteroatom removal (N, S, and O) and hydrogenation of BZT and QN under the catalytic conditions. In the coal system, the addition of NAPH and DMC promoted denitrogenation and hydrogenolysis of QN but did not effect the other reactions. In the QN reaction alone, the promoting effect by the presence of NAPH/DMC on the denitrogenation and hydrogenolysis of QN was observed but the hydrogenation of QN was not affected. The only inhibitor of PN hydrogenation and deoxygenation was Maya TLR whose effect was moderated by

the addition of NAPH and DMC. NAPH hydrogenation was inhibited by the addition of all heteroatomic species coal and residuum, with QN and Maya TLR being the most detrimental.

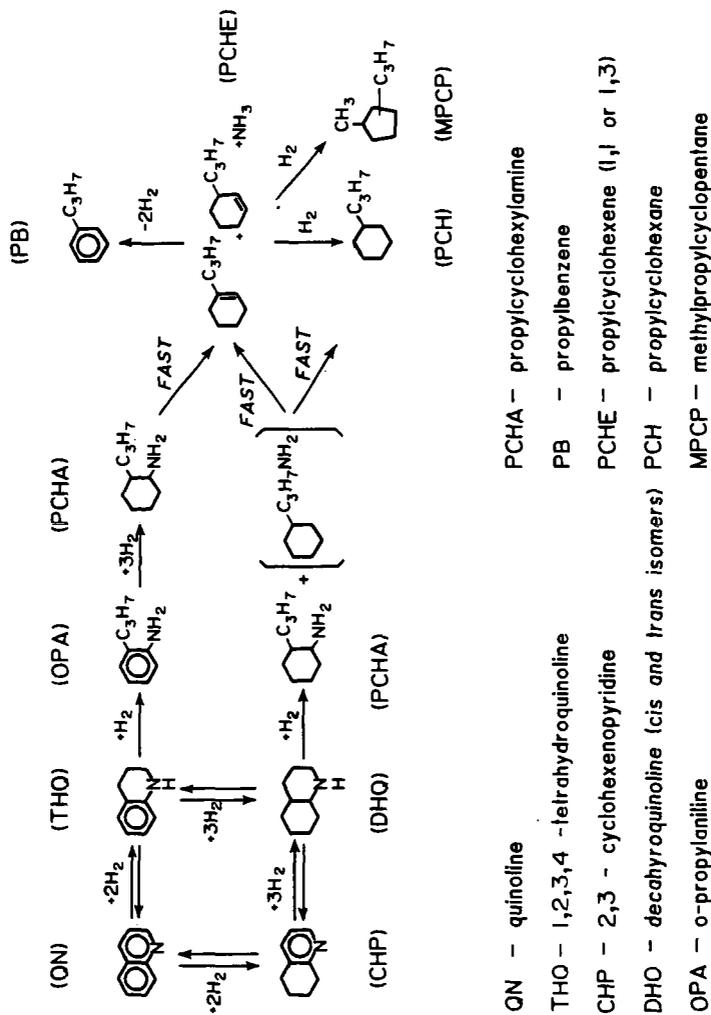
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Figure 1. Reaction Pathway for Quinoline Hydronitrogenation



## COAL/OIL COPROCESSING MECHANISM STUDIES

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### ABSTRACT

Initial coprocessing studies, performed to provide a basis for larger scale tests of coprocessing options using batch one-liter autoclave and continuous hydrotreater facilities at PETC, are described. Areas investigated included the response of coal and petroleum resid combinations to processing under thermal hydrotreatment conditions, the means of increasing the conversion of coal, and the nature of resid demetalation effects. The petroleum resids possessed rather low donable-hydrogen capacities, and the interactions between the resids and coals are weak with respect to promoting formation of liquid products under thermal conditions. Maya ATB was superior to Boscan ATB or North Slope VTB for the conversion of Illinois No. 6 coal to liquid or soluble products. The Maya ATB/Illinois No. 6 coal system responded favorably to the addition of low concentrations of a highly dispersed, unsupported molybdenum catalyst. Extensive demetalation of the liquid product was observed and was a function of the amount of coal added. Results obtained using different coal and resid combinations, under thermal and catalytic conditions, and in the presence of various additives, imply that an absorptive mechanism is operative. The primary interactions leading to demetalation appear to be between the metal complexes of the resid and the insoluble carbonaceous coal-derived material. Demetalation of the liquid product was not observed to be dependent on conversion of the organically complexed metal in the resids to inorganic form.

### INTRODUCTION

The rapid consumption of conventional light petroleum reserves and the increasing need to refine lower quality petroleum feedstocks have recently prompted serious consideration of technology for coprocessing coal with petroleum resids or heavy bitumens. Coprocessing is attractive as a possible route for introducing the processing of coal in an evolutionary manner into existing refinery infrastructures without immediately incurring the large capital investment associated with other coal liquefaction alternatives.

An experimental program was initiated at PETC to obtain fundamental data on the coprocessing of coal with petroleum resids and to achieve a understanding of the observed "synergistic" interactions between coal and petroleum resid feedstocks.<sup>1-4</sup> This work has focused on coprocessing of Illinois No. 6 bituminous coal and, to a lesser extent,

Wyodak subbituminous coal with petroleum resids having widely different properties and coprocessing characteristics. Areas that have been investigated are the response of different coal and resid combinations to processing under thermal hydrotreatment conditions, the means of improving liquid product yields and coal conversions, and the extent and mechanism of liquid product demetalation.

## EXPERIMENTAL

Most of the coprocessing experiments were performed with Illinois No. 6 hvBb coal (>100 mesh) from the Burning Star Mine. A few comparative experiments were carried out with Wyodak subbituminous coals from the Clovis Point or Sarpy Creek Mines. The Clovis Point coal was dried before use. Proximate and ultimate analyses of the feed coals are given in Table 1.

Three petroleum resids were employed: North Slope VTB (950°F<sup>+</sup>), Boscan ATB (650°F<sup>+</sup>), and Maya ATB (650°F<sup>+</sup>). Analyses of these resids are presented in Table 2.

Selected experiments also employed a coal-derived thermal resid, pyrite, activated carbon, and kaolin.

Experiments were carried out in 42-mL shaker bomb microautoclave reactors. In the coprocessing experiments, a coal and a resid were added separately to the reactor. Any additive used was introduced after the coal and resid. After pressure testing, the reactors were charged with the reducing gas and slowly heated to run temperature, usually at a rate of ca. 8°C/min. Heating was achieved by immersion of a bank of five reactors into an electrically heated sand bath. Most experiments were performed with a feed coal concentration of 0-30 wt%, a cold charge pressure of 1200 psig, a reaction temperature of 425°C, and a reaction time of one hour.

The products were removed from the microautoclave reactors and separated into five fractions for analysis according to the scheme presented in Figure 1. The product work-up scheme minimizes the interactions between solvents and liquid products to reduce product contamination by solvent and product losses associated with solvent removal.

Yields of heptane solubles and THF solubles were calculated on the basis of dry weight of the recovered insolubles. Calculated coal conversions of THF solubles are based on maf coal after correcting for the contribution of the petroleum resid to the THF insolubles found in runs with no added coal.

## RESULTS AND DISCUSSION

### Effect of Coal Addition

The interaction of the petroleum resids with Illinois No. 6 bituminous coal under thermal-processing conditions was evaluated in terms of yields of heptane solubles, and coal conversions to THF solubles were evaluated as a function of coal addition. A limited number of experiments were performed with the Wyodak coal for comparative purposes.

The observed changes in heptane-soluble yields with increasing addition of coal to North Slope, Boscan, and Maya resid are shown in

Figures 2,3, and 4, respectively. The lower dashed line in these plots indicates the result expected if the coal simply acted as an insoluble diluent. The results for the North Slope VTB in Figure 2 do not deviate significantly from this line. However, an enhanced yield of heptane solubles is obtained with coal addition to both Boscan ATB and Maya ATB, as described by the upper solid curve (actual experimental results) in Figures 3 and 4. The effect is larger for the Maya ATB than for the Boscan ATB.

Interpretation of the enhanced yields requires knowledge of the relative contributions of the coal vs. resids to the heptane-soluble products. Since the petroleum resids are low in oxygen (if dry) and virtually free of phenolic functionality, relative contributions of coal to soluble product fractions can be monitored following the concentration of phenolic OH. As shown in Figure 5, there is a nearly linear increase of phenolic OH in the heptane solubles with coal addition regardless of resid. The data indicate a relatively weak interaction between Illinois No. 6 coal and the three petroleum resids.

Calculated coal conversions of Illinois No. 6 to THF solubles as a function of coal addition to North Slope VTB, Boscan ATB, and Maya ATB are summarized in Figure 6. The experimental results with coal concentrations less than 10 wt% are highly suspect owing to the small quantity of coal and THF insolubles. However, the remaining results indicate decreasing coal conversions to THF solubles with coal addition upon coprocessing with either North Slope VTB or Boscan ATB. In contrast, about 70% coal conversion was achieved in coprocessing with Maya ATB over the entire range of coal additions.

Based upon a number of reports indicating significant improvements in coal conversion by adding  $H_2S$  to the initial reducing atmosphere,<sup>5-7</sup> the effect of  $H_2S$  addition in coprocessing Illinois No. 6 coal with Boscan ATB and Maya ATB was examined. The results in Table 3 indicate a significant increase (10-15%) in coal conversion to THF solubles with added  $H_2S$ . There is also some improvement in the yield of heptane solubles, although the effect is largely masked by the already large contribution to the heptane solubles from the petroleum resid.

The response of the Illinois No. 6 coal and Maya ATB coprocessing system to addition of an active, highly dispersed, unsupported transition metal catalyst is also shown in Table 3. Molybdenum was added directly into the feed slurry in the form of an aqueous (ca. 12 wt%) solution of ammonium heptamolybdate. Hydrogen sulfide was added to the reducing atmosphere to insure rapid conversion of the molybdenum to the sulfide. Using 1.0% Mo gave virtually complete coal conversion to THF solubles and high heptane-soluble yields of ca. 80 wt%. Similar results were obtained using a catalyst concentration of 0.1 wt% Mo.

#### Metals Removal

One of the most attractive aspects of coprocessing is the potential of processing metal-rich petroleum resids with coal to yield a liquid product of significantly lower metal content. Such resids are currently difficult or impractical to process owing to the detrimental effects of these metals, particularly nickel and vanadium, on conventional upgrading catalysts.<sup>8,9</sup> The role of coal in promoting this demetalation has been investigated by a twofold approach involving monitoring the relative metal (Ni,V) content of the filtered liquid coprocessing

products by X-Ray fluorescence and monitoring the organic vanadium (vanadyl) in the insoluble product by electron spin resonance.

Significant reductions in the metal content of the filtered liquid product were obtained in coprocessing a variety of resid and coal combinations. The observed dependence of the metal (Ni + V) concentrations in the feed slurry is summarized in Figure 7. Similar demetalation effects were also found in experiments with Wyodak coal as indicated in Table 4.

The effect of additives other than coal on the coprocessing behavior of Maya ATB was investigated to gain further insight into the requirements for resid demetalation. As shown in Table 5, coprocessing Maya ATB with 30 wt% Illinois No. 6 coal or a high-surface-area activated carbon resulted in liquid products containing only 10-30 ppm vanadium. Similar results have been observed in coprocessing Maya ATB with cellulose chars.<sup>10</sup> In contrast, coprocessing Maya ATB with coal-derived pyrite, which exerts mild catalytic activity but has low surface area, resulted in an enhanced liquid yield but no significant demetalation above that obtained if only the resid is processed. Likewise, no significant demetalation of the liquid product was achieved by the addition of 30 wt% kaolin, which acts as a low-surface-area diluent. Also, the extent of demetalation of the liquid products in experiments with low concentrations of highly dispersed Mo catalyst is similar to that achieved without the added catalyst, although soluble product yields and coal conversion are considerably higher in the catalytic than the thermal-coprocessing experiments.

The experimental data in Table 5 suggest that a sufficient requirement for resid demetalation appears to be a high-carbonaceous insoluble surface area. There is no particular correlation of metals removal with liquid product yields or coal conversion.

The fate of organic vanadium was further investigated by semi-quantitative ESR procedures. Based on elemental analyses, more than 90% of the vanadium in the feed slurry is recovered in the heptane-insoluble product from coprocessing Maya ATB with 30 wt% Illinois No. 6 coal under the conditions used. The ESR analyses of the quadrivalent vanadium in the heptane insolubles from a variety of microautoclave coprocessing experiments are summarized in Table 6. There is no direct relationship between the amount of ESR-observable vanadyl and the degree of demetalation of the heptane-soluble product fractions. In the thermal microautoclave runs, the vanadium associated with the heptane insolubles remains largely in quadrivalent vanadium complexes even under a hydrogen atmosphere. The ESR spectra of the heptane insolubles from coprocessing Maya ATB with coal or activated carbon were remarkably similar. The addition of pyrite as a catalyst yielded a very lossy heptane-insoluble fraction that was not amenable to ESR analysis. Addition of a highly dispersed molybdenum catalyst resulted in a threefold decrease in ESR-observable vanadium in the heptane insolubles. It is reasonable to assume that the reduction reflects conversion of the organic vanadium into inorganic species (sulfides) or other species not observed by ESR. The ESR spectrum of the quadrivalent organic vanadium remaining in the heptane insolubles from the molybdenum-catalyzed run is similar to that obtained in the absence of an added catalyst.

## CONCLUSIONS

The observed thermal-coprocessing behaviour of petroleum resids is consistent with their limited compatibility with coal-derived materials and an inability to function as efficient hydrogen-transfer solvents. Under thermal-coprocessing conditions with Illinois No. 6 coal, the coal contribution to the heptane-soluble product was low for each of the three tested and varied in a linear manner with coal addition. This appears to be little more than a thermal extraction. There is evidence, particularly in coprocessing Illinois No. 6 with Maya ATB, for an enhanced yield of heptane solubles from the resid with coal addition. Except in coprocessing experiments with Maya ATB, calculated coal conversion to THF solubles fell with increasing coal addition. Under the conditions used, thermal-coprocessing results for Wyodak subbituminous and Illinois No. 6 bituminous coals were similar with respect to soluble product yields. Overall, the thermal-coprocessing experiments indicate the interaction between coal and petroleum resids is rather weak with respect to promoting the formation of liquid products.

The liquid product yields from thermal coprocessing of coal with untreated petroleum resids are too low to justify a completely non-catalytic approach to coprocessing. A limited improvement, particularly with respect to minimizing the yield of THF insolubles, can be realized by simply adding  $H_2S$  to the reducing atmosphere. However, the Maya ATB/Illinois No. 6 coal system responds favorably to addition of low concentrations of active, highly dispersed, unsupported transition metal catalyst. Although no systematic attempt was made to optimize conditions, only a few hundred parts per million of unsupported Mo appear to be necessary to obtain complete conversion to THF solubles and high heptane-soluble yields.

Under thermal-coprocessing conditions in a microautoclave reactor, conversion of organically complexed vanadium to inorganic sulfides or other ESR-unobservable forms occurs to only a limited extent. Minimal catalytic benefit owing to the presence of vanadium in the resid feedstock thus accrues in the absence of an added active hydrogenation catalyst.

Coal addition does facilitate demetalation of the heptane-soluble product from processing petroleum resids. The investigation of the requirements for demetalation in coprocessing indicates that the removal of the resid metals from the soluble product fractions is primarily associated with an interaction of the metal complexes and insoluble carbonaceous components rather than the coal mineral matter. The experimental results strongly suggest that an adsorptive mechanism is initially operative, followed by reactive incorporation of the complexed metal species into the carbonaceous insolubles and by extensive conversion of the metal to inorganic form under appropriate (catalytic) conditions. The primary function of coal is apparently to provide a surface upon which the vanadium species can deposit and undergo further regressive reactions.

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

Table 1. Proximate and Ultimate Analyses of Feed Coals

	Illinois No. 6 ( <u>Burning Star</u> )	Wyodak ( <u>Clovis Point</u> )	Wyodak ( <u>Sarpy Creek</u> )
Proximate Analysis, wt%			
(As Received)			
Moisture	4.2	6.1	17.7
Volatile Matter	36.9	42.3	31.6
Fixed Carbon	48.2	40.8	38.8
Ash	10.7	10.8	11.9
Ultimate Analysis, wt%			
(Moisture Free)			
Carbon	70.2	64.4	62.9
Hydrogen	4.8	4.5	3.9
Nitrogen	0.9	1.0	0.8
Sulfur	3.1	0.9	0.9
Oxygen (Diff.)	9.9	17.7	17.0
Ash	11.1	11.5	14.5
Sulfur Forms, wt%			
Sulfate	0.03	0.02	
Pyritic	1.2	0.2	
Organic	1.9	0.7	

Table 2. Properties of Petroleum Resids

	North Slope VTB (950°F+)	Boscan ATB (650°F+)	Maya ATB (650°F+)
Ultimate Analysis (wt%)			
Carbon	86.1	82.5	84.5
Hydrogen	10.6	10.1	10.6
Oxygen	0.7	0.6	0.3
Nitrogen	0.6	0.7	0.5
Sulfur	2.0	5.6	4.0
Ash	<0.1	0.5	0.1
Ni (ppm)	60	120	70
V (ppm)	130	1300	370
°API	8.9	5.7	8.8
850°F- vol% ASTM D1160	--	19	30
Heptane Insols (wt%) ASTM D3279	4	20	20
$\bar{M}_n$ (VPO, pyridine, 80°C)	920	1250	720
$H_{ar}^*$	0.07	0.08	0.07
$f_a$	0.38	0.41	0.33

Table 3. Effects of H<sub>2</sub>S and Unsupported Mo Catalyst on Coprocessing Illinois No. 6 Coal (30 wt%) and Maya ATB (70 wt%)

Charge Atmosphere

H <sub>2</sub> (vol%)	H <sub>2</sub> S (vol%)	H <sub>2</sub> O(wt%) in Slurry	Cat.(wt%) in Slurry	Heptane- Soluble Yield (wt%)	%Coal Conversion to THF Sols
100	0	-	-	68	73
85	15	-	-	72	84
85	15	5	-	74	85
85	15	-	1.0	81	96
90	10	-	0.1	80	95
100	0	-	0.1	76	88

Note.      Temperature:      425°C  
             Residence Time:      1 hr  
             Charge Pressure:      1200 psig

Table 4. Observed Demetalation of the Filtered Liquid Products from Coprocessing Maya ATB (70 wt%) with Wyodak Subbituminous and Illinois No. 6 Bituminous Coals (30 wt%)

Coal	Coal In Feed Slurry (wt%)	Metals In Filtered Liquid Product (ppm)
Wyodak (Clovis Point)	20	50
	30	20
Illinois No. 6	20	60
	30	10

Note.      Temperature:      425°C  
             Residence Time:      1 hr  
             Charge Pressure:      1200 psig

Table 5. Effect of Various Additives in Processing Maya ATB

Petroleum Resid	Ill. No. 6 Coal (wt%)	Additive (wt%)	% Heptane Solubles in Product	Vanadium in Liquid (ppm)
Maya ATB	0	-	89	200
Maya ATB	30	-	68	20
Maya ATB	0	Deashed Thermal Resid (30%)	74	10
Maya ATB	0	Activated Carbon (30%)	61	30
Maya ATB	0	Coal-Derived Pyrite (30%)	71	210
Maya ATB	0	Kaolin (30%)	62	230
Maya ATB	30	-	72	20 <sup>a</sup>
Maya ATB	30	Mo (0.1%)	80	30 <sup>a</sup>

Note.      Temperature:      425°C  
             Residence Time:    1 hr  
             Charge Pressure:   1200 psig

<sup>a</sup> These runs contained 15 vol% H<sub>2</sub>S in the feed gas.

Table 6. Recovery of Organic Vanadium in Heptane Insolubles from Microautoclave Experiments

Feed Slurry Composition			Initial Reducing Gas Composition		Fraction of Feed Slurry Vanadium	
Petroleum Resid	Additive (30 wt%)	Catalyst (0.1 wt%)	H <sub>2</sub> (vol%)	H <sub>2</sub> S (vol%)	In Heptane Insol as Vanadyl (ESR)	In Heptane Sols (Elemental Analysis)
Maya ATB	Ill. No. 6	---	100	---	0.9 <sub>3</sub>	0.05 <sub>4</sub>
Maya ATB	Activated C	---	100	---	0.9 <sub>2</sub>	0.06 <sub>1</sub>
Maya ATB	Pyrite	---	100	---	0.01 (see text)	0.6 <sub>9</sub>
Maya ATB	Ill. No. 6	---	90	10	0.7 <sub>2</sub>	0.05 <sub>4</sub>
Maya ATB	Ill. No. 6	Mo	90	10	0.2 <sub>7</sub>	0.09 <sub>3</sub>
Boscan ATB	---	---	99	1	0.4 <sub>2</sub>	0.4 <sub>3</sub>
Boscan ATB	---	---	90	10	0.4 <sub>9</sub>	0.3 <sub>8</sub>
Boscan ATB	---	---	75	25	0.4 <sub>8</sub>	0.4 <sub>8</sub>
Boscan ATB	Ill. No. 6	---	90	10	0.8 <sub>2</sub>	0.08 <sub>8</sub>
N. Slope VTB	---	---	100	---	0.1 <sub>9</sub>	0.6 <sub>3</sub>
N. Slope VTB	Ill. No. 6	---	100	---	0.5 <sub>9</sub>	0.07 <sub>7</sub>

Note. Temperature: 425°C  
 Residence Time: 1 hr  
 Charge Pressure: 1200 psig

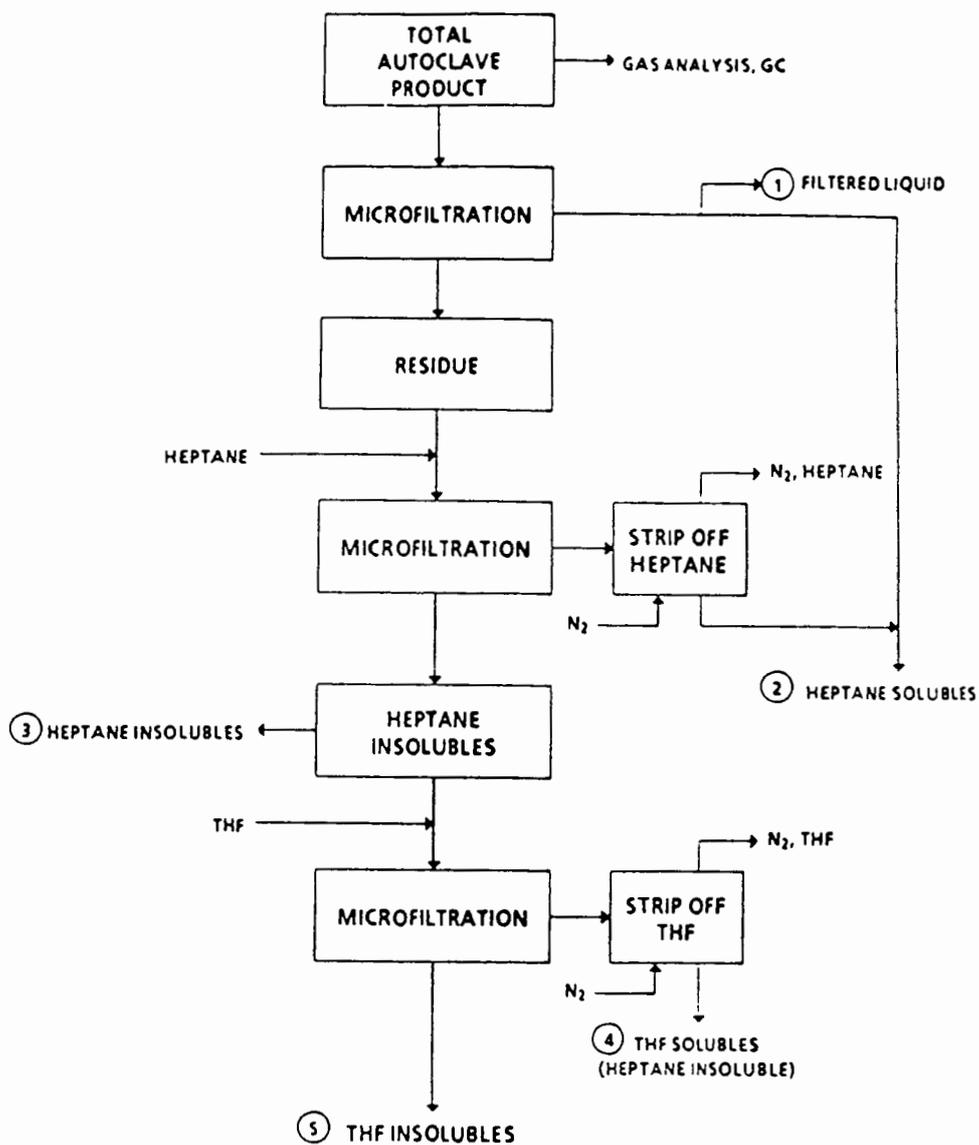


Figure 1. Microautoclave product work-up scheme.

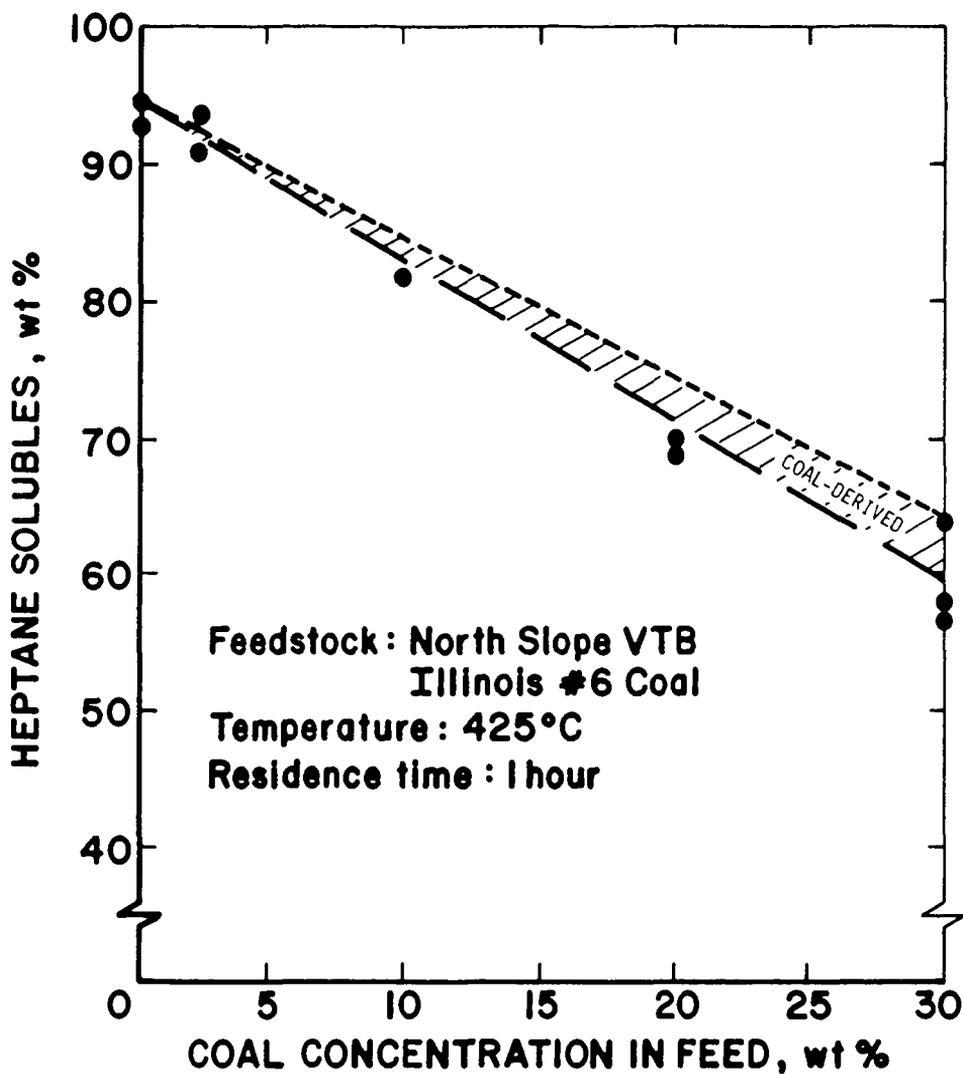


Figure 2. Effect of coal concentration on heptane-soluble yields in coprocessing North Slope VTB with Illinois No. 6 Coal.

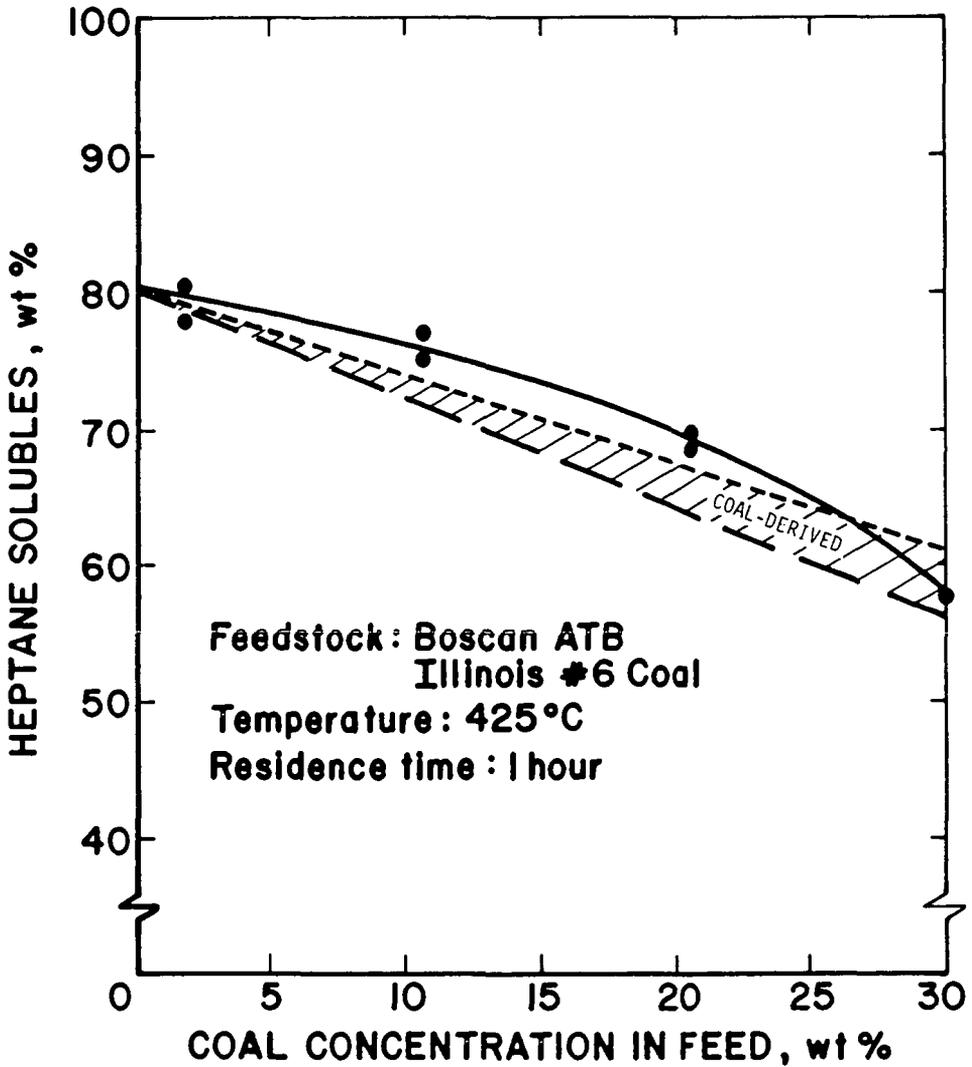


Figure 3. Effect of coal concentration on heptane-soluble yields in coprocessing BOSCAN ATB with Illinois No. 6 Coal.

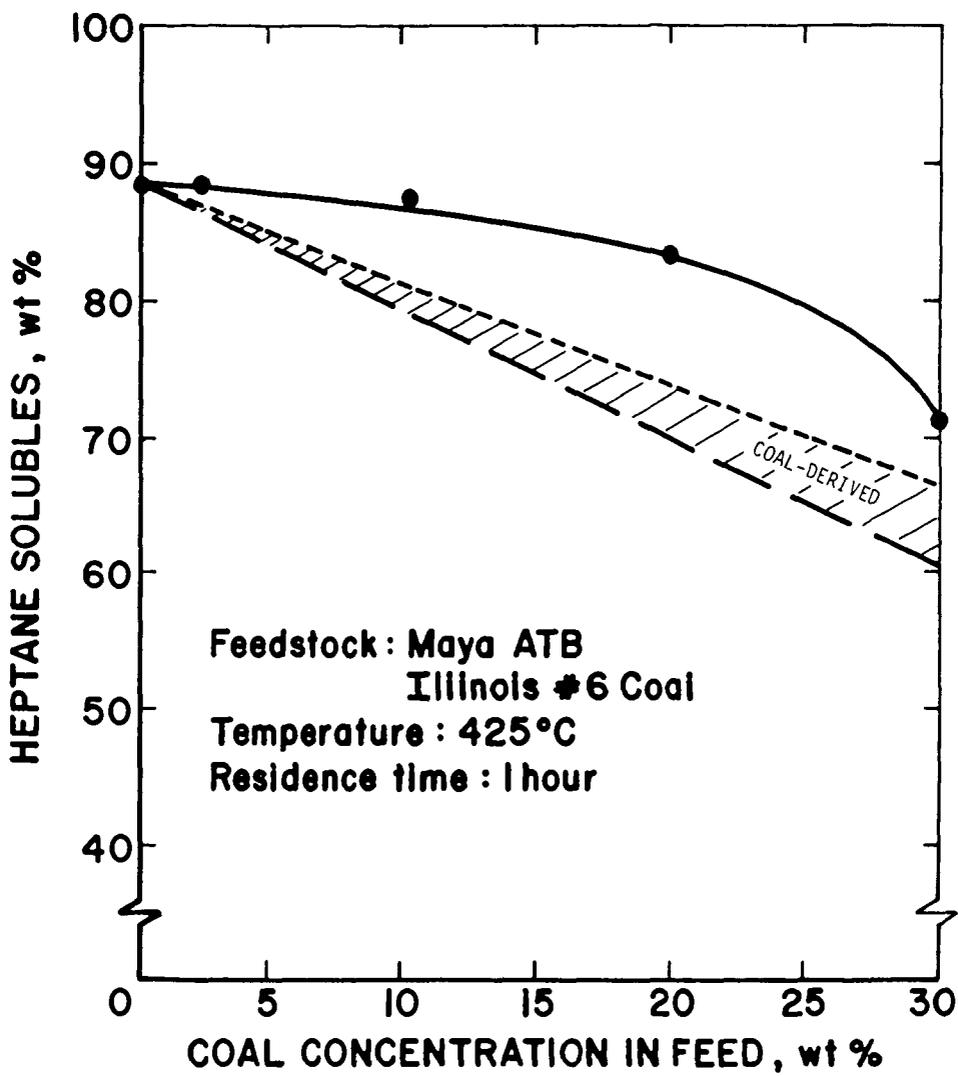


Figure 4. Effect of coal concentration on heptane-soluble yields in coprocessing Maya ATB with Illinois No. 6 Coal.

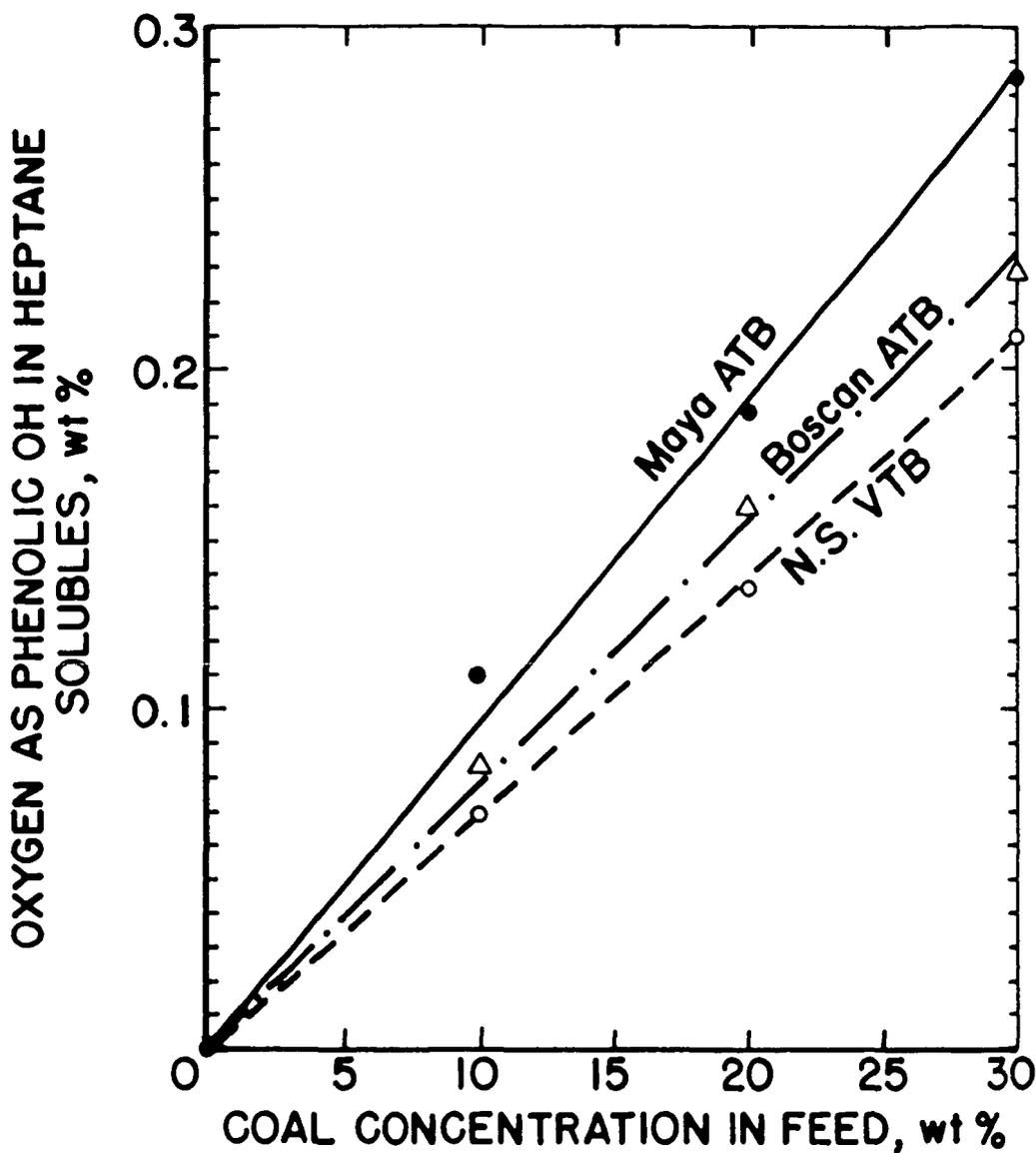


Figure 5. Effect of coal concentration on phenolic OH in the filtered liquid products from coprocessing petroleum residues with Illinois No. 6 Coal.

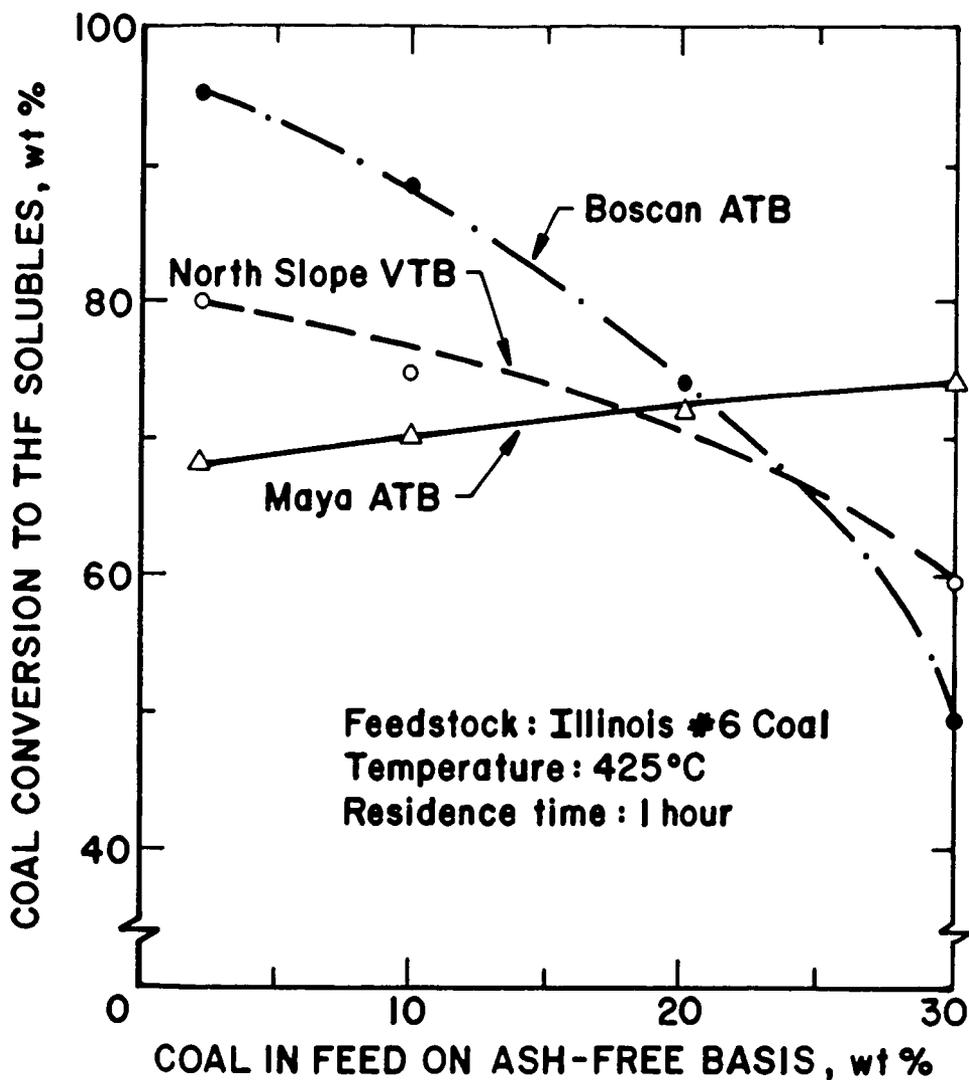


Figure 6. Effect of coal concentration on Illinois No. 6 Coal conversion to THF solubles in coprocessing with petroleum resids.

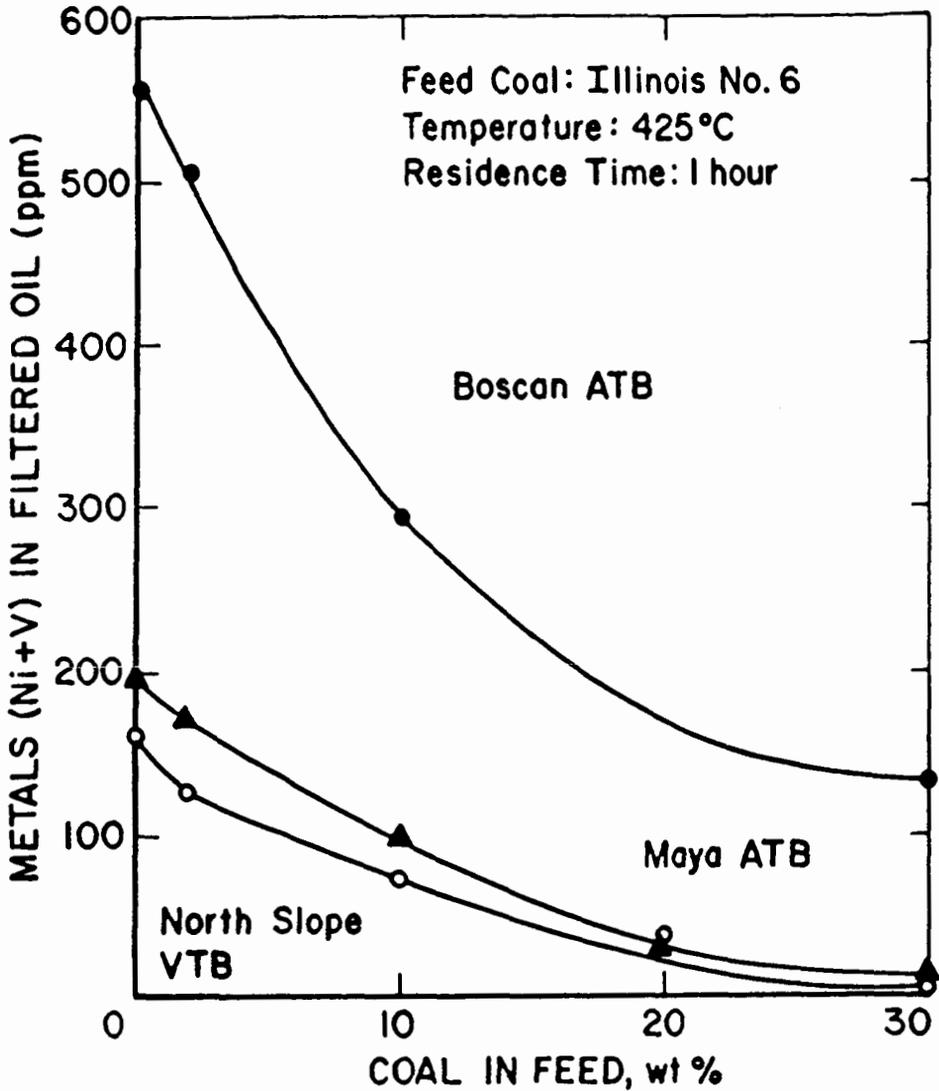


Figure 7. Effect of coal concentration on metals removal.

INTERACTIONS IN THE EXTRACTION  
STAGE OF TWO-STAGE COPROCESSING.

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INTRODUCTION.

In recent years there has been a growing interest in liquefaction processes in which coal recycle solvents are replaced by cheaper petroleum fractions.<sup>1-3</sup> In conventional liquefaction processes there is some evidence that a two-stage process is more advantageous than single stage processes. The Liquid Solvent Extraction (LSE) process of the British Coal Corporation is such a process.<sup>4</sup> Firstly, the coal and solvent are heated in an inert atmosphere before the extract is further upgraded in a second stage involving high pressure hydrogen and a catalyst. The work reported in this paper was undertaken to evaluate the viability of replacing the coal solvent with heavy petroleum fractions in the LSE process.

The results presented here are concerned only with the extraction stage, which in coprocessing is the most important stage. If coal cannot be solubilised to an extractable form poor yields will result however good the upgrading in the hydrocracking stage.

Experimental.

The materials used were Point-of-Ayr (POA) coal and a range of petroleum fractions from various sources. Analytical data are given in Table 1. Samples of coal and petroleum fractions were heated in tubing bombs ( $\sim 15 \text{ cm}^3$ ) with agitation in a fluidised sandbath. Runs were carried out in duplicate. The product was extracted with n-pentane to obtain the % pentane insolubles (% PI). Further extractions were carried out to give the % toluene insolubles (% TI) and quinoline insolubles (% QI).

Table 1 : Analysis of Feed Materials.

Source	Fraction	Wt %				
		C	H	N	S	H/C
Crude "O"	VR > 475°C	85.1	10.5	~	2.95	1.48
Crude "M"	VR 475°C	86.6	12.5	0.35	0.9	1.73
Forties	VR	87.4	11.1	0.45	0.8	1.52
Arabian Heavy	AR	84.3	11.2	0.3	3.9	1.59
Marguerite Lake	AR	83.4	10.4	0.7	5.0	1.50
POA Coal		84.1	5.2	1.8	1.0	0.74

A small number of extractions were carried out in a 250 ml stirring autoclave with a heating rate of  $7^{\circ}\text{C min}^{-1}$ .

The products were extracted with dichloromethane (DCM) and both the soluble and insoluble material was collected and analysed.

#### Pretreatment of Petroleum Crudes.

Whole crudes were vacuum distilled at  $475^{\circ}\text{C}$  and the residue used in coprocessing runs. Vacuum and Atmospheric residues were used as obtained.

The asphaltene fraction of two petroleum fractions was removed and the deasphalted samples coprocessed with POA.

Samples of two of the petroleum residues were hydrogenated prior to use at  $375^{\circ}\text{C}$  or  $425^{\circ}\text{C}$  under 80 atm  $\text{H}_2$  (cold pressure) with NiMo catalyst.

### RESULTS AND DISCUSSION.

#### Thermal Stability of Petroleum Fractions.

The petroleum fractions were heated alone under a variety of reaction conditions. The extraction yields are shown and compared with those of the untreated fractions in Table 2.

Table 2.

Crude	Reaction conditions	% PI	% TI	% QI
VR-M	-	0	0	0
VR-M	$410^{\circ}\text{C}/30$ min	2.7	-	-
VR-M	$440^{\circ}\text{C}/30$ min	5.9	-	-
VR-O	-	-	-	-
VR-O	$380^{\circ}\text{C}/30$ min	22.5	-	-
VR-O	$410^{\circ}\text{C}/30$ min	21.0	-	-
VR-O	$440^{\circ}\text{C}/30$ min	27.4	15.2	5.4
		23.5	10.0	-
HVR-O	None	-	-	-
HVR-O	$410^{\circ}\text{C}/30$ min	11.5	6.4	2.7
VR-FF	None	10.9	-	-
VR-FF	$380^{\circ}\text{C}/30$ min	11.0	-	-
VR-FF	$410^{\circ}\text{C}/30$ min	14.9	-	-
VR-FF	$440^{\circ}\text{C}/30$ min	21.8	4.0	1.0
(VR-FF) <sub>da</sub>	$410^{\circ}\text{C}/30$ min	3.3	-	-
AR-ML	None	22.2	-	-
AR-ML	$380^{\circ}\text{C}/30$ min	19.5	-	-
AR-ML	$410^{\circ}\text{C}/30$ min	21.4	-	-
AR-ML	$440^{\circ}\text{C}/30$ min.	24.0	12.3	3.3
AR-ML	$410^{\circ}\text{C}/10$ min	19.2	-	-
AR-ML	$410^{\circ}\text{C}/2$ h	19.6	7.3	4.0
(AR-ML) <sub>da</sub>	$410^{\circ}\text{C}/30$ min	2.2	-	-
H <sub>1</sub> ARML	$410^{\circ}\text{C}/30$ min	8.8	-	-
"	None	0	-	-
H <sub>2</sub> AR-ML	None	0	-	-
"	$410^{\circ}\text{C}/30$ min	-	-	-
AR-AH	None	15.0	-	-
AR-AH	$440^{\circ}\text{C}/30$ min	13.6	-	-
AR-AH	$440^{\circ}\text{C}/30$ min	16.1	4.5	-

In general, higher reaction temperatures resulted in a small increase in PI but more significantly at 440°C TI were formed. Longer reaction times left the PI unaffected but TI and QI were formed.

Untreated hydrogenated fractions were completely soluble in pentane but on heating considerable PI were formed. These hydrogenated petroleum fractions were less thermally stable than the parent fractions.

#### Effect of Coal/Petroleum Ratio on Extraction Yields.

The extraction yields of compressing runs carried out with a range of coal/petroleum ratios, were measured. During these investigations the reaction conditions were kept constant with a reaction temperature of 410°C and a reaction time of 30 minutes. The results for the coprocessing of VR-FF and AR-ML with POA are shown in Figures 1 and 2 as % insolubles (% INSO) plotted against % POA in the reaction mix. The dashed lines in the figures indicate the % insolubles that would be obtained if the same quantities of coal and petroleum fractions were heated alone under the same reaction conditions. If the experimental points lie on these lines it suggests that no interactions - either positive or negative - have occurred between the coal and petroleum fractions.

In both Figures 1 and 2 it is observed that the experimental points for PI and TI lie on or close to the dashed lines. However, the points for QI lie below the dashed lines. This suggests that VR-FF and AR-ML help to solubilise the coal to a small extent, possibly by providing aromatic radicals that can act as hydrogen shuttlers.

Coprocessing has led to the formation of preasphaltenes and a decrease in the total insoluble material.

Similar results were obtained with other petroleum fractions although the extent of interactions varied with the nature of the petroleum fraction.

The extent of interaction - the difference between the calculated and experimental values of insolubles - was plotted against the % aromaticity of the petroleum fractions (Figure 3). A maximum interaction is noted around 50% aromaticity for coal loadings of 25% and 50%. It might have been anticipated that the greater the aromaticity of the petroleum fractions, the greater the compatibility with coal and so the greater the interaction. The maximum observed at 50% aromaticity might be explained by a concomitant opposing trend. As the % aromaticity of petroleum fractions increases the H/C ratio decreases and so the hydrogen available for shuttling decreases.

#### Effect of Reaction Temperature.

The effect of reaction temperature on the extraction yields of coprocessing runs is shown in Figures 4 and 5. Coprocessing mixes with 25% loading of POA and either VR-FF or AR-ML were heated at 375°C, 410°C and 425°C for 30 minutes. The trends with reaction temperature depend on the petroleum fraction. VR-FF/POA shows a decrease in oil and gas with reaction temperature whereas the changes in oil and gas for the AR-ML/POA runs are very slight. With both petroleum fractions, the total insoluble material decreased as the reaction temperature was increased from 380°C to 410°C but then increased again as the reaction temperature is raised further. In the AR-ML/POA runs the asphaltene content of the product decreased monotonically with reaction temperature but in the VR-FF/POA reactions the variation is <3%. Preasphaltene content in both reactions increased with reaction temperature.

The variations between the petroleum fractions cannot be explained by differences in their thermal stability. They probably result from the complex interactions involved in the reactions between oil and gas/asphaltene/preasphaltene/total insoluble material.

Despite the differences in levels observed the optimum temperature for coprocessing with both petroleum fractions is  $\sim 410^{\circ}\text{C}$ .

#### Effect of Reaction Time.

Coprocessing mixes with 25%, 50% and 75% loadings of POA in AR-ML were heated at  $410^{\circ}\text{C}$  for 10 min, 30 min and 2 h. The results are shown in Figures 6, 7 and 8. The effect of long reaction times was to increase the total insoluble material at the expense of the asphaltene and preasphaltene fractions.

The petroleum/coal ratio also affected the levels with reaction time. This can be seen in Figure 9 where % INSOL are plotted against % POA for a reaction time of 2 h. This plot is considerably different from Figure 1. There appears to be a very negative synergistic effect that is greatest at high loadings of coal.

It is apparent that longer reaction times are not advantageous.

#### Effect of Pretreatment of Petroleum Fractions.

Deasphalted samples of VR-FF and AR-ML were coprocessed with POA in various ratios at  $410^{\circ}\text{C}$  for 30 min. It is clear that the interactions observed with the parent petroleum fractions are no longer present. Particularly notable was the absence of any preasphaltene fraction. The procedure used to prepare these samples removed most of the aromatic material and consequently seriously impaired the ability of the fraction to solubilise the coal.

It was postulated that prior hydrogenation of the petroleum fraction would increase the hydroaromatic content and so increase its ability to donate hydrogen to the coal. The extraction yields for the reactions of hydrogenated VR-0 and AR-ML with POA are given in Figures 12 and 13.

Hydrogenation of VR-0 appeared to have reduced its ability to solubilise coal. All the experimental points lie on the dashed lines. However, the effect of prehydrogenation of AR-ML on its ability to solubilise coal was dramatic. The total insoluble material at 50% POA was reduced to  $\sim 15\%$ . This extent of solubilisation is comparable to that of coal solvents.

#### Extractions in the Autoclave.

The results of % DCMI obtained from coprocessing AR-ML and POA in an autoclave are given in Figure 12. The two values of the % DCMI shown were calculated as follows:

$$\% \text{ DCMI (min)} = \frac{\text{wt. DCMI}}{\text{wt. mix}} \times 100$$

$$\% \text{ DCMI (max)} = \frac{\text{wt. DCMI}}{\text{wt. recovered}} \times 100$$

It was observed that the results follow a similar trend to those obtained in tubing bombs with a reaction time of 2 h. A major problem with extraction in the autoclave is that short contact times are not possible.

It was noted from the gc traces of the DCMS product of coprocessing runs that a considerable amount of the lighter material was coal derived. The peaks observed were not simply a combination of those observed from runs involving coal alone and AR-ML alone. Some major peaks were missing while others new to either materials appeared. This potentially very interesting observation, which agrees well with SEC results reported by Wallace et. al.,<sup>5</sup> will be further examined by gc-ms.

#### Conclusions.

The extraction stage of a two-stage coprocessing operation is very important. Using untreated petroleum fractions, the best coal conversion (d.a.f.) that was achieved was around 30%. This compares poorly with the performance of coal solvents. However, some considerable reaction between the coal and petroleum fractions must take place as indicated by the gc results from autoclave extractions. The greatest promise lies in the result obtained with prehydrogenated AR-ML. The coal conversions (d.a.f.) that resulted with this solvent stream were of the order of 85%. This compares well with the best of coal solvents.

#### Acknowledgments.

We wish to express our thanks to the Coal Research Establishment, British Coal Corporation, for useful discussions and the gift of materials for this work; and the Commission of the European Communities, who are funding this coprocessing programme under grant no. EM3V-0016-U.K.

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- Figure 1. Coprocessing of VR-FF with POA at 410°C for 30 minutes.
- Figure 2. Coprocessing of AR-ML with POA at 410°C for 30 minutes.
- Figure 3. Variation of the extent of interaction between POA/Petroleum fractions with % aromaticity of the petroleum fractions.
- Figure 4. The effect of reaction temperature on the coprocessing of VR-FF/POA with 25% POA and a constant reaction time of 30 minutes.
- Figure 5. The effect of reaction temperature on the coprocessing of AR-ML/POA with 25% POA.
- Figure 6. The effect of reaction time on the coprocessing of AR-ML/POA with a coal levelling of 25% and a constant reaction temperature of 410°C.
- Figure 7. The effect of reaction time on the AR-ML/POA mix with % POA = 50%.
- Figure 8. The effect of reaction time on the AR-ML/POL mix with % POA = 75%.
- Figure 9. Coprocessing of AR-ML with POA at 410°C for 2 h.
- Figure 10. Coprocessing of deasphalted VR-FF with POA at 410°C for 30 minutes.
- Figure 11. Coprocessing of deasphalted AR-ML with POA at 410°C for 30 minutes.
- Figure 12. Coprocessing of prehydrogenated VR-O with POA at 410°C for 30 minutes.
- Figure 13. Coprocessing of prehydrogenated AR-ML with POA at 410°C for 30 minutes.
- Figure 14. Coprocessing of AR-ML with POA at 410°C in the autoclave.

Fig. 1

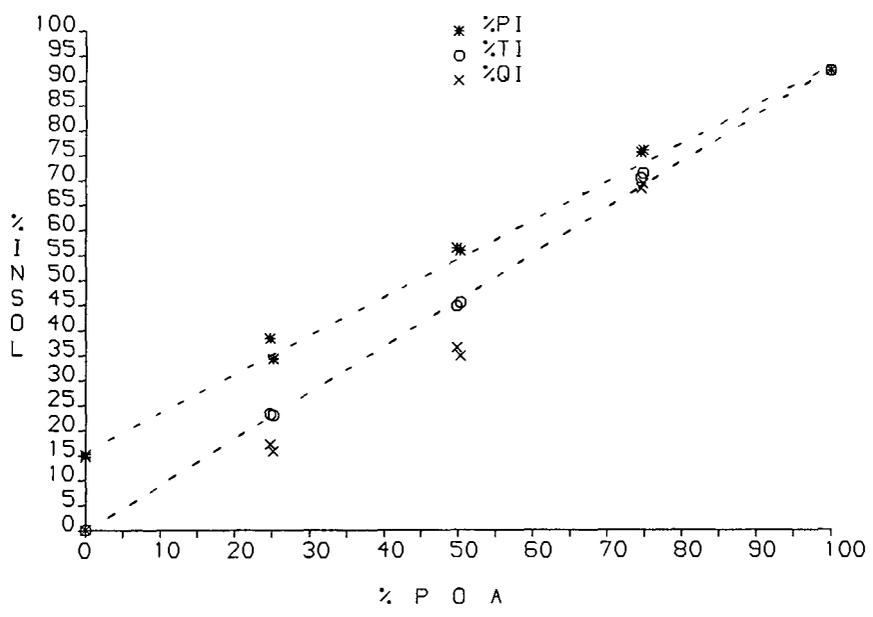


Fig. 2

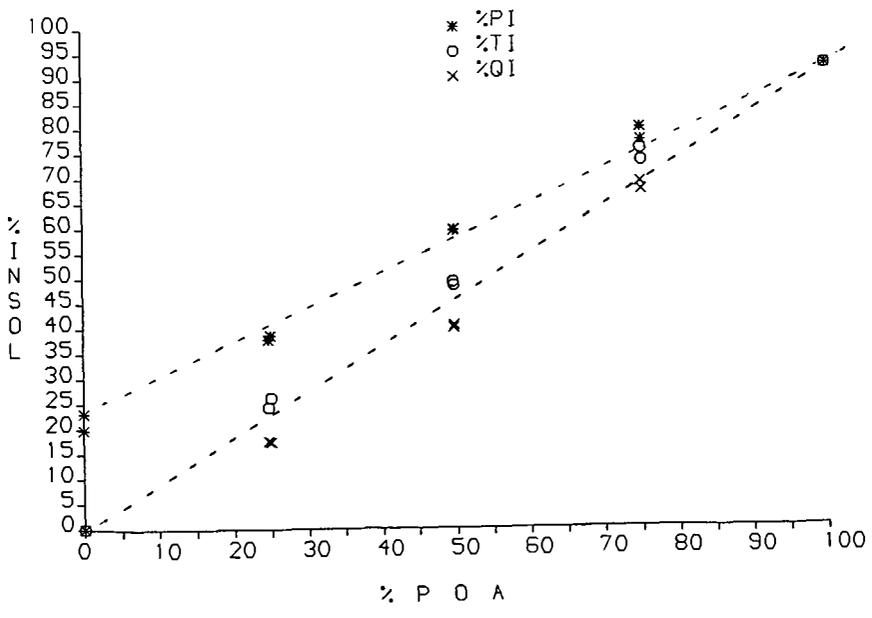


Fig. 3

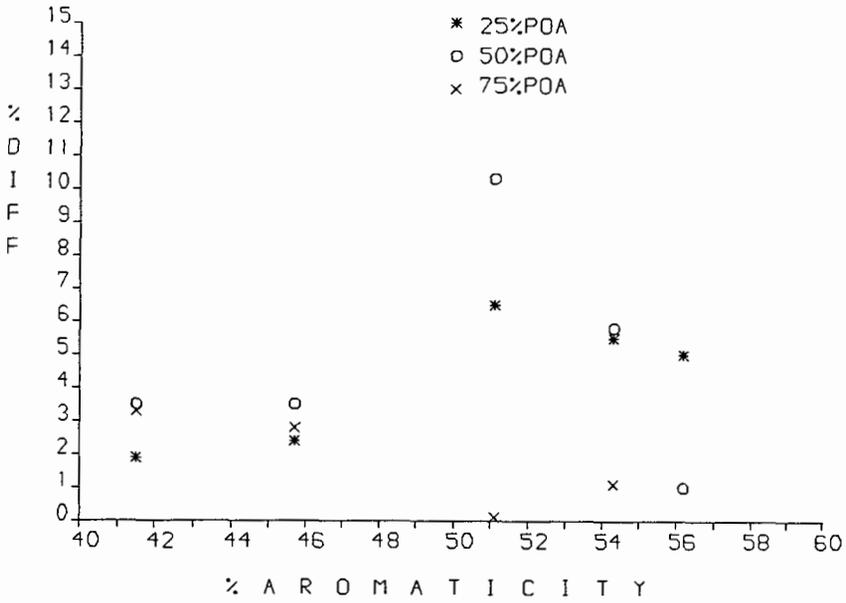


Fig. 4

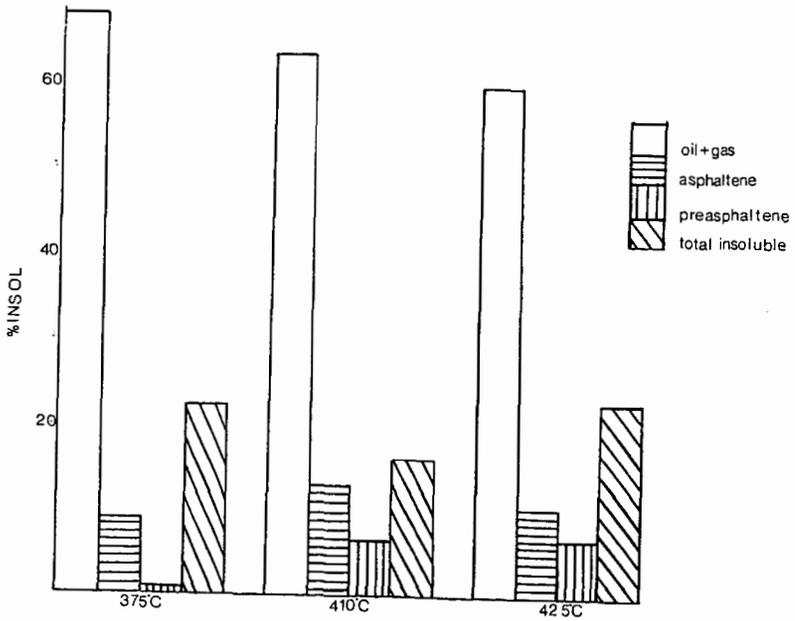


Fig. 5

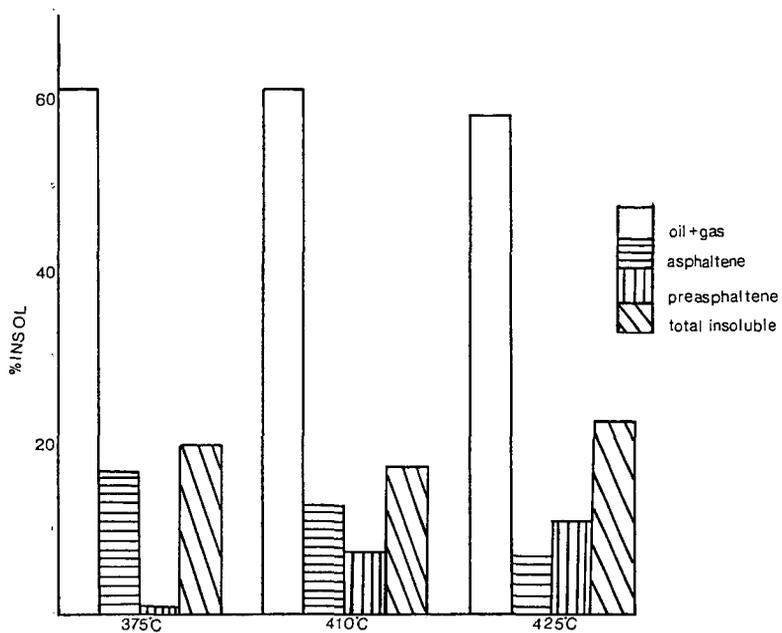


Fig. 6

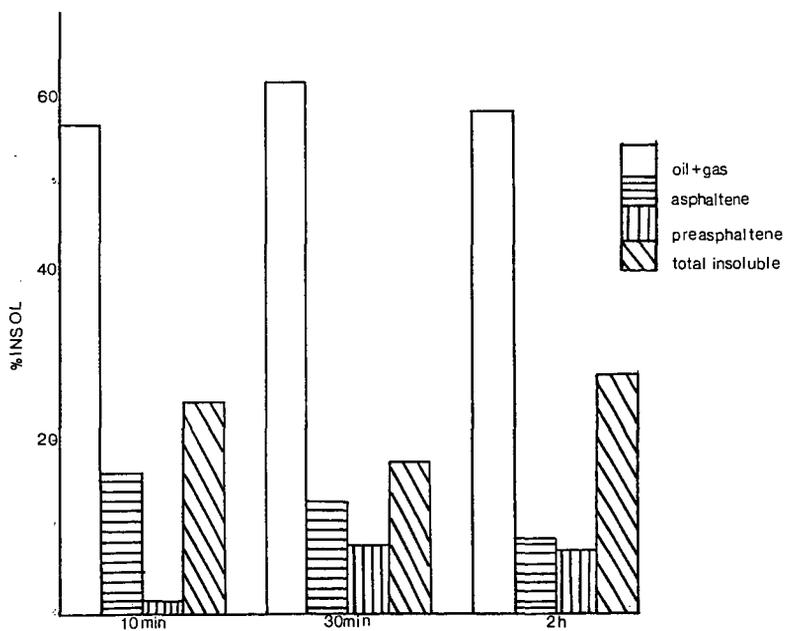


Fig. 7

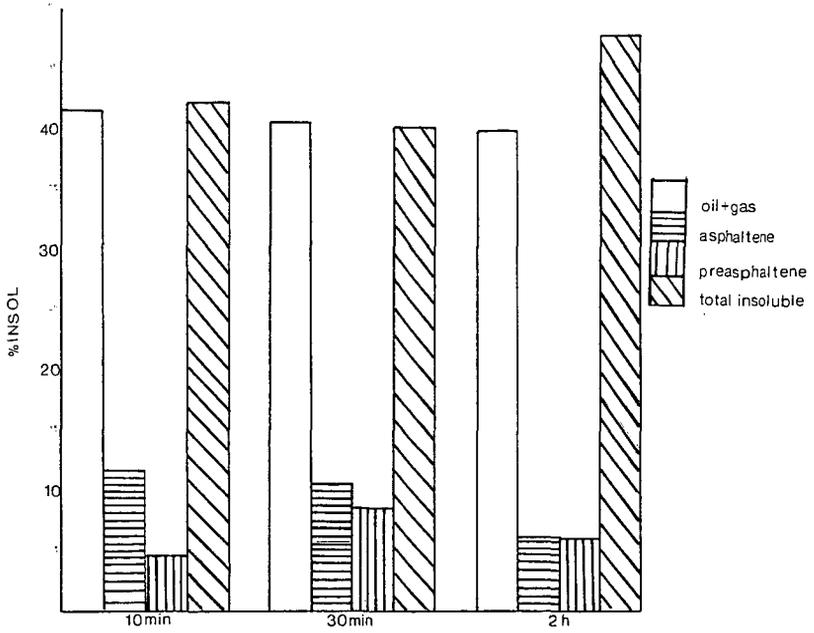


Fig. 8

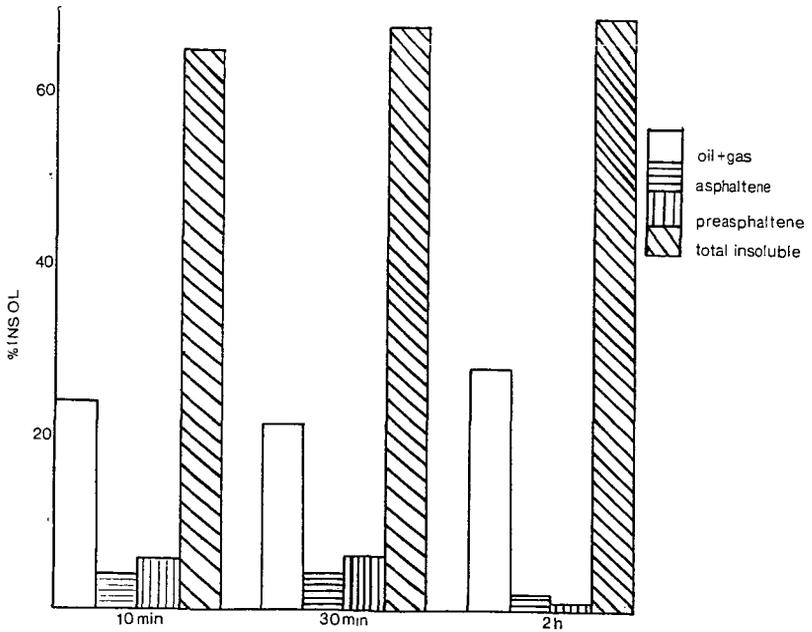


Fig. 9

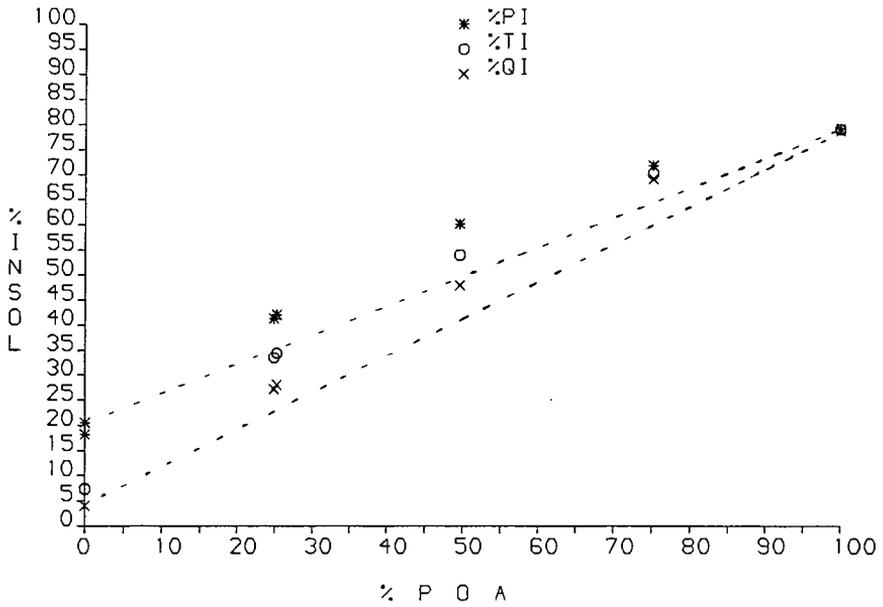


Fig. 10

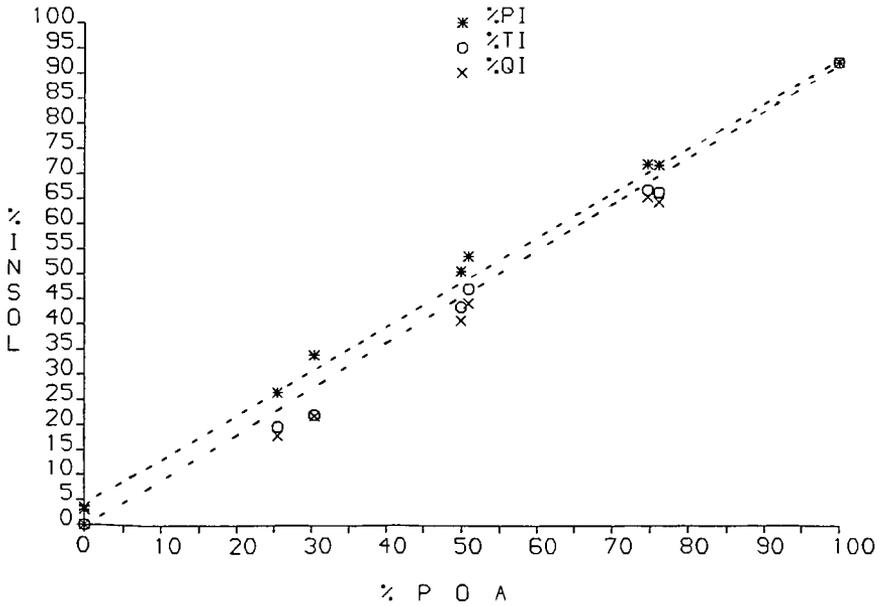


Fig. 11

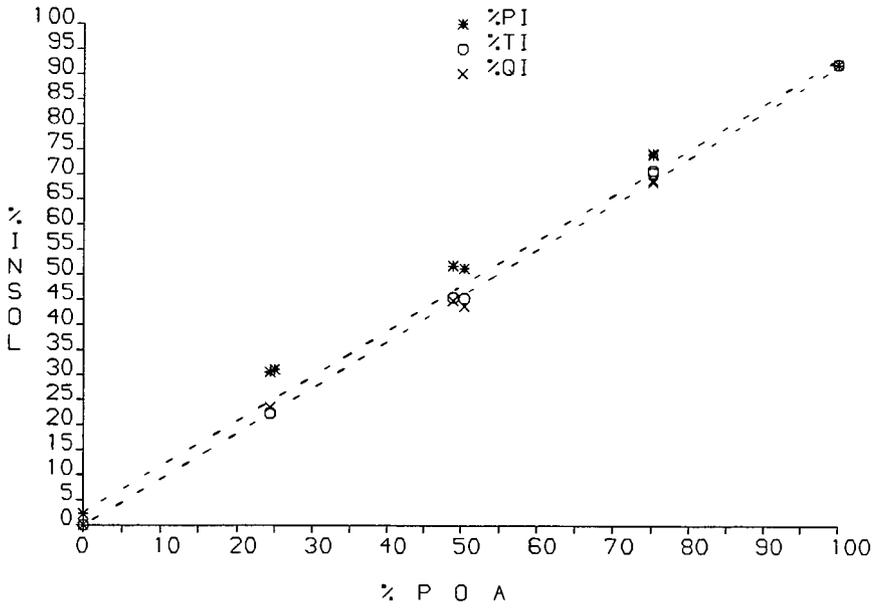


Fig. 12

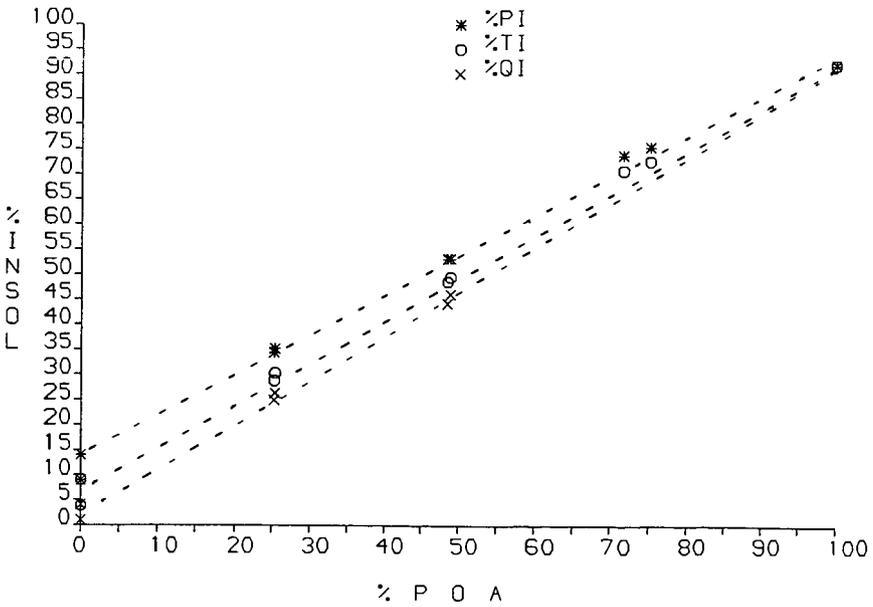


Fig. 13

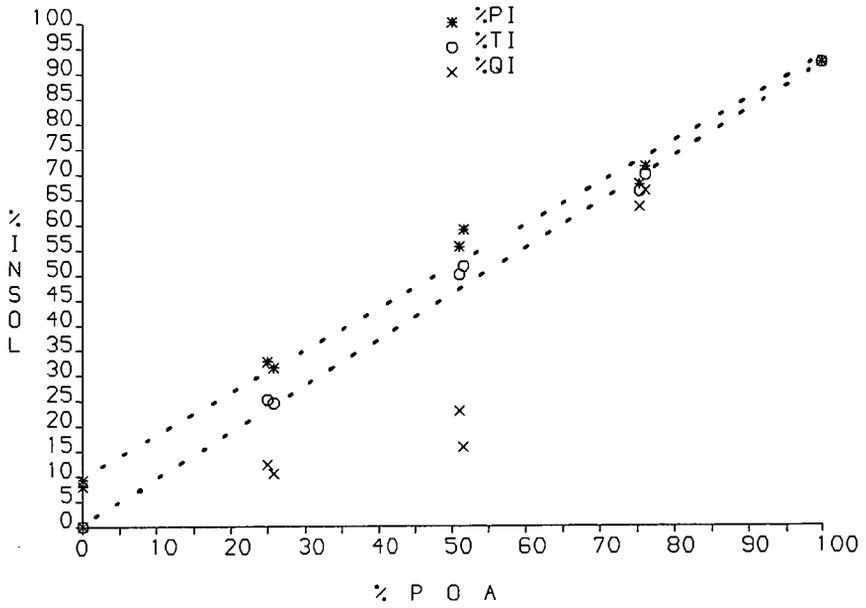
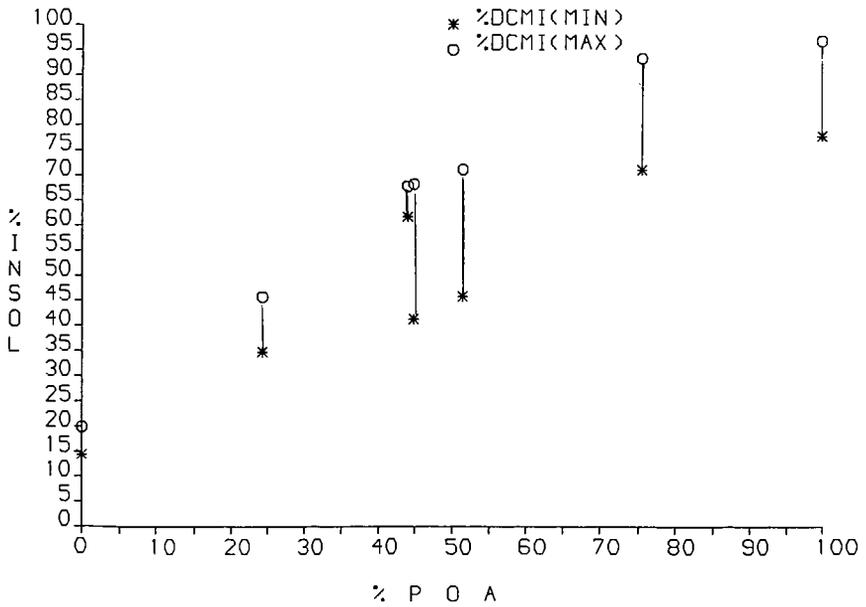


Fig. 14



## COPROCESSING WITH PETROLEUM RESID AND MARTIN LAKE LIGNITE

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### ABSTRACT

Petroleum resids have traditionally been overlooked as fuel sources despite their significant energy content. These products often contain iron, nickel, and vanadium in concentrations which rapidly deactivate or "poison" hydrogenation catalysts. Reacting petroleum resids with coal under liquefaction conditions or "coprocessing" has been proposed as an economic method for the removal of trace metals. Coprocessing involves the upgrading of a petroleum resid in a reaction with coal. While the resid acts as the liquefaction solvent some of the coal is converted to products, and the unconverted coal acts as a sink for metals. This paper will describe the results of tests to determine the increase in liquid product yields, and the reduction in the concentrations of trace metals achieved by coprocessing Arabian resid with Martin Lake lignite. Four batch-autoclave tests were made using various catalysts and conditions. Distillable products comprising 45-60 wt% of the individual product slurries were found to contain 2-8 ppm nickel and vanadium, and 9-41 ppm iron.

### INTRODUCTION

Many petroleum resids contain iron, nickel, and vanadium. These contaminants are found in some resids in concentrations of several hundred parts per million (ppm), and can greatly reduce the value of a resid as a fuel source (1,2). Trace metals in general and vanadium in particular are known to deactivate or "poison" metal-based catalysts used in hydrogenation reactions to upgrade resids (3,4). As a catalyst becomes coated with metals its exposed, active surface area is gradually reduced, resulting in a decrease in catalytic activity (3,5). In order to hydrogenate resids and improve their potential as significant energy sources, trace metals concentrations must be economically reduced to tolerable levels. Several methods for accomplishing this have been studied including "coprocessing" (3,6-14). Coprocessing approaches the upgrading of petroleum resids as a concurrent process with the liquefaction of coal (15-23). While the resid acts as the liquefaction solvent some of the coal is converted to products, and the unconverted coal acts as a sink for metals.

In assessing the feasibility of coprocessing it may be necessary to consider a combination of three parameters rather than one. An ideal coprocessing reaction system would provide a product with minimal trace metals concentrations along with maximum amounts of converted coal and upgraded resid.

## REACTION CONDITIONS

Data for this paper were obtained from the analysis of product slurries from four, two-stage batch autoclave tests with Martin Lake lignite and Lummus Arabian resid. Except for varying catalysts, reaction conditions for all four tests were essentially identical and are listed in Table 1.

TABLE 1  
COPROCESSING REACTION CONDITIONS

	Test 1	Test 2	Test 3	Test 4
Stage 1				
Residence Time (min)	40	40	40	40
Temp (°C)	368	371	367	372
Pressure (psia)	4100	3875	4400	4370
Pressurizing Gas	CO	CO	CO	CO
Stage 2				
Residence Time (min)	10	10	10	10
Temp (°C)	425	423	433	425
Pressure (psia)	2225	2325	2950	2970
Pressurizing Gas	H <sub>2</sub>	H <sub>2</sub>	H <sub>2</sub>	H <sub>2</sub>
Catalyst (both stages)	none	H <sub>2</sub> S	Ammonium Molybdate	none

It should be noted that the autoclave tests described in Table 1 were designated as runs N377, N379, N382, and N383 according to documentation procedures established at UNDEMRC. For the purpose of simplifying discussion, throughout this paper the tests will be referred to as Tests 1, 2, 3, and 4, respectively.

Table 2 provides data relating reactants charged and moisture- and ash-free (MAF) coal conversions achieved for each batch autoclave test. The data indicate that coal reactivity was increased by the presence of the catalysts, especially ammonium molybdate. Tests 1 and 4 were performed under nearly identical conditions to provide data on test-reproducibility, but gave substantially different conversions. There is speculation that the higher conversion achieved by Test 4 was influenced by the presence in the autoclave of residual ammonium molybdate from Test 3. A more complete discussion of the test results in reference to product mix, reaction conditions, and catalyst effects can be found in Rindt, et. al. (24).

## ANALYSIS OF PRODUCT SLURRIES BASED ON PENTANE-SOLUBILITY

To determine trace metals concentrations in coprocessing products as a function of pentane-solubility, samples of the product slurries from Tests 2, 3, and 4 were separated into pentane-soluble and insoluble fractions. Both fractions, and the raw product slurries from each test were analyzed for iron, nickel, and vanadium using an acid digestion technique. The pentane-soluble fraction of Arabian resid, the raw resid, and raw

Martin Lake lignite were also analyzed according to the same procedure.

TABLE 2  
COMPOSITIONS AND RESULTS OF BATCH AUTOCLAVE TESTS

	Test 1	Test 2	Test 3	Test 4
wt as-received coal (g)	134.5	139.6	141.7	142.8
wt MAF coal (g)	93.8	97.8	99.6	100.0
wt solvent (g)	350.5	365.5	372.2	373.7
wt water added (g)	16.7	17.0	18.0	17.4
wt FS* (g)	501.7	522.1	531.9	533.9
% FS that is MAF coal	18.7	18.7	18.7	18.7
wt PS** (g)	472.8	473.9	487.4	464.9
% THFI*** (PS)	11.5	9.7	7.2	11.0
% ash (PS)	4.5	4.4	4.5	4.7
% MAF coal unconverted	35.4	25.3	13.2	29.2
% MAF coal converted	64.6	74.7	86.8	70.8
catalyst	none	H <sub>2</sub> S	ammonium molybdate	none

- \* Feed slurry
- \*\* Product slurry
- \*\*\* Tetrahydrofuran insolubles

Sample sizes ranged from approximately 200 mg for the pentane insolubles, to 600 mg for the pentane solubles, to 1000 mg for the raw product slurries and the resid. The coal sample size was 220 mg. Samples were weighed into 250 mL "Nalgene" plastic containers equipped with screw-on lids. Nitric and hydrofluoric acid were added in 20 and 2 mL amounts, respectively. Lids were placed lightly, as opposed to screwed on the containers, which were then heated in a microwave oven in groups of two, for five minutes on "medium" power. The microwave oven power output was calculated according to a method published by Kingston and Jassie (25), and found to be approximately 330 watts on the medium setting. After cooling, 1 gram of boric and 20 mL of methanesulfonic acid were added to each sample, and the resulting mixtures were heated for 90 minutes at 110°C in the oven of a gas chromatograph. Both heating steps were performed under a hood to safely remove any escaping vapors. The use of methanesulfonic acid is recommended as an effective means of removing metals from porphyrin complexes (26). After vacuum filtration the mixtures were diluted to 100 mL with deionized water and analyzed using inductively-coupled plasma spectroscopy (ICP). Results of the analyses are shown in Table 3.

TABLE 3  
METALS CONTENT BASED ON PENTANE-SOLUBILITY

	Fe (ppm)	Ni (ppm)	V (ppm)
Test 2 product slurry	1700	45	91
pentane solubles	0	0	6
pentane insolubles	13000	190	370
Test 3 product slurry	1800	47	70
pentane solubles	17	4	6
pentane insolubles	16000	210	360
Test 4 product slurry	2400	57	100
pentane solubles	46	0	5
pentane insolubles	13000	180	380
Arabian resid raw	56	37	120
pentane solubles	0	8	28
Martin Lake coal	4300	0	24
NBS 8505 certified*	-	-	390
analyzed**	8	57	460
NBS 1634a certified*	31	29	56
analyzed**	27	31	61

\* Values certified by National Bureau of Standards.

\*\* Values obtained using described analysis.

The bottom two entries in Table 3 refer to Standard Research Materials provided by the National Bureau of Standards, and were included as a means of determining the accuracy of the analytical method. The standards, NBS 8505, vanadium in crude oil (no values for iron or nickel) and NBS 1634a, trace metals in fuel oil residual, were similar in consistency and color to the coprocessing product slurries. Comparison of NBS certified values with values obtained through analysis suggests that the analytical method may yield an error of up to 18%.

Table 4 compares analytically-obtained metals concentration values for the three product slurries with values obtained using a mass balance calculation. The calculations were done using pentane solubilities and the metals concentration values for the pentane-soluble and pentane-insoluble fractions found in Table 3. As an example, the Test 2 calculated value for vanadium was obtained with the following formula:  $74.6\%(6) + 25.4\%(370) = 98$ . Comparison of values for iron suggests that something more than analytical error is contributing to the large difference between analyzed and calculated values. One possible explanation may derive from the digestion procedure since the same amount of acid was used to digest all the samples, regardless of weight or iron concentration. Digestion of the pentane-insolubles, which

contained high concentrations of iron, was done using a small sample (200 mg). While digestion of the pentane-solubles utilized a larger sample (600 mg), the iron in the samples was much less concentrated. In the case of the product slurry samples, the combination of large sample size (1000 mg) and moderately high iron concentration may have resulted in an incomplete digestion due to an overabundance of iron in comparison to acid.

TABLE 4

COMPARISON OF ANALYZED METALS CONTENT TO MASS BALANCE CALCULATED METALS CONTENT OF PRODUCT SLURRIES (PENTANE SOLUBILITY BASIS)

	Pentane Solubility (%)	Fe (ppm)	Ni (ppm)	V (ppm)
Test 2	74.6			
Analyzed value		1700	45	91
Calculated value		3300	48	98
Test 3	77.4			
Analyzed value		1800	47	70
Calculated value		3600	51	86
Test 4	72.7			
Analyzed value		2400	57	100
Calculated value		3600	49	107

#### DISTILLATION OF PRODUCT SLURRIES

The effect of coprocessing on trace metals concentrations was also examined as a function of percent product slurry distillable. Vacuum distillations were carried out using Pyrex glassware with T 14/20 joints. Slow flowing water was used as the first stage condenser cooling fluid. A distillation column approximately 20 cm long was used to reduce the chance of non-distilled sample carryover or "bumping". The apparatus was fitted with a fractionating device and operated under a vacuum of about 5 torr as measured with a mercury-filled McLeod Gauge. Product slurry samples of 10 - 25 g were placed into a 30 ml round bottom flask, heated with a mantle, and stirred with a Teflon-coated magnetic stir bar. As heating progressed the system pressure was slowly reduced. In order to minimize the threat of bumping, the sample was stirred vigorously and the distillation column was warmed to 85°C using glass fabric heating tape. Heating the column allowed low-boiling volatile components to remain in the vapor phase instead of condensing and dripping back into the distillation pot. As the system pressure was gradually reduced to 5 torr, the voltage to the heating mantle was gradually increased to 130 volts, a process that took about 30 - 40 minutes.

The first fraction was collected until the temperature in the distillation head reached 120°C, and is identified as the initial boiling point (IBP) to 120°C fraction. Following collection of

the first fraction the water flow to the condenser was shut off and the condenser was drained. The remainder of the distillation was carried out using air as the condenser cooling fluid. The second fraction was collected over a temperature range of 120-260°C, and the third fraction was collected over a temperature range of 260°C to the "end point". The end point is defined as the temperature at which one or more of the following conditions exist: 1) the temperature in the head piece remains constant, 2) the temperature in the head piece is consistently falling, or 3) decomposition of the sample is evident (the sample remaining in the pot starts smoking). Two other fractions collected were the cold trap fraction and the pot residue. The cold trap fraction refers to the material collected in the cold trap, which is located between the distillation pot and the condenser, and cooled by a slurry bath of dry ice and 2-propanol. This material is a solid while in the cold trap, but becomes a volatile liquid at room temperature. The pot residue refers to the material remaining in the distillation pot after the end point has been reached and the distillation is complete. This fraction contains a solid phase and a very viscous liquid phase.

#### ANALYSIS OF PRODUCT SLURRIES BASED ON DISTILLATION CUTS

The technique used for the digestion of the distillates and residues (developed by David J. Hassett at the University of North Dakota Energy and Minerals Research Center) required a sample size of about 1 g. Placement of the sample in a 100 mL Pyrex volumetric flask was followed by the addition of 10 mL Ultrex concentrated sulfuric acid. The flask was then placed on a hot plate and the mixture was heated. When dense white fumes of sulfur trioxide began to appear, a few drops of concentrated Ultrex nitric acid were added to the mixture. The application of heat continued and dense white fumes of sulfur trioxide again began to appear, at which time several more drops of nitric acid were added. This cycle was repeated until the mixture became clear, or no darker than a dilute straw color. A clear solution indicates that the major portion of the organic matter has been oxidized. After cooling, the solution was diluted to 100 mL with deionized water and analyzed by ICP. A sample of Arabian resid was also distilled, digested, and analyzed according to the same procedure, except that only three distillate fractions were collected. Martin Lake coal was prepared for ICP analysis by two separate methods. One sample was digested and the other was ashed. Table 5 displays the results of these analyses.

Comparison of analytically-obtained values with NBS-certified values for NBS 1634a, trace metals in fuel oil residual, helps demonstrate the reliability of the analytical method. As another check on the analysis, Table 6 compares analytically-obtained metals concentration values for the product slurries and resid with values obtained using a mass balance calculation. The mass balance calculation is similar to the calculation used in Table 4 except that distillate percentages rather than pentane solubilities are used to multiply the metals concentration values in Table 6.

TABLE 5

## METALS CONCENTRATIONS BASED ON PERCENT PRODUCT SLURRY DISTILLABLE

wt% product slurry		Fe (ppm)	Ni (ppm)	V (ppm)
Test 1 Prod. Slurry		4200	34	78
Cold trap	9.6	Below	detection	limits
IBP - 120°C	10.3	Below	detection	limits
120 - 260°C	31.7	7	4	4
260 - 275°C	6.2	75	40	40
Residue	42.2	10200	79	150
Test 2 Prod. Slurry		4000	37	81
Cold trap	4.4	Below	detection	limits
IBP - 120°C	13.6	Below	detection	limits
120 - 260°C	27.8	55	4	4
260 - 285°C	13.8	15	6	6
Residue	40.6	10200	99	180
Test 3 Prod. Slurry		4100	39	75
Cold trap	2.2	Below	detection	limits
IBP - 120°C	9.4	Below	detection	limits
120 - 260°C	30.5	12	4	4
260 - 305°C	16.1	7	6	6
Residue	37.3	10800	94	170
Test 4 Prod. Slurry		2700	30	65
Cold trap	2.7	Below	detection	limits
IBP - 120°C	14.6	Below	detection	limits
120 - 260°C	31.8	74	5	5
260 - 285°C	14.1	9	5	5
Residue	36.8	10500	130	260
Resid		1	36	12
120 - 260°C	26.1	1	2	1
260 - 295°C	16.3	26	2	2
Residue	57.6	14	62	19
Coal digested		3900	6	21
Coal ashed		4000	31	22
NBS 1634a analyzed		32	29	58
NBS 1634a certified		31	29	56

Since analyzed and calculated values are in reasonable agreement for Tests 1 - 3 and the resid, the large differences between values for Test 4 are probably due to a measurement error. With the exception of Test 4 the analyzed and calculated values for iron are very close, unlike the values in Table 4.

TABLE 6

ANALYZED METALS CONTENT COMPARED TO MASS BALANCE CALCULATED METALS CONTENT FOR PRODUCT SLURRIES (PERCENT DISTILLABLE BASIS)

	Fe (ppm)	Ni (ppm)	V (ppm)
Test 1			
Analyzed value	4200	34	78
Calculated value	4300	37	67
Test 2			
Analyzed value	4000	37	81
Calculated value	4200	42	75
Test 3			
Analyzed value	4100	39	75
Calculated value	4000	37	66
Test 4			
Analyzed value	2700	30	65
Calculated value	3900	50	98
Resid			
Analyzed value	1	36	12
Calculated value	13	37	12

This may be due to the digestion technique. While the first technique utilized a standard amount of acid for all samples, the amount of acid used in the second technique was individually determined for each sample based on the amount of oxidizable material contained in the sample. Calculated and analyzed values for nickel and vanadium in the resid are much closer than similar values for the product slurries from Tests 1 - 3. This could be because there were fewer chances for analytical error in the resid analysis since only three distillate fractions were obtained, as opposed to five for the product slurries.

#### COMPARISON OF DIGESTION TECHNIQUES

Table 7 compares analyzed metals concentration values for the product slurries to values that were expected based on feed slurry composition data. All analytical data in Table 7 are the result of analyses using the methanesulfonic acid digestion technique. The metals contents of the coal and resid were used to calculate the total metals content in grams for each slurry charged in the autoclave. By assuming grams metal in feed slurry equals grams metal in product slurry for the three metals, ppm values were calculated based on the weight of total product slurry recovered. Also included in the table is the ratio of expected value to analyzed value for the three metals in each test.

TABLE 7  
 EXPECTED COMPARED TO ANALYZED METALS CONTENTS BASED ON  
 METHANESULFONIC ACID DIGESTIONS

	Fe (ppm)	Ni (ppm)	V (ppm)
Test 2 expected	1300	29	93
Test 2 analyzed	1700	45	91
expected / analyzed	0.76	0.64	1.02
Test 3 expected	1300	28	99
Test 3 analyzed	1800	47	70
expected / analyzed	0.72	0.60	1.41
Test 4 expected	1400	30	104
Test 4 analyzed	2400	57	100
expected / analyzed	0.58	0.53	1.04

Table 8 also compares analyzed metals contents of the product slurries to expected metals contents based on feed slurry composition data. All analytical data in Table 8 are the result of analyses using the Ultrex acid digestion technique.

TABLE 8  
 EXPECTED COMPARED TO ANALYZED METALS CONTENTS BASED ON  
 ULTREX ACID DIGESTIONS

	Fe (ppm)	Ni (ppm)	V (ppm)
Test 1 expected	1100	28	15
Test 1 analyzed	4200	34	78
expected / analyzed	0.26	0.82	0.19
Test 2 expected	1200	30	16
Test 2 analyzed	4000	37	81
expected / analyzed	0.30	0.81	0.20
Test 3 expected	1200	29	16
Test 3 analyzed	4100	39	75
expected / analyzed	0.29	0.74	0.21
Test 4 expected	1200	31	16
Test 4 analyzed	2700	30	65
expected / analyzed	0.44	1.03	0.24

The most consistent relationship between analyzed and expected values in either Table 7 or Table 8 is evident in the comparison

of ratios for Tests 1 - 3 in the Ultrex acid digestion matrix. Although the analyzed values do not match the expected values, they are reasonably precise and consistent in their variation from the expected values. (Data from Test 4 do not correlate well with data from Tests 1 - 3, but, as previously discussed, it appears likely an error was made, in either the processing or analysis of the Test 4 product slurry.) The ratios displayed in Table 8 indicate that a greater degree of analytical precision is achievable through the use of the Ultrex acid digestion. The consistent variation in analyzed values suggests that a consistently performed step in the reaction process is responsible for the inaccuracy of the analyzed values. The higher than expected analyzed values for iron may be a result of storing the product slurries in metal cans upon their removal from the autoclave.

#### COMPARISON OF PRODUCT RECOVERY METHODS

Pentane extraction and distillation were compared as methods of recovering the largest product yield with the lowest metals concentrations possible. Table 9 displays metals contents as a function of pentane solubility, along with coal conversions achieved for tests 2, 3, and 4. Pentane solubility and pentane-solubles metals contents are also included for the Arabian resid.

TABLE 9  
METALS CONTENT AS A FUNCTION OF PENTANE-SOLUBILITY

	Pentane Solubility (%)	Fe (ppm)	Ni (ppm)	V (ppm)	% MAF coal converted
Test 2	74.6	0	0	6	74.7
Test 3	77.4	17	4	6	86.8
Test 4	72.7	46	0	5	70.8
Resid	80.3	0	8	28	

The data in Table 9 suggest that coprocessing may have potential as a means of reducing nickel and vanadium concentrations in the pentane-soluble fraction of Arabian resid. Since the feed slurries for the autoclave tests contained approximately 72% resid by weight, if no metals were removed during coprocessing, the pentane-soluble fraction of the product slurries should contain about 72% of 28 ppm, or 20 ppm vanadium. (Although this calculation is meaningful, it is not absolutely correct since it does not account for some gas production during the reaction and slight differences in pentane solubilities.)

Table 10 displays metals contents as a function of total product slurry distillable, along with coal conversions for the four tests. Similar data is included for the resid.

TABLE 10

## METALS CONTENT AS A FUNCTION OF TOTAL DISTILLATE

	% Distillable	Fe (ppm)	Ni (ppm)	V (ppm)	% MAF coal Converted
Test 1	45	15	7.8	7.8	64.6
Test 2	54	32	3.5	3.5	74.7
Test 3	54	8.7	1.7	1.7	86.8
Test 4	60	41	3.8	3.8	70.8
Resid	42	11	2.0	1.4	

## CONCLUSIONS

On the basis of this preliminary study, coprocessing appears to have merit as a means of reducing catalyst-poisoning metals concentrations in petroleum resid. However, in order to properly evaluate coprocessing, coal conversion and extent of resid-upgrading need to be assessed in terms of reaction cost and product value. Also, a larger, more accurate analytical data base is required to validate the metals concentration values.

According to this study, pentane extraction of the product slurry provides a greater usable product yield than distillation, and the pentane-soluble product contains iron, nickel, and vanadium in concentrations comparable to those of the distillate product. However, because of more and greater inconsistencies in data acquired using the methanesulfonic acid digestion, in order to properly compare product recovery methods it would be necessary to analyze a sample matrix based on pentane-solubility using the Ultrex acid digestion.

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## STABLE CARBON ISOTOPE ANALYSIS OF COAL/PETROLEUM COPROCESSING PRODUCTS

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### ABSTRACT

Coproprocessing involves the simultaneous upgrading of coal and petroleum resid by catalytic hydroconversion. To obtain a kinetic/mechanistic description of the process, it is useful if not necessary to be able to distinguish the relative contributions of coal and petroleum to the product mixtures. In this paper, the method of stable carbon isotope ratio analysis is shown to be sufficiently sensitive to determine the relative concentrations of coal and petroleum carbon in coprocessing products. Selective isotopic fractionation does not appear to occur to a significant extent, although additional work is needed to confirm this preliminary conclusion. Application of the method to the coprocessing of Wyodak and Illinois 6 coals with a Lloydminster resid by the Signal Research/UOP process is shown to yield valid results of use in process interpretation and optimization.

### INTRODUCTION

A noteworthy recent entry in the list of developing synthetic fuels processes is the concept of coal/oil coprocessing. In coprocessing, a petroleum resid is used as the vehicle to convey coal to a reaction vessel which simultaneously converts the two to distillate mixtures which are either finished products or suitable feeds for more conventional petroleum refinery processes. The incentive for the development of coprocessing lies in its potential to replace a portion of the petroleum feedstock with a lower cost hydrocarbon source while minimizing the recycle requirements which increase the capital costs of a grassroots coal liquefaction plant. To the extent that coprocessing can be integrated with existing refinery capacity, it may find some near-term application if conventional feedstocks are unavailable. A chemical or physical synergy has also been reported by some investigators who observe better results for coprocessing than for the processing of either individual feedstock. An excellent overview of industrial and academic research in the area can be found in the preprints of the American Chemical Society's "Symposium on Coprocessing and Two-Stage Liquefaction" held at the society's Fall 1986 National Meeting (1).

In the development of hydrocarbon conversion processes, it is useful if not essential to be able to describe the hydrogenation, cracking and heteroatom (O,N,S) removal reactions which control product yields and qualities. Ideally, these reactions would be known in sufficient detail to allow a kinetic/mechanistic model to be derived which would assist in data interpretation and process optimization. For coprocessing, the development of such a model is complicated by the presence of two feedstocks greatly different in composition. The ability to distinguish the reactions of the coal and petroleum components of the feed would be a useful tool in process development.

This paper describes the validation and application of the measurement of stable carbon isotope ratios to quantitatively determine the relative concentrations of coal- and petroleum-derived components in coprocessing products. The method relies on the difference between their  $^{13}\text{C}/^{12}\text{C}$  ratios to calculate the ratio of the coal and petroleum carbon in product mixtures

containing the two. Since the carbon contents of these materials are typically 85% to 90%, this provides an excellent estimate of the overall mass compositions. The measurement of carbon isotope ratios is standard practice in the petroleum industry and its application is conceptually straightforward. However, several significant questions must be resolved. First, is the method sufficiently precise and are the differences between the carbon isotope ratios of the relevant materials large enough to obtain experimentally meaningful results? Second, does selective isotopic fractionation occur, or do all the products retain the ratio of their individual parent feedstock? Third, do actual applications confirm the utility of the method by providing meaningful process results? The work described in this paper addresses these three questions.

#### CARBON ISOTOPE RATIOS OF COAL AND PETROLEUM RESIDS

Carbon isotope ratios are determined by quantitatively converting the carbon in a sample to CO<sub>2</sub> and measuring the relative amounts of the isotopically different CO<sub>2</sub> species. The resulting ratio, corrected for oxygen isotopes, is compared to that of a standard material and the result is reported as the relative difference.

$$\delta = \left( \frac{(^{13}\text{C}/^{12}\text{C})_{\text{Sample}}}{(^{13}\text{C}/^{12}\text{C})_{\text{Standard}}} - 1 \right) \times 1000$$

The standard used in this work is a Peedee belemnite (PDB)(2), a Cretaceous marine organism whose shell consists of calcium carbonate. Therefore, all ratios are reported relative to PDB. Experimental details have been reported elsewhere (3).

If the carbon isotope ratios of the feedstocks are known and are not identical, the percentage of coal or petroleum carbon, for example, in a coprocessing product can be calculated as

$$\% \text{ Petroleum Carbon} = \left( \frac{\delta \text{ Sample} - \delta \text{ Coal}}{\delta \text{ Petroleum} - \delta \text{ Coal}} \right) \times 100$$

This equation requires a sufficient difference between the carbon isotope ratios of the coal and petroleum to be of practical use. Table 1 presents the  $\delta$  values for the coals and petroleum resids used in the work reported here. Despite the variation in the coal rank from subbituminous (Wyodak) to hvAb (Pittsburgh), the carbon isotope ratios of the coals are essentially the same. By contrast, the resids show a considerable range, although all have absolute values greater than those of the coals. Table 1 also provides the standard deviations, based on at least triplicate analyses, for these feedstocks. These values give a good indication of the intrinsic precision of the analytical method, and are comfortably small relative to the differences between the coal and petroleum resids.

#### VALIDATION OF METHOD

A critical assumption in the application of this method is that significant isotopic fractionation does not occur. That is, the coal- or petroleum-derived

portion of the product mixture must retain the same carbon isotope ratio as the parent feed. Although significant isotope fractionation is not expected (3), some work has been initiated to verify this assumption. In the first test, a light oil, heavy oil and vacuum resid from the LC-Fining of an Arab Heavy crude, supplied by Lummus, were analyzed. The results, shown below, indicate that the products are not substantially different. Comparison to the feed material would have been desirable, but a valid feed sample was not obtained.

<u>LC-Finer Products</u>	<u><math>\delta \pm \text{Std Dev}</math></u>
Light Oil (600°F <sup>-</sup> )	-27.01
Heavy Oil (600°F <sup>-</sup> )	-26.76
Vacuum Resid (975°F <sup>+</sup> )	<u>-26.86 <math>\pm</math> 0.11</u>
Average	-26.87 $\pm$ 0.09

In a second test of isotopic fractionation, a set of petroleum samples, supplied by R. Lett of PETC (DOE) were analyzed. These samples consisted of a Maya atmospheric tower bottoms (ATB) and its heptane soluble and insoluble fractions. The results, below, indicate the insensitivity of the carbon isotope ratio to this type of solubility fractionation.

	<u><math>\delta \pm \text{Std Dev}</math></u>
Maya ATB	-27.66 $\pm$ 0.08
Heptane Solubles	-27.66 $\pm$ 0.08
Heptane Insolubles	<u>-27.28 <math>\pm</math> 0.07</u>
Average	-27.53 $\pm$ 0.22

As a further investigation of the possibility of isotopic fractionation, products from the Wilsonville coal liquefaction pilot plant made during operations with Illinois 6 (Burning Star coal) were compared. The results below are for a first-stage vacuum tower distillate (V-178) from Integrated Two-Stage Liquefaction operations and for resids (850°F<sup>+</sup>) from two different runs. KMV-203 is a heavy deashed thermal resid from Run 245. V-131B is a pasting solvent resid from Run 247.

	<u><math>\delta \pm \text{Std Dev}</math></u>
V-178	24.14 $\pm$ 0.03
KMV-203 (Run 245, 850°F <sup>+</sup> )	23.79 $\pm$ 0.03
V-131B (Run 247, 850°F <sup>+</sup> )	<u>23.8 <math>\pm</math> 0.1</u>
Average	23.91 $\pm$ 0.20

Again, the product isotope ratios are in good agreement, despite the fact that these products were made during different runs many months apart. The isotope ratios are also in reasonable agreement with the values for Illinois 6 coal given in Table 1, although neither of these Illinois 6 samples was obtained from Wilsonville.

Finally, carbon isotope ratios were determined for two samples of Lloydminster resid provided by Signal Research/UOP. These samples were prepared by distillation of a single feedstock.

Resid	Vol % Overhead (D-1160)	mol wt (amu)	$\delta$
17-R7	5.0	1117	-29.81
18-R8	26.5	755	-29.94

Despite their considerably different boiling ranges, these resids have equivalent carbon isotope ratios.

Although these results are not definitive, they indicate that selective isotope fractionation, at least to a first approximation, is not occurring to a great extent as a result of hydroprocessing, distillation, or solubility fractionation. No gas samples were analyzed, and previous work indicates that selective isotope enrichment of the gas may be significant, particularly at low gas yields (4). However, this effect is not expected to significantly alter the carbon isotope ratios of the distillate and residual liquids which are the main reaction products. While this remains a necessary area for further investigation, the possible effects of selective isotopic fractionation are ignored, with some reason for confidence, in this report.

#### APPLICATION TO SIGNAL RESEARCH/UOP COPROCESSING RUNS

Signal Research/UOP (UOP) is developing a coprocessing technology that employs a proprietary slurry-phase catalyst in a single-stage reactor. To evaluate the utility of the carbon isotope method in a practical application, a set of four feedstock samples and vacuum overhead and toluene-soluble vacuum bottoms products from sixteen continuous coprocessing runs were obtained from UOP. The toluene-insoluble portions of the vacuum bottoms, containing unconverted coal, ash and catalyst, were removed by UOP specifically to provide samples free of their proprietary catalyst. Reaction conditions and yield data are given in Table 2. Additional data were given elsewhere (3). These data were supplied by UOP. Table 3 gives the carbon isotope analyses and coal carbon as a percentage of total carbon in the vacuum overheads and bottoms, as calculated from the carbon isotope analyses.

UOP made two sets of runs, one with Illinois 6 coal and one with Wyodak coal. All the run periods reported here used a Lloydminster resid designated 18-R8. The carbon isotope data were used to calculate the ratios of coal carbon to total carbon in the two analyzed products. By comparing these values to the percentage of coal carbon in the total feed, it is possible to calculate a "selectivity" as the ratio of the measured percentage of coal carbon to that of the feed mixture. A value greater than one indicates that the given fraction is selectively enriched in coal carbon relative to petroleum carbon; a value less than unity indicates that the fraction is relatively enriched in petroleum carbon. A value equal to one indicates that, per carbon atom, the coal and petroleum respond similarly. Figures 1 and 2 show the selectivities for the runs with Wyodak and Illinois 6 coals. The selectivities are plotted versus vacuum bottoms yields, with increasing vacuum bottoms yields generally representing decreasing processing severity. The results show a clear distinction between the two coals. For the Wyodak coal, the vacuum overheads are consistently enriched in coal carbon, while the bottoms are depleted. This indicates that, per carbon atom, the Wyodak coal is more readily converted to distillate at these conditions than the petroleum resid. The Illinois 6 coal, by contrast, shows little average selectivity for the vacuum overheads, indicating that its carbon conversion to distillate is

similar to that of the resid. There is some suggestion in the Illinois 6 data that the vacuum bottoms are depleted in coal carbon at low conversion (high vacuum bottoms yields) and enriched at high conversion. Since coal conversion from toluene insolubles to soluble resid increased with increasing severity, this increase in coal carbon may simply reflect this higher conversion.

Table 4 gives the percentages of coal carbon and petroleum carbon fed which are converted to overhead and bottoms products. These numbers are based on the carbon contents and yields of the products and their relative proportions of coal and petroleum carbon. Comparing the conversions of coal and petroleum carbon to vacuum overheads with reaction temperature (Table 2) by linear regression analysis yields the following results.

#### Coal Carbon Conversion to Vacuum Overheads

Illinois 6 Coal:      % Conv =  $-402 + 1.051 T$  ( $^{\circ}\text{C}$ ),  $R^2 = 0.89$   
Wyodak Coal:        % Conv =  $-270 + 0.778 T$  ( $^{\circ}\text{C}$ ),  $R^2 = 0.81$

#### Resid Carbon Conversion to Vacuum Overheads

Both Coals:        % Conv =  $-296 + 0.804 T$  ( $^{\circ}\text{C}$ ),  $R^2 = 0.77$

This analysis of the data underscores the significant difference in the coprocessing behaviors of the Wyodak and Illinois 6 coals. By contrast, a single linear equation appears to adequately describe the temperature response of the resid conversion regardless of the coal with which it was coprocessed. These experiments were not specifically designed to demonstrate the effect of temperature in coprocessing, and other reaction conditions were simultaneously varied. However, the results indicate that carbon isotope ratios can be used to independently assess the relative reactions of coal and petroleum in coprocessing. Additional work is required to fully exploit the value of this technique to process development.

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TABLE 1. CARBON ISOTOPE RATIOS OF COPROCESSING FEEDS

Coals	$\delta$ ‰
Illinois 6 (Burning Star)	-24.32 $\pm$ 0.07
Illinois 6 (UOP)	-24.34 $\pm$ 0.04
Wyodak (Sarpy Creek)	-24.66 $\pm$ 0.06
Wyodak (UOP)	-24.36
Pittsburgh (McElroy)	-23.80 $\pm$ 0.1
Pittsburgh (Ireland)	-23.68 $\pm$ 0.01
<u>Petroleums</u>	
Lloydminster Resid (17-R7)	-29.81
Arab Heavy Vacuum Resid	-26.21 $\pm$ 0.28
Athabasca Vacuum Resid	-29.50 $\pm$ 0.2
Maya Atmospheric Tower Bottoms	-27.66 $\pm$ 0.08

TABLE 2. OPERATING CONDITIONS, CONVERSIONS, YIELDS AND ANALYSES - UOP COPROCESSING TESTS

Test No.	Operating Conditions			Product Yields, wt % of MAF Feed	
	Resid/MAF Coal wt Ratio	Space Velocity (a)	T, °C	Vacuum Overhead	SoTable Bottoms
<u>Illinois 6 Coal</u>					
16-0915	1.5	B	414	31.6	54.7
14-0905	1.5	B	425	45.1	41.6
15-0907	1.5	B	434	49.0	38.0
4-0513	2	1.25B	425	41.0	45.5
3-0508	2	B	413	32.2	54.3
2-0502	2	B	426	48.0	39.8
6-0522	2	B	431	49.4	36.5
5-0521	2	0.75B	424	45.2	39.7
<u>Wyodak Coal</u>					
10-1111	2	1.25B	427	48.0	34.5
7-1102	2	B	414	42.0	41.0
9-1108	2	B	425	46.6	35.9
8-1107	2	B	426	48.9	35.8
12-1118	2	B	431	53.5	30.9
11-1116	2	0.75B	425	48.5	33.5

(a) Overall space velocity, based on both coal and petroleum. "B" refers to proprietary base conditions.

TABLE 3. CARBON ISOTOPE ANALYSIS - UOP COPROCESSING SAMPLES

Test No.	Carbon Isotope Analyses $\delta^{13}C, \%$		Coal Carbon as % of Total Carbon	
	Vacuum Overhead	Soluble Vacuum Bottoms	Vacuum Overhead	Soluble Vacuum Bottoms
<u>Illinois 6 Coal Products</u>				
16-0915	-27.88	-27.93	36.8	35.9
14-0905	-27.61	-27.78	41.6	38.6
15-0907	-27.60	-27.48	41.8	43.9
4-0513	-28.14	-28.13	32.1	32.3
3-0508	-28.11	-28.35	32.7	28.4
2-0502	-28.18	-27.85	31.4	37.3
6-0522	-28.21	-27.88	30.9	36.8
5-0521	-28.19	-27.87	31.2	37.0
<u>Wyodak Coal Products</u>				
10-1111	-27.89	-28.67	36.1	22.3
7-1102	-27.87	-28.86	36.4	19.0
9-1108	-27.88	-28.78	36.3	20.4
8-1107	-27.89	-28.66	36.1	22.5
12-1118	-27.83	-28.58	37.1	23.9
11-1116	-27.95	-28.46	35.0	26.1

TABLE 4. CONVERSION OF COAL AND PETROLEUM CARBON TO VACUUM OVERHEADS - SIGNAL/UOP COPROCESSING

Test No.	% Conversion to Vacuum Overhead	
	Coal Carbon	Resid Carbon
<u>Illinois 6 Coal</u>		
16-0915	30.5	33.6
14-0905	49.3	44.5
15-0907	54.2	48.5
4-0513	42.2	42.8
3-0508	33.6	33.3
2-0502	48.1	50.5
6-0522	48.6	52.3
5-0521	47.6	47.7
<u>Wyodak Coal</u>		
10-1111	60.0	46.9
7-1102	53.6	41.4
9-1108	59.5	45.5
8-1107	61.5	47.9
12-1118	68.8	51.6
11-1116	59.1	48.4

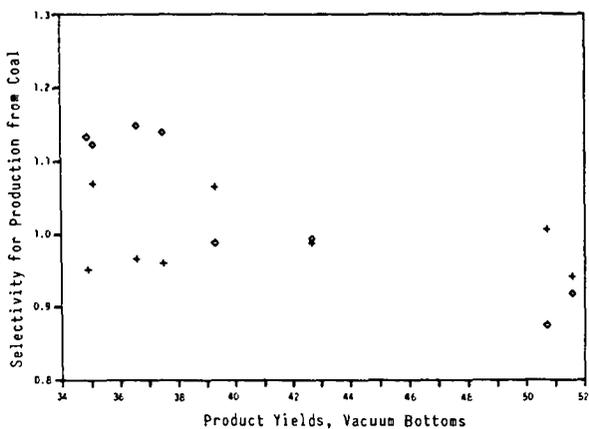


Figure 1. Selectivity vs Vacuum Bottoms Yields, UOP/Signal Research Coprocessing of Illinois 6 Coal, + - Vacuum Overhead, ◇ - Vacuum Bottoms.

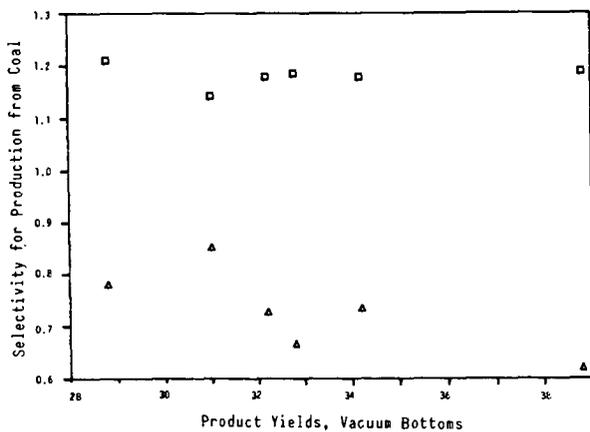


Figure 2. Selectivity vs Vacuum Bottoms Yields, UOP/Signal Research Coprocessing of Wyodak Coal, □ - Vacuum Overhead, △ - Vacuum Bottoms.

## NATURAL VARIATIONS OF $^{13}\text{C}$ ABUNDANCE IN COAL AND BITUMEN AS A TOOL TO MONITOR CO-PROCESSING

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### INTRODUCTION

The use of coal to facilitate the generation of transportation grade fuel from bitumen, heavy oil or petroleum resids is a topic of continuing research.<sup>(1-3)</sup> In order to optimize the upgrading process one needs to know in what proportion each feedstock contributes to each product fraction. Conventional analytical methods are neither able to distinguish the contribution from either feedstock in the synthetic products, nor measure the subtle changes in product character in response to differing process conditions.

The inherent difference in the  $^{13}\text{C}/^{12}\text{C}$  ratio between most coals and bitumen can be utilized as an isotopic tracer to assess the efficacy of co-processing. For example Vesta coal and Athabasca bitumen have sufficiently distinct  $^{13}\text{C}/^{12}\text{C}$  ratios<sup>(4)</sup> that the measured  $^{13}\text{C}/^{12}\text{C}$  of any product will accurately reflect the proportion of feed incorporated into the product. From the elemental analysis and the  $^{13}\text{C}/^{12}\text{C}$  ratio of the feedstock and products one can calculate the amount of carbon derived from coal (CDC) in each product fraction.<sup>(4-5)</sup> Analogously the amount of bitumen derived carbon (BDC) can also be independently calculated. In this study the natural variation in  $^{13}\text{C}$  concentration was utilized as an isotopic tracer to evaluate co-processing efficiency of a one litre stirred autoclave under differing process conditions. Process variables examined were coal concentration, several iron based catalysts ( $\text{Fe}_2\text{O}_3$ ;  $\text{Fe}_3\text{O}_4$  impregnated with  $\text{TiO}_2$ ,  $\text{SnO}_2$ , or  $\text{ZnO}$  and a sludge obtained from a nickel refinery) and temperature.

### EXPERIMENTAL PROCEDURE

Coal and bitumen with or without catalyst (3 wt% of Fe, based on daf. coal) were placed in a one litre magnadrive stirred autoclave equipped with an internal cooling coil. The autoclave was pressurized with  $\text{H}_2$  (8.6 MPa. ambient temperature) and heated at  $8^\circ\text{C}$  per minute to the reaction temperature. The slurry was reacted at operational temperature ( $\pm 1^\circ\text{C}$ ) for 45 minutes. Dried Vesta subbituminous coal (100 mesh) and the  $+350^\circ\text{C}$  fraction of Athabasca bitumen were used as feeds. The major component fractions of Athabasca bitumen are shown in table 1 and the elemental and isotopic analyses are listed in table 2. Iron based catalysts were prepared by co-precipitation (atomic ratio of 1:1) as described by Tanabe *et al.*<sup>(6)</sup> The sludge was obtained from Sheritt Gordon's Fort Saskatchewan nickel refining plant ( $\text{Fe}_2\text{O}_3$  74.1 wt%; Ni 19200 ppm., Co 3580 ppm., Mo 169 ppm.).

Table 1. Component Distribution of Bitumen ( $+350^\circ\text{C}$ )

Fraction	Wt% Carbon
Distillate	14.9
Maltene	61.5
Asphaltene	23.6
Residue	0.0

Table 2. Elemental Analyses (wt%) of Vesta Coal and Athabasca Bitumen (+350°C)

Fraction	Coal	Bitumen
Carbon	71.6	82.4
Hydrogen	5.0	10.1
Nitrogen	1.7	0.5
Sulphur	1.0	4.9
Ash	17.0	0.7
Moisture	0.7	0.0
$\delta^{13}\text{C}$	-26.35	-30.46

† Values expressed in terms of PDB(7)

$\delta^{13}\text{C}$  of NBS 22 is -29.81 parts per thousand (ppt.) with respect to PDB.

In experiments involving changes in coal concentration 125 grams of stripped Athabasca bitumen (-350°C fraction removed by distillation) was co-processed with 0, 8, 15, 30 and 60 grams of vacuum dried Vesta subbituminous coal at an operational temperature of 430°C. A second set of autoclave runs was performed in which 125 gram aliquots of stripped bitumen were co-processed with 0, 10, and 18 grams of Vesta coal. After reaction, the -300°C fraction was directly removed from the autoclave and trapped by condensation in an ice water trap, distilled to -177°C then characterized using GC-MS. The influence of iron based catalyst upon coal solubilization was the second process variable examined. Coal (60 grams), stripped bitumen (125 grams), and various catalysts (no added catalyst,  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3/\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3/\text{SnO}_2$ ,  $\text{Fe}_2\text{O}_3/\text{ZnO}$  or nickel sludge) were reacted at 430°C. The third process variable examined was the influence of temperature upon co-processing. Three autoclave runs were performed in which 125 grams of stripped Athabasca bitumen were reacted with 60 grams of Vesta coal and  $\text{Fe}_2\text{O}_3$  catalyst (3 wt% of Fe based on daf. coal weight) at 415°C, 430°C and 445°C.

The following fractions were isolated from the co-processed material: distillate (-524°C), maltene (n-pentane soluble), asphaltene (n-pentane insoluble - toluene soluble), and residue (toluene insoluble). Each product's elemental composition and  $^{13}\text{C}/^{12}\text{C}$  ratio was measured.(4) Product gases were collected and analysed by GC. All the  $^{13}\text{C}/^{12}\text{C}$  ratios were expressed in terms of the  $\delta^{13}\text{C}$  notation of Craig(7) equation 1:

$$1) \quad \delta^{13}\text{C} = \left( \frac{(^{13}\text{C}/^{12}\text{C})_{\text{sample}} - (^{13}\text{C}/^{12}\text{C})_{\text{ref.}}}{(^{13}\text{C}/^{12}\text{C})_{\text{ref.}}} \right) \times 1000$$

## RESULTS AND DISCUSSION

### Mass Balance Calculation

Contrast between the  $^{13}\text{C}/^{12}\text{C}$  ratio of coal and bitumen may be utilized as a natural isotopic tracer to monitor coal or bitumen incorporation into synthetic product fractions. A two end member mixing model<sup>(8)</sup> can be algebraically derived to calculate the make up of the co-processed products, equation 2.

$$2) \% \text{ COAL INCORPORATION} = \left( 1 - \frac{\delta^{13}\text{C}_{\text{prod}} - \delta^{13}\text{C}_{\text{coal}}}{\delta^{13}\text{C}_{\text{bit}} - \delta^{13}\text{C}_{\text{coal}}} \right) \times 100 \%$$

Two hydroprocessing experiments were performed using only bitumen in order to examine whether any isotopic shift would occur due to processing. Bitumen (125 grams) was processed at 430°C and bitumen (125 grams with 3 wt% Fe<sub>2</sub>O<sub>3</sub>) was processed at 445°C. Distillate (200°C to 524°C), maltene, asphaltene and residue fractions were found to be enriched (0.16, 0.37, 0.31 and 1.12 ppt. respectively) in  $^{13}\text{C}$  relative to unprocessed bitumen fractions.<sup>(4)</sup> The naptha fraction was enriched in  $^{12}\text{C}$ , (table 3). Such measurements serve as blanks and need to be substituted for  $\delta^{13}\text{C}_{\text{bit}}$  in equation 2. In this study the calculated yields of carbon summed over all the fractions is within  $\pm 2\%$  of the weight of the original charge.

Table 3: Isotopic Ratio of the Naptha Fraction (-177°C)

0 grams coal	-31.14 ppt.
10 grams coal	-30.99 ppt.
18 grams coal	-30.95 ppt.

† Values expressed in terms of PDB<sup>(7)</sup>

$\delta^{13}\text{C}$  of NBS 22 is -29.81 ppt. with respect to PDB.

Formation of crack gases enriches the residues in  $^{13}\text{C}$  but the  $^{12}\text{C}$  enrichment in the naptha is enigmatic. Two pathways for  $^{12}\text{C}$  enrichment are possible; that large moieties have isotopic heterogeneity, or alternatively that the  $^{12}\text{C}$  enrichment may result from a thermal process. Athabasca bitumen has been biodegraded to the stage where many of the original components, i.e. (alkanes and steranes) found in crude oils are no longer present.<sup>(9)</sup> However C<sub>27</sub> to C<sub>29</sub> steranes are released from the asphaltene fraction of Athabasca bitumen by hydropyrolysis<sup>(10)</sup> suggesting that the asphaltene fraction of bitumen may have incorporated alkanes from the original crude which are released upon thermal degradation. Recent work by Cyr *et al.*<sup>(11)</sup> indicates that in the highest molecular weight fraction (MW 16900) of Athabasca bitumen the aromatic core of the asphaltene is surrounded by alkyl chains with a mean length of 12. In nondegraded crude oil the alkane fraction is isotopically enriched in  $^{12}\text{C}$  relative to the whole crude, while the cycloparaffin and aromatic fraction are relatively uniform.<sup>(12)</sup> These observations suggest that the observed  $^{12}\text{C}$  enrichment of naptha may result from thermal degradation of moieties which have incorporated a portion of the original alkane fraction.

Alternatively, selective enrichment of a low molecular weight product fraction in  $^{12}\text{C}$  by C-C bond scission is known to occur.<sup>(13-15)</sup> Pyrolysis of n-C<sub>18</sub>H<sub>38</sub> at 500°C for one hour produced methane enriched in  $^{12}\text{C}$  relative to the source by 15 ppt. The C<sub>2</sub> to C<sub>4</sub> gases showed similar but less pronounced enrichment with Sackett<sup>(15)</sup> suggesting that for C<sub>2</sub>, C<sub>3</sub> and C<sub>4</sub> the isotope shift was 1/2, 1/3 and 1/4 that of methane respectively.

## Effect of Variations of Coal-Bitumen Ratio

Varying amounts of coal were co-processed with bitumen. Coal and bitumen incorporation into a product fraction has been calculated and plotted against the weight% of coal in the slurry, (figures 1,2). Co-processing experiments utilizing coal to bitumen ratios less than 15 wt%, exhibit a noticeable increase in distillate yield (14% to 17%) over and above distillate yields obtained by hydrotreatment of bitumen alone, (figure 1). Graphically there appears to be an antithetic correlation between bitumen-derived distillate and bitumen-derived maltene products. Increased distillate yield corresponds with a decrease in in the bitumen-derived maltene fraction. The shift to a more positive  $\delta^{13}\text{C}$  value with increasing coal concentration, (table 3), indicates that coal is incorporated into the  $-177^\circ\text{C}$  naptha fraction. For coal concentrations greater than 8 wt% the BDC incorporated into the maltenes are in excess of the maltene yields obtained from processing of bitumen alone. Increase in the maltene's BDC corresponds with a decrease in the BDC present in the asphaltene fraction. With increasing coal concentration, bitumen's incorporation into the asphaltene fraction decreases. Graphically it is more pronounced for low coal concentrations, (figure 1). Slurry compositions of 8 to 26 wt% coal show only a slight decrease in bitumen incorporation into asphaltenes over the entire range. The isotopically determined BDC yield of the distillate, maltene and asphaltene fractions suggest that the increase in distillate yields for coal-bitumen ratios of 4% to 8% is derived from the thermal degradation of the asphaltene and maltene fractions. The proportion of distillate derived solely from bitumen shows no appreciable change in yield for coal concentration in excess of 15 wt%, (figure 1). Higher coal concentration, however appear to enhance asphaltene conversion to maltene and residue fractions. The increase in bitumen's incorporation into residue parallels a measured increase in coal incorporation into residue, (figure 2). The sharp increase in residue is in part due to polymerization reactions (as evidenced by the increase in the bitumen-derived component of the residue), and in part by coal saturation in the slurry (as evidenced by the three fold increase in the coal-derived residue).

With increasing coal concentration, coal's contribution to each product fraction increases. Calculated yields of distillate ( $-524^\circ\text{C}$ ) solely derived from coal are observed to increase in near linear fashion with coal concentration, (figure 2). Incorporation of coal derived carbon (CDC) into the maltene fraction appears to be largely independent of coal concentration. For coal concentrations of 0 wt% to 15 wt%, a large relative increase in the coal derived proportion of the asphaltene exists. For concentrations in excess of 15 wt%, the amount of coal-derived asphaltenes appear to level off.

The naptha fraction recovered from three co-processing experiments for which 0, 10 and 18 grams of Vesta coal were reacted with 137, 126 or 126 grams of stripped bitumen was characterized using GC-(P(O)NA column) and GC-MS by means of retention times and library search of compounds. We have now identified, by means of GC-MS, in the naptha fraction of the 10 grams coal co-processing experiment, oxygen and sulphur bearing hydrocarbons; 2-3 dimethylthiophene, 2-4 dimethylthiophene, 2-3-4 trimethylthiophene, 2-3-5 trimethylthiophene, dimethylphenol and methylbenzothiophene.

## Effect of Iron Based Catalyst

The effect of select metal oxides catalyst upon coal solubilization was the next process variable examined. The different catalysts affect the make-up of the synthetic liquids, (table 4). In all experiments the weight of feedstocks co-processed was held constant, 60 grams Vesta coal (35.4 grams carbon) and 125 grams of stripped Athabasca bitumen (102.3 grams carbon).

Table 4: Effect of Iron Based Catalyst (CDC, BDC\* in grams)

Fraction	Blank		Fe <sub>2</sub> O <sub>3</sub>		Fe <sub>2</sub> O <sub>3</sub> /TiO <sub>2</sub>		Fe <sub>2</sub> O <sub>3</sub> /SnO <sub>2</sub>		Fe <sub>2</sub> O <sub>3</sub> /ZnO		Sludge	
	CDC	BDC	CDC	BDC	CDC	BDC	CDC	BDC	CDC	BDC	CDC	BDC
Distillate	7.3	52.7	6.7	46.1	6.5	46.1	7.7	46.1	8.8	54.2	7.6	49.6
Maltene	2.4	22.7	4.0	40.8	2.4	43.7	3.2	44.1	2.8	31.8	2.1	41.2
Asphaltene	9.7	9.5	17.6	11.8	18.7	11.6	13.5	8.7	12.2	11.3	16.5	10.4
Residue	13.5	5.8	5.7	0.2	6.7	0.1	10.4	1.8	10.5	2.2	7.6	0.8
Gas**	2.1	4.4	1.5	4.3	1.3	4.3	1.2	4.3	1.6	4.3	1.0	4.3
% Yield***	98.9	98.1	100.3	100.9	100.6	103.4	101.7	102.6	101.4	101.5	98.3	103.9

\* Feeds: 60 g of coal (35.4 g carbon), 125 g of bitumen (102.3 g carbon)

\*\* From GC analysis

\*\*\* Based on carbon in the feed

The contribution of both coal-derived carbon (CDC) and bitumen derived carbon (BDC) as calculated from  $\delta^{13}\text{C}$  mass balance are listed for each product fraction. Isotopically calculated coal and bitumen contribution to the product fraction agree within 98 to 103% of the initial feedstock charge, (table 4).

Distribution of the CDC in both catalyzed and catalyst free experiments for the distillate and maltene fractions ranged from 6.5 to 8.8 grams, and 2.1 to 4.0 grams respectively. These results suggest that CDC incorporation into the maltene and distillate fractions may be largely independent of catalyst. Catalyst showed varying abilities to convert coal to asphaltene. Fe<sub>2</sub>O<sub>3</sub> alone or Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> or sludge converted coal more effectively than did Fe<sub>2</sub>O<sub>3</sub>/SnO<sub>2</sub> to Fe<sub>2</sub>O<sub>3</sub>/ZnO; 16.5 to 17.6 grams for the former, 12.2 to 13.5 grams for the latter. For bitumen upgrading, large differences in the BDC incorporation into the residue exists. Feedstock bitumen, (table 2) contains negligible toluene insoluble material (residue), so BDC incorporation into the residue fraction must be due to coking. The blank run (no added catalyst) produces both a high coke yield (5.8 grams) and a high distillate yield (52.9 grams). Addition of catalyst strongly inhibited the formation of coke, 0.1 to 0.2 grams with Fe<sub>2</sub>O<sub>3</sub> alone or with Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub>, 0.8 grams with sludge and 1.8 grams to 2.2 grams with Fe<sub>2</sub>O<sub>3</sub>/SnO<sub>2</sub> or Fe<sub>2</sub>O<sub>3</sub>/ZnO. Bitumen incorporation into residue appears to be closely related to distillate yield for experiments with added catalyst. The higher the residue yield, the more distillate obtained. Addition of Fe<sub>2</sub>O<sub>3</sub>/ZnO substantially increased distillate yield (54.2 grams), increased coke yields relative to other catalysts and decreased BDC incorporated into maltene fraction.

#### Effect of Temperature

Coke inhibition by Fe<sub>2</sub>O<sub>3</sub> catalyst upon bitumen upgrading was investigated at three different temperatures, 415°C, 430°C and 445°C. The contribution of CDC and BDC to each product fraction is presented in (table 5). An initial charge of 60 grams of Vesta coal (35.4 grams carbon) and 125 grams of stripped Athabasca bitumen (102.3 grams) were used in all experiments.

Table 5: Effect of Temperature (BDC\* and CDC in grams)

	(415°C)		(430°C)		(445°C)	
	CDC	BDC	CDC	BDC	CDC	BDC
Distillate	5.9	37.5	6.7	46.1	11.1	60.4
Maltene	2.5	52.2	4.0	40.8	3.5	18.9
Asphaltene	11.7	13.7	17.6	11.8	13.8	10.8
Residue	12.3	0.1	5.7	0.2	7.2	2.1
Gas**	-	3.6	1.5	4.3	3.0	3.9
% Yield***	90.3	104.5	100.3	100.9	102.4	92.0

\* Feeds: 60 g of coal (35.4 g carbon),  
126 g of bitumen (103.1 g carbon),  
3 wt% Fe<sub>2</sub>O<sub>3</sub> (based on daf coal wt.)

\*\* From GC analysis

\*\*\* Based on feed carbon

Increasing operational temperatures from 415°C to 430°C increased coal incorporation into the maltene and asphaltene fractions (2.5 to 4.0 grams and 11.7 to 17.6 grams respectively), at the expense of the residue (decreased from 12.3 to 5.7 grams). Little change is observed in the coal derived distillate. At 415°C a large proportion of coal remains unreacted, 12.3 grams of coal derived residue out of an initial coal charge of 35.4 grams. Yields of BDC incorporated into distillate fraction increases with increasing temperature (37.5 to 46.1 grams) while bitumen contribution to the maltene and asphaltene fraction decreased (52.2 to 40.8 grams and 13.7 to 11.8 grams respectively).

Co-processing of bitumen and coal at 445°C generated significantly more distillate, but also more insoluble material. Coal derived distillate increased from 6.7 to 10.4 grams. Whereas coal incorporation into the residue fraction increased from 5.7 to 9.4 grams. The increase in distillate and residue was at the expense of a twofold decrease in CDC in the maltene and asphaltene fractions (4.0 to 1.4 grams and 17.6 to 9.6 grams respectively). With co-processing at 445°C an increase in bitumen's incorporation into distillate was also observed (46.1 to 60.4 grams). Coke formation in terms of insoluble matter (residue) sharply increased from .2 grams (430°C) to 2.2 grams (445°C). Increased distillate and residue yields correspond with a sharp decrease in maltene (40.8 to 18.9 grams). The asphaltene fraction remained nearly constant, 11.8 grams at 430°C to 10.8 grams at 445°C.

## CONCLUSIONS

A stable isotope mass balance techniques was used to investigate the efficiency of single stage coal-bitumen co-processing for the solubilization of coal. The results indicate that during co-processing:

- 1) Uncatalyzed co-processing of coal-bitumen mixtures comprising of 5 to 10 wt% coal enhance bitumen conversion to distillate by 14 to 17%. Concordantly the bitumen derived component of the asphaltene fraction decreases from 32 to 49% with respect to yields obtained in the hydrotreatment of bitumen alone. Coal concentrations of 15 to 26 wt% result in no appreciable increases in distillate over processing of bitumen
- 2) Increase in coal concentration from 0 to 26 wt% results in a progressive increase in coal incorporation into the distillate, maltene, asphaltene and residue fractions; and that a change in coal concentration from 15 to 26 wt% results in a threefold increase in coal derived residue.
- 3) In the naptha fraction of co-processing experiment (5 wt% coal) dimethyl thiophenes, trimethyl thiophenes, dimethyl phenol and methyl benzothiophene have been detected using GC-MS. No contrast exists in compound types as determined by GC between coal-bitumen and bitumen only runs. Isotopic mass balance calculations indicate that coal is incorporated into these fractions.
- 4) Coal incorporation in the distillate and maltene fractions appears to be independent of the iron based catalyst used.
- 5) Iron based catalyst strongly inhibits coke formation from bitumen and increases coal solubilization into asphaltene fractions.
- 6)  $\text{Fe}_2\text{O}_3/\text{ZnO}$  and  $\text{Fe}_2\text{O}_3/\text{SnO}_2$  increased residue yield from bitumen with respect to  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3/\text{TiO}_2$ , and nickel sludge.
- 7) Sludge from nickel refining can be used as an effective coal solubilization catalyst.
- 8) Autoclave reaction temperature of  $445^\circ\text{C}$  increased bitumen's conversion to distillate by 31% with respect to distillate yield obtained in co-processing at a temperature of  $430^\circ\text{C}$ . However a sharp increase in bitumen coking is observed in experiments processed at  $445^\circ\text{C}$ .

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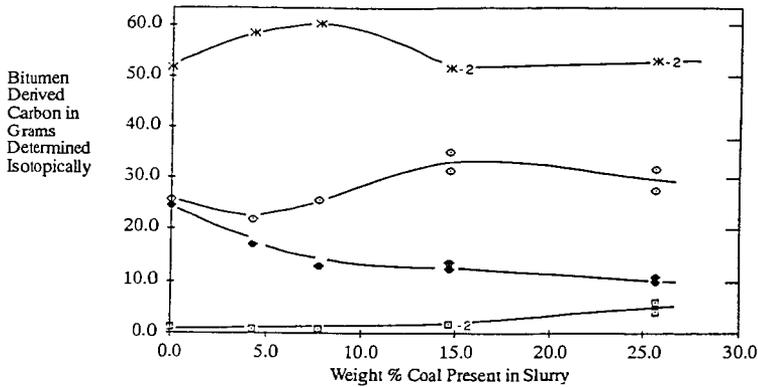


Figure 1 Variation in the isotopically determined amount of bitumen derived carbon incorporated into each synthetic liquid as a function of coal concentration in the slurry. Symbols: \* - Distillate; ○ - Maltene; ● - Asphaltene; □ - Residue.

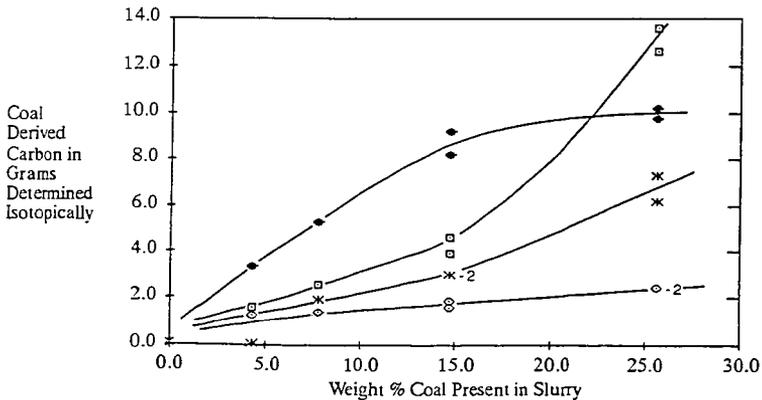


Figure 2 Variation in the isotopically determined amount of coal derived carbon incorporated into each synthetic liquid. Symbols: \* - Distillate; ○ - Maltene; ● - Asphaltene; □ - Residue.

## Characterisation of Reactants and Products in Coal-Petroleum Co-processing

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### INTRODUCTION

Over the last few years a number of processes have been developed for the direct liquefaction of coal to distillate fuels. Typically these processes involve thermal degradation of the macromolecular coal structure followed by hydrogenation to stabilise the degraded material and adjust the hydrogen to carbon ratio of the products. One such process, developed by British Coal, is Liquid Solvent Extraction (LSE) (1). This is a two stage process in which coal is firstly digested in a process derived solvent. The resulting coal liquids are then hydrocracked and distilled to give a range of light oil fractions and a residue which is recycled to the extraction stage. Since the solvent stream is generated from the final coal-derived products the extent of hydrocracking has to be limited. In principle this problem could be alleviated by supplementing or replacing the recycle solvent stream with heavy petroleum fractions which are cheap and have a higher H/C ratio than the coal derived solvents.

In this paper we report on the preliminary results from an EEC funded project to examine the viability of incorporating petroleum oils into the existing LSE process. Methods have been developed for the characterisation and assesment of potential solvent streams and also for the determination of product distributions in co-processed mixtures.

### SAMPLES AND EXPERIMENTAL

The petroleum samples investigated so far include two atmospheric residues ('A' and 'B'), one vacuum residue ('C') and two whole crudes ('O' and 'M'). The crudes O and M were distilled to give vacuum residues boiling > 475°C whilst the three distillation residues were investigated as received.

The distillation residues were characterised by fractionation on silica into saturate, aromatic and polar compound classes (2). The aromatic fractions were further separated into mono, di and poly aromatics on neutral alumina (3). The C-5 and C-7 asphaltene contents of the crudes and residues were also determined. The <sup>1</sup>H NMR spectra of all fractions were recorded and form the basis for assessing solvent quality.

Point-of-Ayr (POA) coal was co-processed in two and three component systems containing petroleum fractions and petroleum fractions/anthracene oil respectively under a range of conditions. This work forms a separate part of the project and is discussed more fully in a separate paper by Caygill *et al* (4).

In order to assess the relative contributions of coal and petroleum derived asphaltenes in the co-processed residue size exclusion chromatography has been used. Briefly, mixtures with differing proportions of coal and petroleum derived asphaltenes were introduced onto an analytical scale PL Gel SEC column with UV detection. From the combined, overlapping, coal and petroleum peak areas a calibration graph was constructed and used to determine the relative contributions of the two asphaltenes to the co-processed residues.

To make a direct comparison between differing solvents a Solvent Dissolving Index was determined for the POA coal. Essentially, the coal was processed in a tubing bomb reactor (420 °C for 60 mins.) using hydrogenated anthracene oil (HAO) as a hydrogen donor solvent. In a series of runs the HAO was progressively diluted with naphthalene thus causing a progressive dilution of hydrogen donors.

## RESULTS AND DISCUSSION

Chromatographic analysis of the petroleum residues (eg. atmospheric residue A; Table 1) indicates that they contain a large amount of saturates. Although these materials are generally regarded as not participating in the liquefaction reactions, if present in large quantities they may have an anti-solvent effect and therefore their removal is desirable (5). Whilst removal of n-alkanes is facilitated by the use of urea adduction, removal of branched and cyclic alkanes presents more of a problem.

Table 1  
Analytical Data For Atmospheric Residue A

	Total	Asph.	Sats.	Arom.	Polars	
%	-	21.2	13.6	54.3	15.8	-
C	83.3	83.0	86.7	84.0	80.2	80.4
H	10.0	8.25	12.9	10.1	9.6	9.5
N	0.8	1.35	0.3	0.5	1.2	0.7
S	6.4	8.05	0.0	3.8	4.5	5.5
H/C	1.44	1.19	1.79	1.44	1.44	1.42
H <sub>AR</sub>	6.1	9.3	1.8	8.5	7.5	7.0
H <sub>α, 2</sub>	0.5	1.9	0.0	2.0	3.0	1.9
H <sub>α</sub>	16.0	18.9	6.5	23.6	20.6	16.3
H <sub>β</sub>	57.3	51.9	63.9	55.3	53.9	56.6
H <sub>γ</sub>	20.2	18.1	27.8	10.6	15.0	18.2

Removal of asphaltenes from the residues reduces the aromaticity of the remaining material. This is likely to make the remaining n-pentane solubles less suitable as a process solvent. Aromatic species probably participate in hydrogen shuttling reactions and increase radical lifetimes, thus enhancing the probability of radical stabilisation by hydrogen transfer (6). The nature of the aromatic groups in the asphaltene and polar fractions is currently being investigated by electrochemical methods (7).

Figure 1 shows the superimposed SEC traces obtained from a coal liquid and a petroleum derived asphaltene injected onto the column separately. Considerable overlap of the two components is evident and precludes the measurement of coal/petroleum asphaltene ratios in co-processed mixtures directly from the chromatogram. However, since the UV detector is more sensitive to coal derived asphaltenes than petroleum derived fractions, the total peak area is dependent on the ratio of the two types of asphaltene in the mixture. Figure 2 shows a plot of peak area verses percentage of coal derived asphaltene for mixtures of different coal and oil derived asphaltenes. It should be noted that, although the asphaltenes were obtained from different sources, all of the points fall broadly on the same straight line. A least squares treatment of the data gives a gradient of  $0.100 \pm 0.008$  %coal/unit area. For individual samples, however, the fit is significantly better (eg.  $0.090 \pm 0.002$  %coal/unit area). Using the plot as a calibration it is possible to estimate the proportions of petroleum and coal derived asphaltene in a co-processed product stream.

Atmospheric residue A was co-processed with Point-of-Ayr coal (48.7% POA/410 °C/30 mins.) and the asphaltenes separated from the product mixture. Using the

calibration it was estimated that, of the 8.1% of asphaltene obtained, 62% of it was coal derived. This result agrees well with the findings of Steer et al (8) using isotopic mass balance calculations. The high percentage of coal contributing to the asphaltene is likely arise from the progressive breakdown of the coal structure to preasphaltenes, asphaltenes and then n-pentane solubles thus causing a preferential increase in coal derived species in the high molecular mass fractions.

Figure 3 shows the SDI calibration for POA coal and HAO with naphthalene as a diluent. The horizontal region of the plot indicates that the solvent mixture contains an excess of hydrogen donors. At higher naphthalene concentrations the extraction yield gradually decreases until the minimum extraction is reached at 100% naphthalene (ie no hydrogen donors). The Solvent Dissolving Index is defined as 0 at 100% naphthalene and 20 at the onset of maximum extraction.

In the standard SDI method developed by Clarke et al (9) the test liquefaction solvent is diluted with naphthalene (typically 50%). For the analysis of potential petroleum derived solvents the presence of naphthalene may result in erroneously high dissolving index due to it increasing the average aromaticity of the solvent mix and, therefore, its ability to solubilise the highly aromatic coal derived species.

#### ACKNOWLEDGEMENTS

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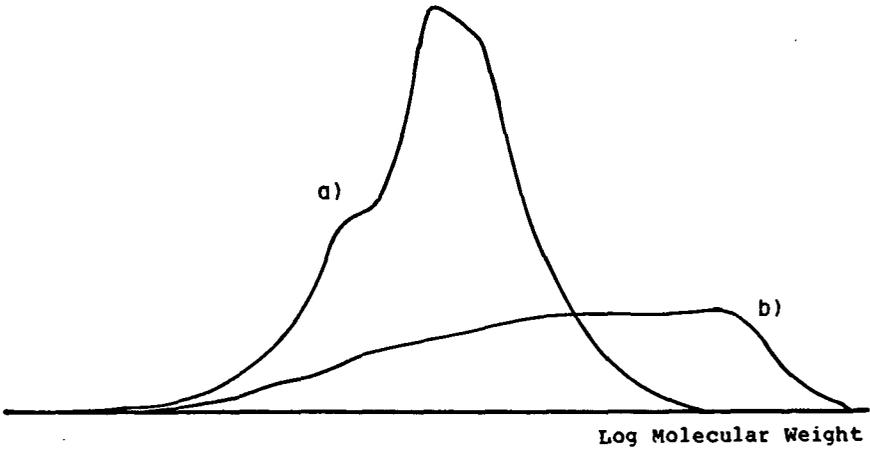


Figure 1. Superimposed SEC Traces from a) Coal Derived and b) Petroleum Derived Asphaltenes.

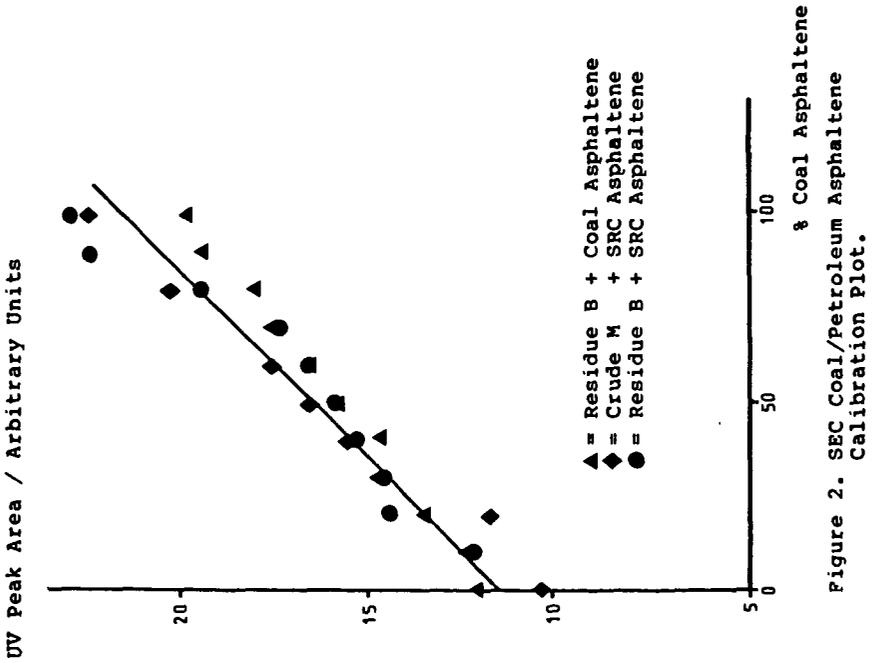


Figure 2. SEC Coal/Petroleum Asphaltene Calibration Plot.

## HYDROTREATING OF COPROCESSING DERIVED LIQUIDS

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### ABSTRACT

One task of a program, jointly sponsored by Electric Power Research Institute; Hydrocarbon Research, Inc.; Alberta Research Council and Ontario-Ohio Synthetic Fuels Corporation, was to determine the response of various coprocessing derived liquids to hydrotreating. The liquids were collected from an ebullated bed bench unit test performed by HRI. The feedstock was a 1:1 mixture of Ohio No. 5/6 coal and Cold Lake atmospheric resid. The product liquids were separated by distillation into naphtha (IBP to 185°C), distillate (185-343°C) and gas oil (343-470°C).

Scoping tests were performed in a fixed bed hydrotreater to determine suitable conditions for the production of reformer feedstock naphtha and diesel quality distillate. Variables investigated included temperature, pressure and space velocity. A Berty CSTR was employed to measure the kinetics of heteroatom removal from the distillate and gas oil. The resulting products met the specifications for synthetic crude oil feedstocks.

### INTRODUCTION

The Alberta Research Council (ARC) has been investigating various coprocessing options to develop a new market for the subbituminous coal reserves and heavy oil/bitumen deposits which are located within the Province of Alberta (1). One promising process option for this purpose is the Hydrocarbon Research Inc., (HRI) coal/oil coprocessing technology which uses hydrocracking over an ebullated bed of supported catalyst to convert coal and heavy oil resids to distillable liquid products (2). In 1985, ARC joined a consortium of Electric Power Research Institute (EPRI), Ontario-Ohio Synthetic Fuels Corporation (OOSFC) and HRI, to develop this technology (Ontario-Ohio Synthetic Fuels Corporation received financial assistance from the State of Ohio, Coal Development Office). Phase I of the program confirmed that both bituminous and subbituminous coals could be converted to high quality liquid synthetic crude oils when coprocessed with heavy oil resids such as Cold Lake atmospheric tower bottoms. Coal conversions exceeded 94% under preferred conditions while distillable oil yields approached 75 wt%.

In 1986, a second phase of the program was initiated with the same contributors. The key objectives of the program were to test alternate feedstocks, to determine catalyst replacement rates and to answer specific questions regarding aspects of the chemistry of the upgrading pathways. One subtask was to investigate processing conditions for the secondary upgrading of distillable oil product fractions. The following paper reports on the activities completed by ARC on the hydrotreating of these coprocessing derived liquids.

### EXPERIMENTAL

The distillable liquid product from a bench unit run completed by HRI in their New Jersey facility was separated by distillation into naphtha (IBP-185°C), middle distillate (185-343°C) and a gas oil (343-470°C). The bench unit run was performed on a 1:1 blend of Ohio No. 5/6 coal (dry basis) and Cold Lake atmospheric resid. Properties of these distilled liquids are shown in Table 1. These liquids approached

but did not meet specifications set by synthetic crude refiners or ASTM product requirements (diesel, No. 2 fuel oil).

All three fractions were initially hydrotreated in a Berty continuous flow stirred tank reactor (300 ml). Conditions were preselected based on historical data and literature reports. The required specifications for gas oil were met using a presulfided Amocat 1C catalyst. However, all the target specification for naphtha and middle distillations could not be achieved with this catalyst. It was therefore replaced with the more active Shell 324 or Shell 424 catalysts. Even then some target specifications were still unobtainable so the program was completed using a fixed bed reactor.

For the Berty reactor, five hours were allowed for the system to reach steady state. Product was then collected over a 2-3 hour period. Fresh presulfided catalyst (40 g) was charged into the reactor prior to each test. In the fixed bed reactor a two-hour period was adequate to reach steady state. This was followed by a 1 hour yield period. Conditions were then adjusted and the procedure repeated. In this manner, three runs could be completed within a single working day. A single charge of presulfided Shell 424 (50 g) was used throughout the fixed bed tests. Void space was packed with a silicon carbide filler. The operating parameters investigated were temperature, liquid hourly space velocity (LHSV), reported as g feedstock per g catalyst per hour, and hydrogen partial pressure.

Once conditions to produce a naphtha reformer feedstock had been established (Table 2), a production run was performed in the fixed bed hydrotreater. Over a 7 hour yield period, sufficient naphtha (about 0.5 litre) was produced to test the response of this material to reforming. The test unit for the reformer runs was the same fixed bed hydrotreater as had been used in the hydrotreating studies. Three flow rates were subsequently investigated, again in a single day of operation. The catalyst was Cyanamid PR-7, which was predried but otherwise untreated.

## RESULTS AND DISCUSSION

The key objectives of the study were to determine suitable conditions for the production of feedstocks which would be acceptable to synthetic crude refineries or conditions to meet ASTM product specifications (No. 2 fuel oil and diesel fuel). The liquid products derived from the HRI coal/oil coprocessing technology are generally superior to those derived from many other upgrading processes. The catalytic conditions in the ebullated bed ensure that a high proportion of the heteroatoms are removed and that substantial hydrogen addition occurs. The conditions required for secondary hydrotreating therefore are less severe than those for most synthetic crude oils. Commercial coking-derived, synthetic crude oils are presently hydrotreated on site to meet pipeline specifications and again at the refinery to meet process specifications. The quality of the ebullated bed products ensures that on site hydrotreating can be eliminated.

The middle distillate and gas oil used in this study already met the sulfur specifications for synthetic feedstocks and fuels without additional hydrotreating. Nitrogen levels were excessive, however, and the cetane number was low (Table 2). Hydrotreating conditions were therefore selected to bring these properties to acceptable levels.

A secondary objective of the programme was to determine kinetic data for the desulfurization and denitrification reactions. However, the conditions were not initially selected for this purpose, so much of the data was within too narrow a range. Also sulfur analyses were highly scattered especially for the Berty reactor. Product samples were routinely flushed with helium gas to remove dissolved hydrogen sulfide but results were often still high. This effect disappeared after two runs with the fixed bed unit, suggesting that the catalyst may have been the source of the interference. These problems were not resolved within the constraints of the program

and the data was insufficient to complete a kinetic study.

#### NAPHTHA

In the fixed bed unit, nitrogen specifications (1 ppm) for production of a reformer feedstock were met whenever the hydrogen pressure exceeded 10.3 MPa (1500 psi) and temperature was greater than 315°C. To reduce the sulfur to the desired level required a minimum of 13.8 MPa and 330°C. The hydrogen consumption was calculated from the hydrogen content of the feed and product; values ranged from 0.4 to 1.0 g/100 g feed (300 - 700 SCF/bbl). The conditions selected for the production run were 13.8 MPa, 345°C and a liquid hourly space velocity of 1.40 hr<sup>-1</sup>. Conditions were more severe for the Berty reactor but a reformer feedstock could be prepared from this unit.

The naphtha from the production run had over 50% naphthenes which indicated that it should be an excellent reformer feedstock. The conditions in the reformer (Table 2) were adequate to almost completely convert the naphthenes with a moderate gas yield (about 11%). Only two thirds of the naphthenes were converted to the desired aromatics, however, so that these components (43%) were slightly below specifications. Theoretically this would give a low octane number, but the gravity (42°API) was encouragement for a more acceptable research octane number (~99).

#### MIDDLE DISTILLATE

The end use of this fraction was assumed to be either diesel or No. 2 fuel oil. Nitrogen specifications for synthetic crude were readily obtained in both the fixed bed hydrotreater and Berty reactor. Over 95% of the nitrogen was removed even at 6.9 MPa (Fig. 1). This condition was insufficient to improve the cetane index or reduce the aromatic content to the level ascribed by Sullivan (3) or Kriz (4).

The cetane index reported here is an adapted version of ASTM procedure D-976. This method is based on the true 50% boiling point of the liquid and the gravity. The hydrotreating experiments did not produce sufficient liquid for a true boiling point distillation determination. It was therefore replaced by a simulated distillation. The calculated cetane index of the feedstock by this method was 37.5, similar to that previously published (2) by HRI for this fraction. An engine test gave a cetane number of 32.1 which showed the limitations of the cetane index method. To account for these limitations, a cetane index of 42 was set as the target specification.

The hydrogen pressure had to exceed 10.3 MPa before a significant change in cetane index and aromatic content was achieved. The temperature required was 330°C or higher. A space velocity of 2.0 would meet nitrogen specifications (Fig. 2) but not cetane index. Conditions vary greatly, therefore, dependant upon the end use of the product. The aromatic content of the product as close to 10% at the acceptable cetane index and this satisfied the predicted value of Sullivan. No runs came close to the 4% imposed by Kriz. Hydrogen consumption to make diesel grade product was approximately 1-1.2 g/100 g (700-850 SCF/Bbl) at preferred operating conditions.

#### GAS OIL

No tests were run on the fixed bed unit with this feedstock. The targetted specifications could be obtained with the Berty reactor. Based on the earlier experience with the naphtha and middle distillate, mild conditions of less than 370°C, 10.4 MPa and LHSV of greater than 2.0 hr<sup>-1</sup> should provide an acceptable product with either Shell 324 or Amocat 1C in a fixed bed. The requirements for the hydrotreating of gas oil are not highly stringent since it must subsequently be subjected to a cracking process. Up to 70% nitrogen removal was possible at the above conditions. Hydrogen consumption was about 0.7 g/100 g (500 SCF/Bbl).

## CONCLUSIONS

Operating ranges for hydrotreating and reforming of coprocessing derived liquid were established. All product fractions met target specifications for a synthetic crude oil feedstock or commercial product.

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Table 1  
Properties of Coprocessing Derived Liquids

		Naphtha (L0-4749)	Middle Distillate (L0-4750)	Gas Oil (L0-4751)
Carbon	%	83.8	87.1	87.4
Hydrogen	%	13.7	12.1	11.1
Nitrogen	ppm	165	1022	4000
Sulfur	ppm	120	334	1630
API gravity	°	49.7	28.3	17.0
13C aromaticity	%	5	23	30
Distillation	°C			
IBP		57	151	323
50%		131	268	368
90%		177	338	402
FBP		253	387	(470)

Table 2

## Product Quality and Reactor Conditions

	Product Quality		Operating Conditions				Hydrogen Consumption (SCF/Bbl)
	Nitrogen (ppm)	Sulfur (ppm)	Temperature (°C)	Pressure (MPa)	LHSV (hr <sup>-1</sup> )		
Naphtia							
Target	1	10	380	10.4	1.0		
Berty	1	12	330+	13.8	1.4		
Fixed Bed	1	10					~500
Reformer							
	Nitrogen (ppm)	Aromatics (%)	Yield (%)				
Target	1	45(PONA)	--				
Fixed Bed	1	43(PNA)	88	500	1.7	2.0	
Distillate							
	Nitrogen (ppm)	Aromatics <sup>a</sup> (%)	Cetane Index				
Target	200	10(4)	40 <sup>b</sup>				
Fixed Bed	10	10	42	330+	13.8	1.0	700-850
Berty	93	19	38				
Gas Oil							
	Nitrogen (ppm)	Gravity API					
Target	1200	18					
Berty	1130	18.4		370	10.4	2.0	~500

<sup>a</sup>Carbon 13 NMR<sup>b</sup>Cetane number

FIGURE 1  
Hydrogen Pressure vs Conversion Parameters (345°C)

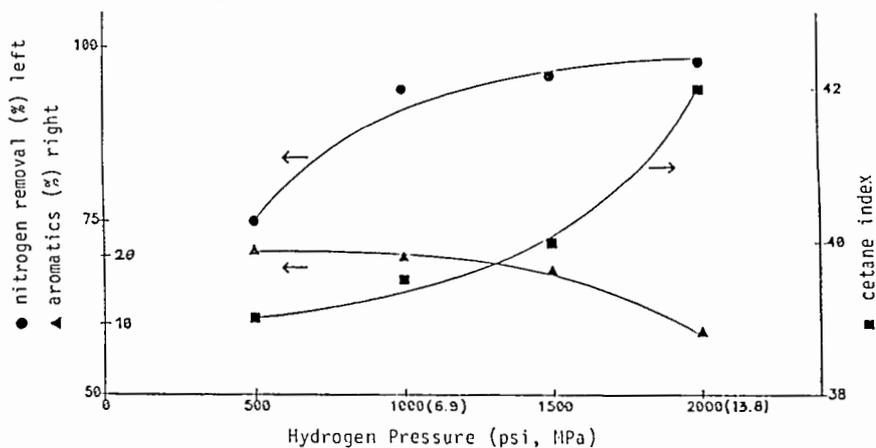
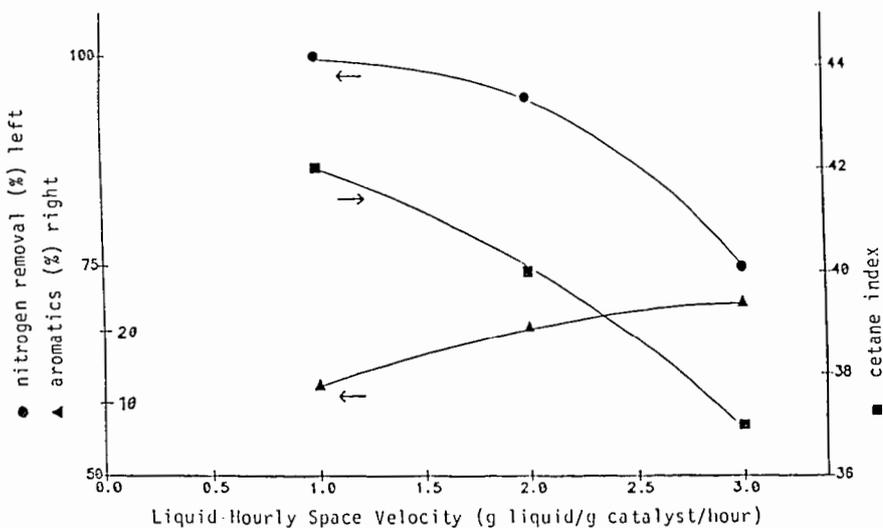


FIGURE 2  
Space Velocity vs Conversion Parameters (345°C)



## KINETICS OF HEAVY OIL/COAL COPROCESSING

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### INTRODUCTION

A number of studies have been reported on coprocessing of coal and oil sand bitumen, petroleum residues and distillate fractions in catalytic and non-catalytic processes (Moschopedis et al., 1984ab, Ignasiak et al., 1984, Kelly et al., 1984, Fouda et al., 1982, MacAurthur et al., 1985, Curtis et al., 1984). The studies described the effects of feedstock characteristics, process chemistry and operating variables on the product yield and distribution; however, very few kinetic data were reported in these investigations. This paper presents the kinetic data and modelling of the CANMET coal/heavy oil coprocessing process.

CANMET has been conducting research and process development work on coprocessing of Canadian heavy oil/bitumen and coal since 1979 including studies of the kinetics and mechanisms of coprocessing. As a continuation of the program, CANMET and Lobbe Technologies undertook a project on mathematical modelling of coprocessing kinetics with emphasis on the development of reaction engineering models for improved process performance and operation. The results of that project were reported in much detail elsewhere (Szladow et al., 1987).

### EXPERIMENTAL

The coprocessing experiments were conducted in a continuous-flow stirred-tank coprocessing reactor unit. A detailed description of this unit was given by Fouda et al. (1982). The applied reactor equations were those for CSTR, based on conclusions from the exploratory runs which investigated the effect of impeller speed on the yield of reaction products.

Alberta subbituminous coal and Cold Lake, Alberta, vacuum bottoms (+454°C) were used as the feedstock. The coal was ground to -200 mesh and slurried with heavy vacuum bottoms by mixing about 30 percent of coal and 70 percent of heavy oil (d.a.f. slurry basis). A disposable iron sulphide catalyst was added in the amount of approximately 5 percent on a d.a.f. slurry basis.

The experimental conditions were designed using a Latin Square statistical design at three levels of temperature and space velocity. The range of process conditions included:

Temperature: 400 to 455°C  
 Nominal Slurry Space Velocity: 0.50 to 1.54 kg/L/hr  
 Reactor Pressure: 2000 psig  
 Run Duration: 80 to 180 min.  
 Total Feed Processed: 402 to 600g  
 Coal Concentration: 29.71 to 33.38 m.a.f. Wt% feed

The coprocessing products were analyzed for four liquid fractions, solvent soluble and insoluble fractions, gaseous products, hydrogen consumption, and coal and pitch conversion. Distillate products were also analyzed for composition and specific gravity. The residue (+525°C) was analyzed for elemented composition and ash content. A summary of the product definitions and separation procedures is depicted in Figure 1. The percent recovery of the input feed was between 96.40 and 105.02 percent with the mean of 100.78 and standard deviation of 2.84 percent. These accurate mass balances for the product yield facilitated high predictive capabilities of the developed models.

Two different types of models were formulated for predicting the yield structure of coprocessing products: 1) models which had sequential characteristics; and 2) models with parallel characteristics, where most coprocessing products were generated from the initial lumps (Figure 2). In the sequential models, the distillate products always reached a maximum beyond which addition of more hydrogen resulted in generation of C1-C4 hydrocarbon gases. In the parallel models, the yield of distillate products continuously increased - within the range of coprocessing conditions - and the selectivity of products was determined by the relative rates of their formation.

A set of generalized lumped kinetic model equations was derived for an n-component reacting mixture in a stirred-tank reactor:

$$\frac{F_{in} (1 - \phi)}{(1 - \epsilon) \rho_P V_R} (x_{i,0} - X_i) = r_i'$$

where  $F_{in}$  = rate of total feed input, kg/hr (d.a.f.)  
 $\phi$  = mass fraction of product flashed at reactor T,P  
 $\rho_P$  = average density of products, kg/L  
 $V_R$  = reactor volume (to the dip tube), L<sup>3</sup>  
 $\epsilon$  = gas holdup  
 $X_{i,0} = F_{i,in} / F_{in}$   
 $r_i' = F_{i,out} / F_{in}$   
 $r_i$  = rate of formation (disappearance) for component "i" in terms of fractional conversion,  $X_i$ , hr<sup>-1</sup>

The equations were solved using a Least Square method and the product yield structure for each coprocessing component. The computer algorithms first solved the normal equations developed for the rate parameters,  $k_{ij}$ , and later, solved for the rate constant coefficient  $A_{ij}$  and  $E_{ij}$ . This approach provided information on how the calculated rate constants,  $k_{ij}$ , change with the alternative reaction networks. The approach also permitted better understanding of the physical meaning underlying the regressed rate constants and the postulated product yield structures for coprocessing.

A number of studies have been published documenting the pitfalls of using lumped kinetic models for reacting mixtures, in general (Liu et al., 1973, Luss et al., 1971) and for coal liquefaction in particular (Szladow et al., 1981, Prasad et al., 1986). The most common pitfalls reported were the loss of information about the kinetics of individual reactions, different rate expressions for the grouped as opposed to individual species rate equations, little theoretical significance underlying the overall (lumped) activation energies, and the frequent discrepancy between the order of the rate expressions for lumps and for reacting species. Several investigators also showed methods which overcome these difficulties for complex reacting mixtures, (Golikeri et al., 1974, Lee, 1978, Bailey, 1972). These methods were later extended to coal liquefaction (Szladow et al., 1982, Prasad et al., 1986).

Bearing in mind the above limitations of lumped kinetics, the CANMET coprocessing data and product lumping were reviewed to establish whether the product lump definitions were dependent on the severity of the process. The analysis of variance which was performed indicated that product characteristics did not change with the severity of coprocessing reactions. Also, analysis of activation energies for THFI using methods reported by Szladow et al. (1981) showed that one initial lump is sufficient for expressing coal reactivity.

Over twenty different reaction networks were developed and tested based on ANOVA tables and Multiple Classification Analysis of the coprocessing products. A significant number of the networks predicted the coprocessing data structure and met the identified constraints on the rate coefficients. The selection of suitable models was based, therefore, on three criteria:

1. How much of the total variance was explained by the model.
2. How much of the grouped product's variance was explained by the model.
3. How well the model predicts the yields of coprocessing products or how accurate the model is.

First, criterion 1 was used, later, as specific difficulties were addressed, criteria 2 and 3 were reviewed. This approach allowed a systematic evaluation of the models, in conjunction with the interpretation of the rate constants and reaction paths.

Special difficulties were also experienced with modelling preasphaltenes. Figure 3 depicts the effect of temperature on the yield of preasphaltenes. As the temperature increased from 400 to 425°C the yield of preasphaltenes increased; however, the yield of preasphaltenes decreased as the temperature increased from 425 to 450°C, indicating a change in the sign of the temperature coefficient (activation energy). This led us to believe that two mechanisms may be responsible for preasphaltenes formation: one essentially being a chemical reaction mechanism of THFI conversion, with the rates increasing with temperature, and the second representing an adduct formation between preasphaltenes and oils, for which the rate decreases with temperature.

Cronauer et al. (1979) and Sato (1976) reported similar effects for coal liquefaction. They observed a net negative yield of oil at low

primary liquefaction products. Our analysis of the CANMET experiment revealed that other coals also exhibit similar "reverse" temperature effects at lower temperatures. At high temperatures, the adduct seemed to disintegrate.

To account for the two opposed mechanisms, one would have to postulate independent rate expressions for chemical reactions and for adduct formation of preasphaltenes. Considering, however, that preasphaltenes constitute only a small fraction of the overall coprocessing products (5 to 10 percent), we decided to retain the parallel structure for preasphaltenes reactions, with only one reaction path leading to its formation. This approach had resulted in somewhat inaccurate modelling of preasphaltenes, but it allowed modelling of the remaining coprocessing reactions.

The final choice of parallel and sequential models is presented in Figure 4. Model 52 has a strong parallel characteristic for the yield of distillate fractions with the prime coprocessing products (light gas oil, naphtha and hydrocarbon gas) constituting the termination lumps for the coprocessing network. Model 61 has sequential characteristics with the exception of the formation paths for the C1-C4 group.

The regressed rate constants for Model 52 and 61 are shown in Table 1. Both models predicted the coprocessing yield data accurately (Figures 5 and 6). The amount of variance explained by the models is shown in Table 2. Model 52 explains 84.4 percent of the total variance. For individual components the variance explained exceeds or is close to the target variance for preasphaltenes, asphaltenes, oils, naphtha and the C1-C4 group. Model 61 explained 81.4 percent of total variance and achieved target variance for THFI, asphaltenes and oils and was close for the C1-C4 group. Interestingly enough, when tested without path #8, Model 61 could not predict the C1-C4 yield accurately.

In the final step, Model 52 was improved by adding two more reaction paths to meet the limiting conditions, i.e., at infinite time distillate fractions should be converted to lighter products (Figure 7). Model 53 explained 90.0 percent of variance, which is very satisfactory, considering the difficulties with modelling preasphaltenes. Model 53 also explained most of the individual component variance except for light gas oil and naphtha.

#### **SUMMARY AND CONCLUSION**

A number of reaction networks were evaluated for CANMET coprocessing. The final choice of model was a parallel model with some sequential characteristics. The model explained 90.0 percent of the total variance, which was considered satisfactory in view of the difficulties of modelling preasphaltenes.

The models which were evaluated showed that the kinetic approach successfully applied to coal liquefaction and heavy oil upgrading can be also applied to coprocessing. The coal conversion networks and heavy oil upgrading networks are interrelated via the forward reaction paths of preasphaltenes, asphaltenes, and THFI and via the reverse kinetic paths of an adduct formation between preasphaltenes and heavy oil.

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**Table 1. RATE CONSTANT COEFFICIENTS  
FOR MODEL 52 , 61, AND 53**

Rate Constant	MODEL 52		MODEL 61		MODEL 53	
	<u>Ai</u>	<u>Ei</u>	<u>Ai</u>	<u>Ei</u>	<u>Ai</u>	<u>Ei</u>
1	1.24E10	33,020	5.33E13	44,040	1.24E10	33,020
2	8.31E23	76,180	5.23E03	12,030	9.11E23	77,730
3	1.84E12	39,030	8.33E08	29,390	1.84E12	39,030
4	1.72E12	40,000	9.48E18	61,030	1.51E12	40,000
5	4.97E17	58,910	5.56E09	31,990	4.17E17	59,610
6	4.06E19	63,400	7.90E06	23,310	4.06E19	63,400
7	7.90E06	23,510	6.53E02	13,860	7.90E06	23,510
8	2.28E14	47,470	1.50E06	55,000	2.28E14	47,470
9	-	-	-	-	3.51E19	66,400
10	-	-	-	-	4.52E16	59,900

**Table 2. PERCENT OF VARIANCE EXPLAINED BY  
MODELS 52, 61 AND 53**

	<u><math>\sigma(i)</math></u>	<u><math>F(i)^1</math></u>	<u>MODEL 52</u>	<u>MODEL 61</u>	<u>MODEL 53</u>
THFI	15.5	92.1	90.4	92.8	91.5
PA	53.5	91.7	96.3	<0	93.1
A	30.6	52.4	54.0	55.3	52.6
OIL	38.1	65.9	95.4	96.6	96.0
HGO 1+2	12.1	94.1	47.2	75.1	90.6
LGO	5.9	98.8	71.5	75.2	78.4
NAPHT	6.1	99.4	91.6	88.4	72.7
C1-C4	10.9	99.7	98.5	98.7	98.9
TOTAL	N/A	92.5	84.4	81.4	90.0

<sup>1</sup> target, based on standard deviations for individual components

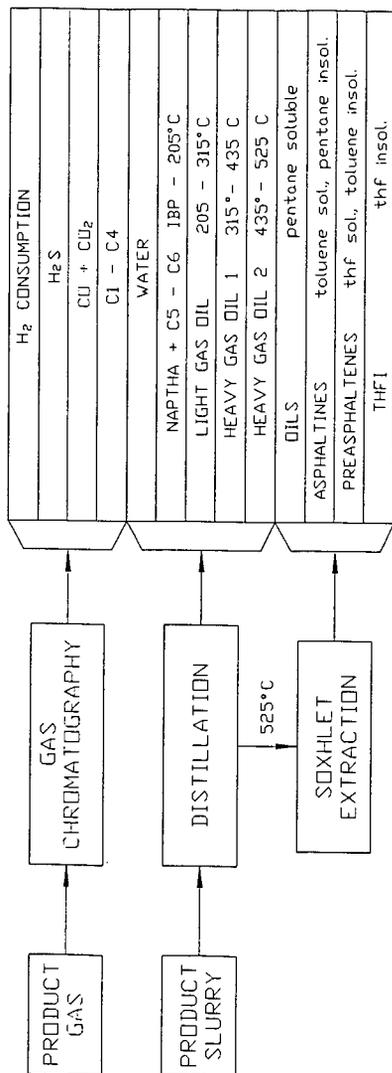


Figure 1. PRODUCT DEFINITION

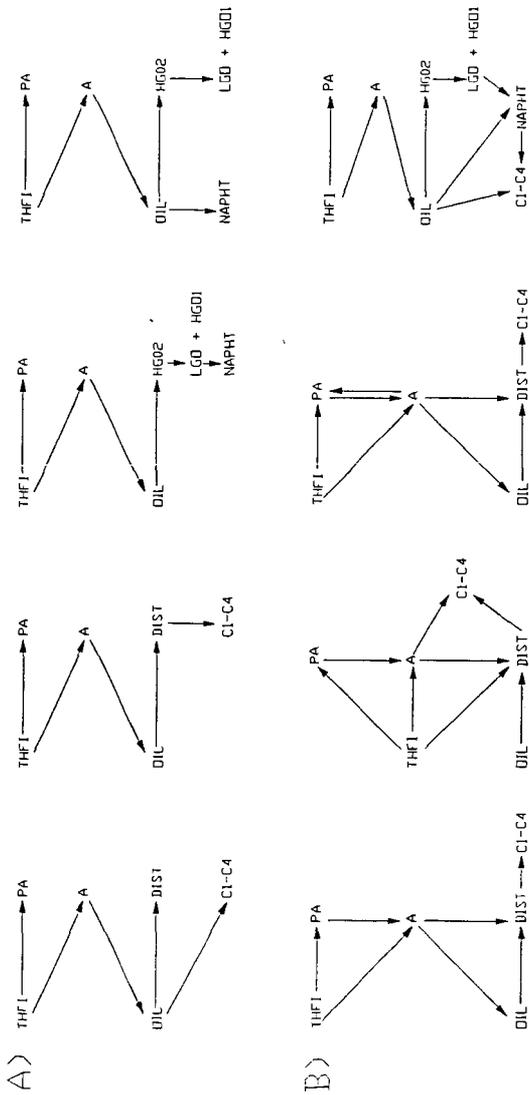


Figure 2. EXAMPLES OF SEQUENTIAL (A) AND PARALLEL (B) KINETIC STRUCTURES FOR COPROCESSING

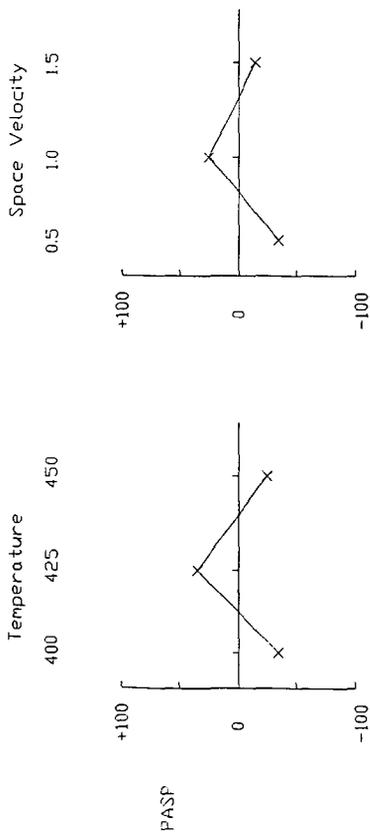


Figure 3. THE EFFECTS OF TEMPERATURE AND SPACE VELOCITY ON PREASPHALTENES COPROCESSING PRODUCTS

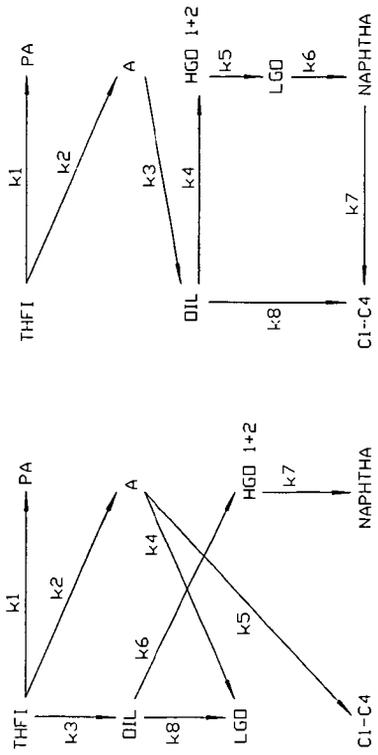


Figure 4. MODELS 52 AND 61

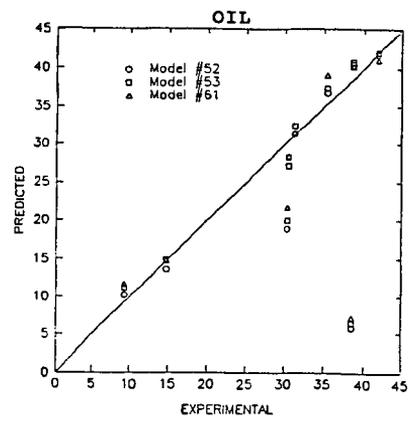
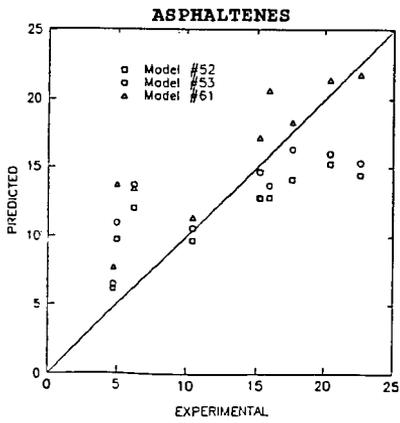
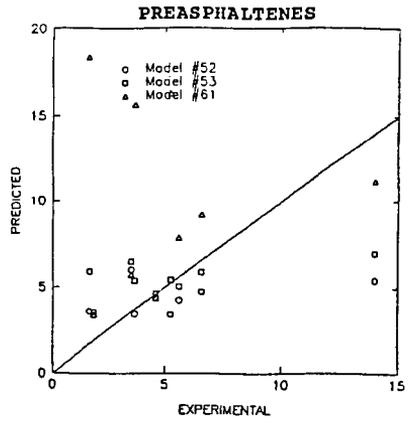
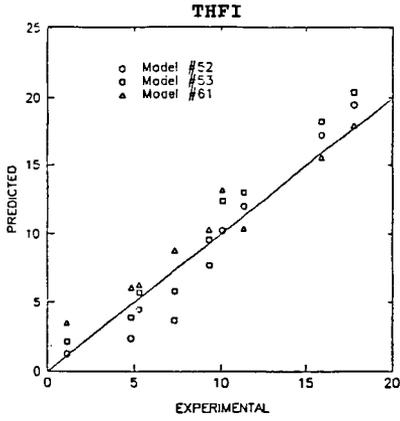


Figure 5. PREDICTED vs EXPERIMENTAL DATA

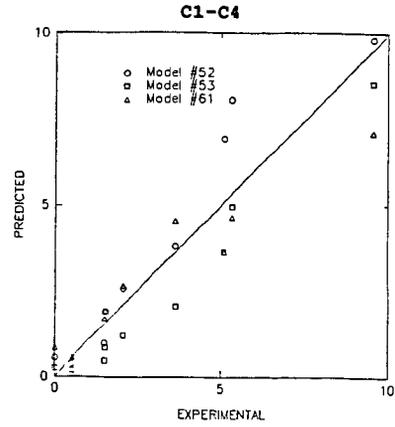
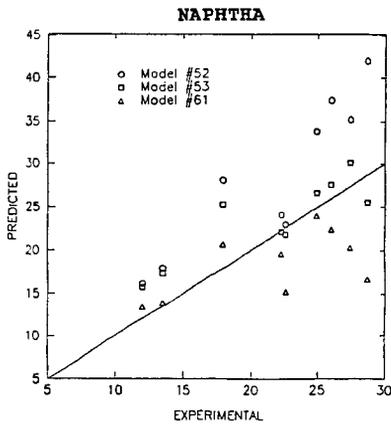
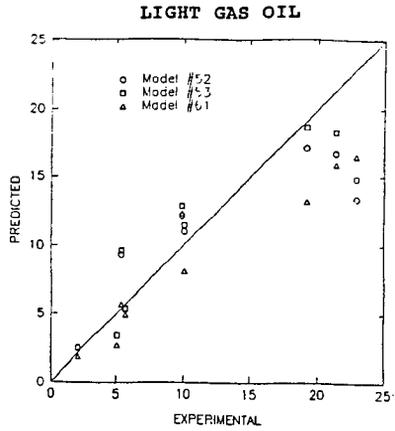
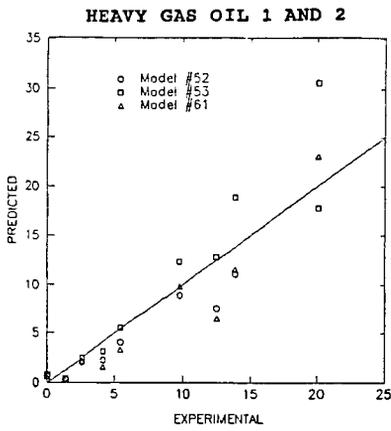


Figure 6. PREDICTED vs EXPERIMENTAL DATA

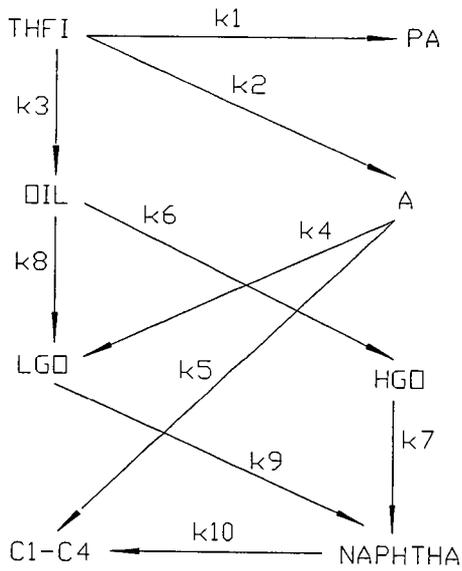


Figure 7. MODEL 53

LOW SEVERITY CO-PROCESSING USING  
HOMOGENEOUS BASIC NITROGEN PROMOTORS

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INTRODUCTION

The possibility of dissolving coal at low severity reaction conditions has intrigued researchers for many years. As early as 1921, Fischer and Schrader (1) reported production of an ether-soluble material by liquefying coal at 350°C using carbon monoxide and water as reducing agent. More recently, other groups including the Pittsburgh Energy Technology Center (2-5), the North Dakota Energy Research Center (6-10), Stanford Research Institute (11-14), Carbon Resources, Inc. (15,16), and the Colorado School of Mines (17-19) have investigated various methods of low severity dissolution. Their efforts have been prompted by the fact that many incentives exist for converting coal at milder conditions than utilized in present day technology. Several of these incentives are listed below:

- \* Reduced hydrocarbon gas make resulting in reduced feed gas consumption and enhanced hydrogen utilization efficiency
- \* Suppressed retrogression of primary coal dissolution products resulting in enhanced distillate and residuum product quality
- \* Production of high boiling residuum which is less refractory and thus amenable to upgrading in a conventional second-stage hydrocracker
- \* Substitution of less expensive off-the-shelf vessels, piping, and pumps in place of expensive, custom-designed units
- \* Less severe slurry handling and materials of construction problems as a result of lower operating temperatures and pressures.

In searching for effective coal dissolution promoters to be evaluated at low severity co-processing conditions, we concluded that, based on results from high severity studies, basic nitrogen compounds warranted extensive study. Atherton and Kulik (20,21) summarized data from several high severity liquefaction studies using 1,2,3,4-tetrahydroquinoline (THQ) in which THF coal conversions in the range of 85-100 wt% (MAF basis) were obtained with Wyodak subbituminous coal and Illinois 6 bituminous coal at reaction temperatures of 400°-450°C. However, distillate yields from these experiments were much lower than expected, and nitrogen material balance measurements indicated significant adduction of the THQ into non-distillable products.

Thus, while basic nitrogen compounds appear attractive as coal dissolution promoters, the adduction problem limits their usefulness in high severity co-processing. We hypothesized that utilizing basic nitrogen compounds at lower severity would reduce adduction sharply, but that effectiveness towards promoting coal dissolution would remain high.

Our first low severity co-processing experiments to test this hypothesis were conducted using Wyodak subbituminous coal and either unhydrotreated or mildly hydrotreated shale oil each containing approximately 1.0 wt% heterocyclic basic nitrogen (19). Mild hydrotreatment of the shale oil prior to co-processing greatly improved both liquid yield and THF soluble coal conversion. Yield and nitrogen balance results suggested that significantly less adduction of nitrogen compounds in the shale oil occurred at low severity reaction conditions compared with earlier high severity coal/shale oil co-processing experiments.

The success of these preliminary runs provided the incentive to begin a more fundamental study on the use of basic nitrogen compounds to promote coal dissolution and increase distillate yields at low severity reaction conditions. Initial results from model compound studies are reported in this paper.

#### EXPERIMENTAL PROCEDURE

Kentucky 9 bituminous coal and Wyodak subbituminous coal were used as feed coals in the low severity co-processing experiments. Ultimate analysis data for these coals is presented in Table I. Coal samples were vacuum-dried to less than 1.0 wt% moisture content before use.

Cold Lake atmospheric residuum was used as co-processing heavy oil. Available characterization data for this feedstock, designated A-8, are shown in Table II. Sample A-8 has been extensively studied as a co-processing feed and performs well at low severity reaction conditions (19). The seven model nitrogen compounds listed in Table III were evaluated as coal dissolution promoters. Each compound was ACS reagent grade and was used without further purification. These compounds were chosen to provide a wide range of base strength as measured by aqueous  $pK_b$  values. For convenience, the coding system shown in Table III will be used to reference each of the seven model nitrogen compounds.

Runs were completed using either commercial grade hydrogen or carbon monoxide. Each feed gas contained 1.0 mole% krypton used as an inert tracer. Distilled water in an amount equal to 50 wt% of the MAF feed coal was added to runs using carbon monoxide feed gas.

Table IV lists the reaction conditions used in this study. A majority of the runs were completed at the low severity conditions shown. However, for comparison purposes, several runs were also completed at conventional high severity conditions.

Co-processing experiments were performed using a 300 cm<sup>3</sup> Autoclave Magnedrive II batch reactor interfaced to an Apple IIe personal computer for temperature control. The computer was also routinely used for temperature and pressure data acquisition during a run. Reactor heatup time to 330°-350°C reaction temperature was approximately 30 minutes. At the end of a run, water was circulated through cooling coils immersed in the reactor contents, allowing cooldown to temperatures below 200°C in less than 20 minutes.

After cooling the reactor to near room temperature, gaseous products were recovered in evacuated stainless steel vessels and analyzed for light hydrocarbon gases and carbon oxide gases using a Carle Model 111H refinery gas analyzer. The krypton tracer concentration was also measured and used as a tie element for determining product gas yields.

The liquid-solid product slurry was removed from the reactor using toluene as a wash solvent and quantitatively centrifuged to separate solids from the liquid product (termed "decant oil"). The residue (termed "centrifuge residue") contained unconverted coal and mineral matter coated with liquid product. Toluene added during slurry recovery and centrifugation was quantitatively removed during distillation. Decant oil samples were distilled to a 454°C endpoint using an ASTM-type microdistillation apparatus. Portions of the centrifuge residue and decant oil 454°C+ residuum were extracted in a Soxhlet extraction apparatus using cyclohexane, toluene, and tetrahydrofuran. Standard elemental analyses for carbon, hydrogen, nitrogen, sulfur and ash content were performed on all liquid and solid product samples. Oxygen content was determined by difference.

Detailed quantitative measurements of individual model nitrogen compounds in 454°C- distillate samples were performed using an HP 5890 capillary gas chromatograph interfaced with an HP 5790B quadrupole mass spectrometer. These data helped provide a measure of nitrogen compound losses by thermal degradation or adduction.

## RESULTS AND DISCUSSION

### Effect of Model Nitrogen Compound Addition

Low severity co-processing experiments were completed to evaluate the seven model nitrogen compounds listed in Table III as coal dissolution promoters. THF soluble coal conversion results from these runs are shown in Figure 1. The greatest improvement in coal conversion was noted using 1,2,3,4-tetrahydroquinoline (THQ) (N1) and dipropylamine (N2). Addition of piperidine (N4), 4-piperidinopyridine (N5), or diphenylamine (N7) had little effect on the extent of coal dissolution. Similar results were observed using hydrogen gas at low severity reaction conditions.

As shown in Figure 2, addition of each model nitrogen compound significantly influenced the yield of C<sub>4</sub>-454°C liquids obtained at low severity liquefaction conditions. Once again, 1,2,3,4-tetrahydroquinoline (N1) and dipropylamine (N2) strongly enhanced process performance, while addition of each of the remaining five nitrogen compounds (N3-N7) reduced the liquid yield obtained. These results are entirely consistent with preliminary nitrogen adduction data showing that neither THQ nor dipropylamine adducted at low severity reaction conditions while approximately 10-15 wt% 4-piperidinopyridine was adducted into the insoluble organic matter fraction.

A comparison of the data presented in Figures 1 and 2 also shows that no direct one-to-one correlation between the levels of coal conversion and liquid yield can be developed. This result has commonly been observed when using nitrogen compounds as conversion promoters, and points out the fact that conversion data alone cannot be used to infer information about liquid yields. Rather, distillations must be performed and used in material balance calculations to provide a direct measure of recoverable liquids.

### Effect of Reaction Severity

Figure 3 summarizes coal conversion and liquid yield results from a series of THQ (N1) and dipropylamine (N2) addition experiments using Kentucky 9 coal and hydrogen gas at both low and high severity reaction conditions. Increased reaction severity resulted in a THF soluble coal conversion increase of approximately 22 wt% for the THQ runs, but only about 5 wt% increase for the dipropylamine runs. As

shown, the liquid yield was much more sensitive to an increase in reaction severity, with yield increases of about 30 wt% and 53 wt% for the THQ and dipropylamine addition runs, respectively. Much of the increase noted can be attributed to increased cracking of the A-8 heavy oil at high severity conditions.

Preliminary nitrogen balance data for the high severity runs suggested that about half the THQ was adducted into the IOM fraction, and that over 90 wt% of the dipropylamine was cracked to ammonia and propane. In the absence of these losses, liquid yield results for the high severity runs would be higher than shown in Figure 3. Nevertheless, these data substantiate our hypothesis that compounds such as THQ and dipropylamine can be identified which remain effective coal dissolution promoters at low severity co-processing conditions. Improving low severity liquid yields will apparently require a second stage catalytic hydrocracker to process the high boiling residual material produced in the low severity co-processing first stage. Based on previous studies from our laboratory, this residuum should be very reactive and easily converted to distillable liquids.

#### Effect of Coal Rank and Feed Gas Composition

Additional low severity co-processing runs were completed to study the effects of coal rank (subbituminous vs. bituminous) and feed gas ( $H_2$  vs.  $CO/H_2O$ ) on the performance of THQ (N1) and dipropylamine (N2) as coal dissolution promoters. Results from these experiments are summarized in Figures 4 and 5. For the Kentucky 9 bituminous coal runs, use of hydrogen and either THQ or dipropylamine slightly improved both coal conversion and liquid yield. Conversely, significantly better wyodak coal conversion and liquid yield were achieved using  $CO/H_2O$ , a result which would be expected based upon aqueous water-gas shift chemistry. Additional coal samples, including several Argonne premium coals will be studied to expand the coal rank relationships shown in Figures 4 and 5.

#### SUMMARY AND CONCLUSIONS

Results of low severity co-processing experiments completed to date clearly demonstrate the potential for using homogeneous basic nitrogen compounds to promote coal dissolution and increase liquid yields without significant nitrogen losses via adduction or thermal degradation. Both 1,2,3,4-tetrahydroquinoline and dipropylamine significantly improved coal conversion and distillable liquid yields, although, in general, no direct relationship between improvements in conversion and yield structure can be inferred. A comparison of liquid yields from low severity and high severity experiments suggests that a two-stage process consisting of a low severity coal dissolution first stage followed by a second stage catalytic hydrocracker would improve coal conversion and liquid yield while, at the same time, minimizing nitrogen losses via adduction or thermal degradation. Work to evaluate this co-processing concept is currently underway.

#### ACKNOWLEDGEMENT

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Table I

ULTIMATE ANALYSIS OF FEED COALS

<u>Ultimate Analysis, wt% dry basis</u>	<u>Kentucky 9</u>	<u>Wyodak</u>
Carbon	69.7	61.4
Hydrogen	4.7	4.0
Nitrogen	1.4	1.0
Sulfur	4.2	0.7
Oxygen (difference)	9.2	18.6
Ash	<u>10.8</u>	<u>14.3</u>
Total	100.0	100.0

Table II  
 PROPERTIES OF COLD LAKE ATMOSPHERIC RESIDUUM

<u>Distillate Fraction</u>	<u>Wt%</u>
Water	0.0
177°C-	0.4
177°-260°C	4.1
260°-343°C	4.1
343°-454°C	10.9
454°C+	80.5
<u>Ultimate Analysis, wt% dry basis</u>	
Carbon	84.2
Hydrogen	12.0
Nitrogen	1.0
Sulfur	1.1
Oxygen (difference)	1.7
Ash	0.0
<u>Solvent Solubility, wt%</u>	
Tetrahydrofuran	100.0
Toluene	100.0
Cyclohexane	100.0

Table III  
 MODEL NITROGEN COMPOUNDS STUDIED

<u>Compound</u>	<u>Aqueous pK<sub>b</sub></u>	<u>Code Symbol</u>
1,2,3,4-tetrahydroquinoline	8.97	N1
dipropylamine	3.00	N2
7,8-benzoquinoline	9.20	N3
piperidine	2.88	N4
4-piperidinopyridine	8.04	N5
5,6-benzoquinoline	10.05	N6
diphenylamine	13.23	N7

Table IV  
CO-PROCESSING REACTION CONDITIONS

	<u>Low Severity</u>	<u>High Severity</u>
Reaction Temp. (°C)	344	440
Feed Gas	CO/H <sub>2</sub> O, H <sub>2</sub>	H <sub>2</sub>
Initial Pressure (psig)	850	1000
Maximum Pressure (psig)	1500	2000
Time at Temp. (min)	30	30
Coal/A-8/Nitrogen Compound Feed Ratio	1/1.5/0.5	1/1.5/0.5

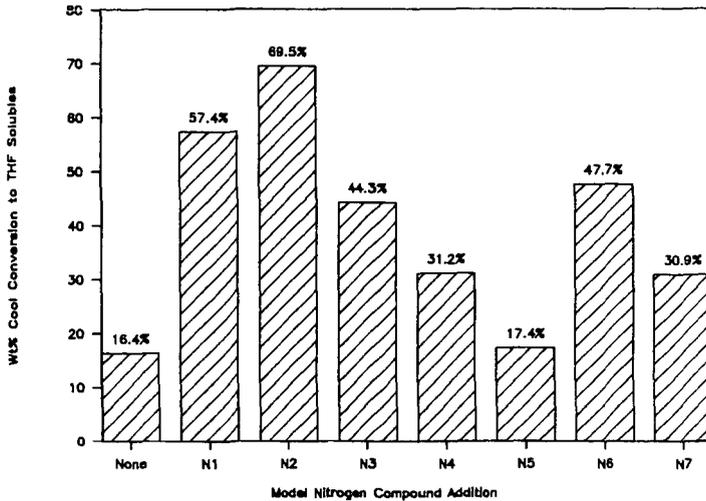


Figure 1. Effect of Model Nitrogen Compound Addition on Low Severity Conversion of Kentucky 9 Coal With Carbon Monoxide Feed Gas

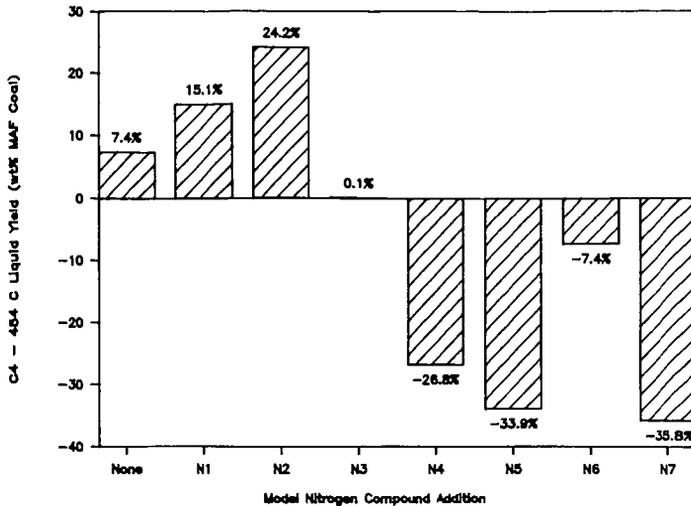


Figure 2. Effect of Model Nitrogen Compound Addition on Distillate Liquid Yield from Low Severity Co-Processing of Kentucky 9 Coal with Carbon Monoxide Feed Gas

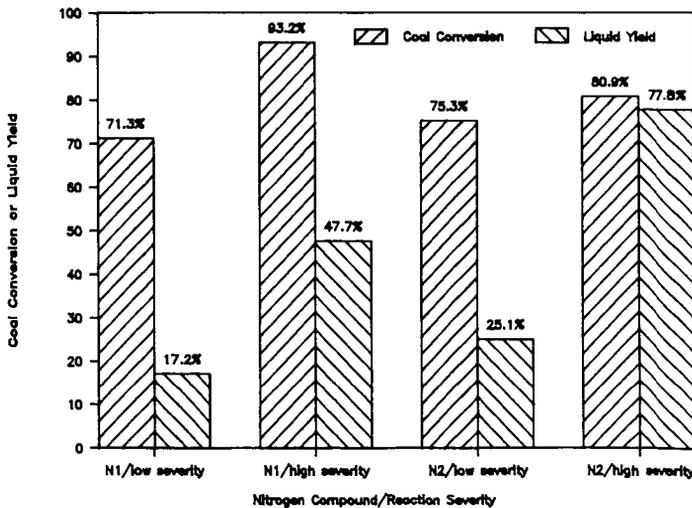


Figure 3. Effect of Model Nitrogen Compound Addition and Reaction Severity on Kentucky 9 Coal Conversion and Distillate Liquid Yield with Hydrogen Feed Gas

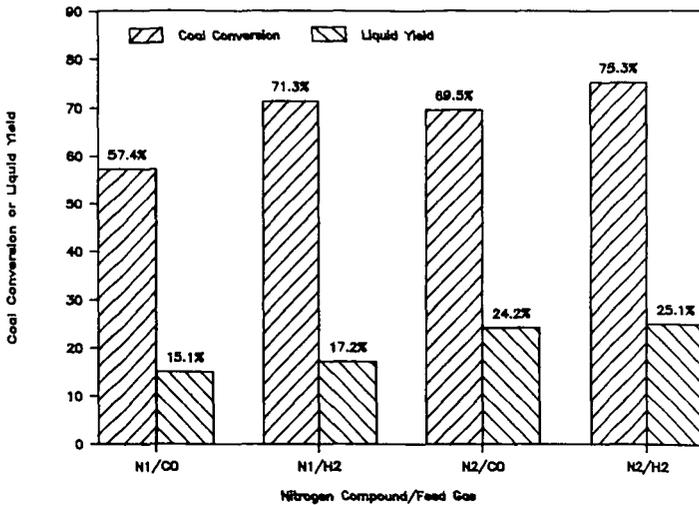


Figure 4. Effect of Model Nitrogen Compound Addition and Feed Gas on Kentucky 9 Coal Conversion and Distillate Liquid Yield at Low Severity Co-Processing Conditions

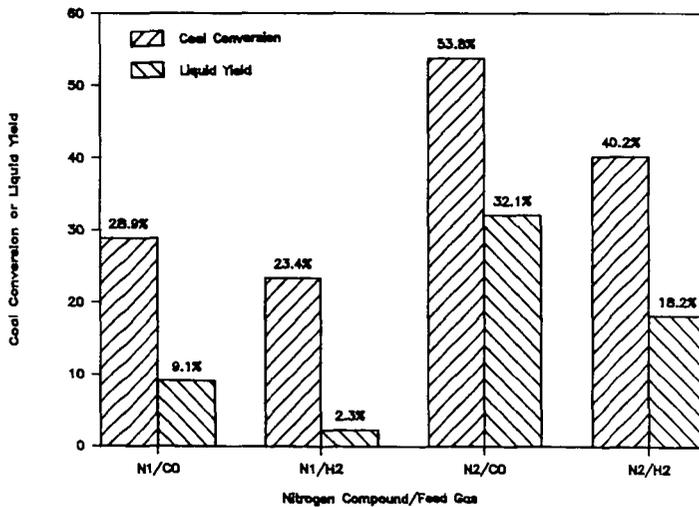


Figure 5. Effect of Model Nitrogen Compound Addition and Feed Gas on Wyodak Coal Conversion and Distillate Liquid Yield at Low Severity Co-Processing Conditions

## COPROCESSING COAL LIQUIDS WITH PETROLEUM RESID

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### ABSTRACT

A series of bench-scale experiments was run to determine the advantages and disadvantages of processing coal liquids with petroleum resid. Standard resid, blends of resid containing 15 and 40% coal-derived liquids (from Wilsonville), plus the neat coal-derived component of the blends were evaluated. The parameters evaluated were: (1) Hydrogen Consumption; (2) Conversions (1000+°F, hydrodesulfurization (HDS), hydrodenitrogenation (HDN), and Ramsarbon removal (HDR)); (3) Catalyst Activity; (4) Unit Operability; and (5) Product Quality (total liquid product plus 360-, 360-650, 650-1000, and 1000+°F fractions).

The major findings are: (1) Hydrogen consumption and HDN increased with increasing coal liquids but HDS and HDR were independent of feed; (2) Coal liquids did not accelerate catalyst deactivation; (3) Unit operability increased with increasing coal-liquids content of the feed; (4) Aromaticity of the 360-, 360-650, and 650-1000°F fractions all increased with increasing coal liquids.

### INTRODUCTION

As part of its synfuels development program, Amoco has been doing research to improve the economics of converting coal into liquid fuels using the technique known as direct coal liquefaction.<sup>(1-3)</sup> Direct liquefaction is a proven technology--used by Germany to produce liquid fuels during World War II. However, it is not economic at the current price of crude oil and there is no current commercial source of coal liquids. The economics of coal liquefaction would improve if existing petroleum refinery units could be used to upgrade coal-derived liquids rather than building a grass-roots facility. The research program described herein was conducted to determine the advantages and disadvantages of processing coal liquids with petroleum resids.

### EXPERIMENTAL

#### Feedstocks

Maya-containing 1000+°F resid blend (Feed A) was chosen as the resid benchmark. Coal-derived liquid (containing about 50% 1000+°F material and designated Feed B) obtained from the Wilsonville, Alabama pilot plant was used to make the blends. The feedstocks containing 15% and 40% coal liquids were designated Feed C and Feed D respectively. The inspections of these feeds are shown in Table I.

## Reactor

An automated continuous resid hydroprocessing pilot plant was used. High pressure hydrogen enters through a pressure stepdown and metering device and exits through an outlet pressure control loop so that hydrogen pressure and flow can be controlled within narrow limits. The existing gases pass either into a gas sampling device or through a scrubber and into a wet test meter. Feed is added by a positive displacement pump. Feed and hydrogen flow concurrently upflow through a vertical pipe reactor. The pipe reactor is heated by four independently fired and controlled heating zones. Reactor temperature is measured in a centrally located axial thermocouple well by a travelling thermocouple. Feed exits from the top of the reactor and is collected in either of the following two ways:

1. In normal operation, feed exits through a high pressure gas-liquid separator via a Research Control Valve (RCV) with a control loop that maintains a constant liquid level in the high pressure separator. In this mode, product liquid is collected continuously in a glass bottle at atmospheric pressure.
2. Under some process conditions, solids are formed which plug the RCV making the unit inoperable in that mode. The high pressure receiver is used when high solids conditions are encountered. In this mode, product liquid is held in a heated (about 300°F) Hoke vessel at the system pressure until the vessel is drained and the product is collected (typically every 24 hours).

## Reaction Conditions and Sequence of Feedstock Testing

Only feedstock and reactor temperature were varied. Kept constant were liquid feedrate, pressure, and hydrogen flow rate. The feedstock comparison started with a reactor temperature of "base". Sequentially, data were obtained with Feedstocks A (0% coal-liquids), C (15% coal liquids), D (40% coal-liquids), and then with A (0% coal-liquids) again to determine catalyst deactivation. The temperature was then raised to "base + 20°F" continuing with Feedstock A (0% coal-liquids) and then sequentially testing as was done at "base". At the end of the "base + 20°F" test sequence, the program was expanded to also test the 100% coal-liquids feed, Feed B. This experimental program was designated Run 17-258.

## RESULTS

Table II shows the average total liquid product inspections for each feedstock in the sequential order the feeds were run; the standard deviation for each inspection is given in parenthesis. The inspections listed in Table II are: °API, percent Shell hot filtration (SHFT), percent hexane insoluble; also percents sulfur, nitrogen, and Ramscarbon.

Table III shows the mass balance data: percent C<sub>1</sub>-C<sub>4</sub> gas-make, total hydrogen consumption (SCF/B) and weight percent product recovered.<sup>4</sup> Table IV shows the conversions obtained with each feed, again in the sequential reaction order. Sulfur, nitrogen, and Ramscarbon conversions are the averages for the run period.

Inspections on the 360-, 360-650, 650-1000, and 1000+°F fractions (collected by atmospheric distillation of the 650-°F fractions and vacuum distillation of the 650+°F material) have been obtained for each of the feedstocks after reaction at each

temperature. The data from reaction at "base" and "base + 20°F" are shown in Tables V and VI respectively.

#### Unit Operability

Figure 1 shows the effect of coal-liquids and reaction temperature on SHFT during normal operation through the RCV. Our data clearly show that operability increases with increasing coal-liquids content and the improved operability with added coal liquids is much more pronounced at the higher temperature.

In normal operation, the reaction product continually exits the unit through a separator, the level of which is controlled by a research control valve (RCV). During periods of good operability, flow through the RCV is smooth and the liquid product has a low value for an inspection called the Shell Hot Filtration Test (SHFT). SHFT is a measure of the amount of solids formed. At "base temperature" operation through the RCV was possible with either 0, 15, or 40% coal-liquids giving average SHFT inspections of about 1.2, 0.8, and 0.6, respectively. At "base + 20°F" operability was fine with 15, 40 and 100% coal-liquids resulting in SHFT inspections of 0.8, 0.5, and 0.2, respectively.

In contrast, operation at "base + 20°F" with Feed A was impossible; the RCV plugged and had to be by-passed by using the high pressure receiver. The SHFT inspections of these high pressure receiver products, about 0.88, are lower than the SHFT of 1.2 obtained at "base". Since operability should improve with lower SHFT inspections, the SHFT data obtained from operation with the high pressure separator do not accurately reflect unit operability and cannot be compared with data obtained during operation through the RCV. We do not know why the SHFT inspections are not comparable.

#### Catalyst Activity

The use of coal liquid-containing feeds had no unusual effect on catalyst activities. Catalyst activity only declined with time on stream at a given temperature, with deactivation increasing with increasing temperature, as would be expected for any feed.

The data for denitrogenation have the lowest experimental error and are used to show our results, but similar trends were followed for sulfur and Ramscarbon reduction.

Figure 2 shows the relative denitrogenation reactivity for each of the feeds in the sequential order which they were run. Relative reactivity is defined as the ratio of 1st-order rate constants to Day 69 for reaction at base and the ratio to day 105 for reaction at "base + 20°F". As is seen, the reactivity of benchmark Feedstock A at "base" was identical before and after running the coal-liquid blends. The reactivity at "base + 20°F" was slightly lower after running the blends, but the decline was very small and is attributed to the expected catalyst deactivation at this temperature and not to the use of coal liquid-containing feeds.

The explanation for the greater denitrogenation of the coal liquids-containing feeds is unknown. One possibility is that the nitrogen-containing compounds in the coal liquids are inherently easier to denitrogenate than those in the petroleum resid. Alternatively, the greater denitrogenation of the coal liquids-containing feeds might simply be a result of their greater amounts of 1000-°F material present (14, 25, and

50% in Feeds C, D, and B, respectively, versus 8% in A); previous studies have shown that ease of upgrading increases as boiling point of the feed decreases.

#### Conversions and Hydrogen Uptake

The percent conversions of 1000+°F material to 1000-°F material, nitrogen removal, Ramscarbon removal, and sulfur removal for each coal liquid-containing feed plus Feed A at "base" and "base + 20°F" are shown in Figures 3-6 respectively. Conversion of 1000+°F material is calculated (correcting for 1000-°F material in the feed) from one actual distillation of combined product collected over each run period. Nitrogen, Ramscarbon, and sulfur conversions are calculated from inspections of daily products and then averaging the results. Hydrogen uptake is shown in Figure 7. Hydrogen uptake is the average of mass balance calculations taken during each run period.

All conversions with the 15 and 40% blends of coal liquids were always equal to or greater than the conversion with Feed A alone, indicating that no penalty in conversion would result from the addition of coal liquids. Also, the 1000+°F conversions of the blends were higher than those of the straight A and B feeds. This suggests the possibility of a synergistic interaction, but the data do not warrant a definitive statement to that effect. C<sub>1</sub>-C<sub>4</sub> gas make appeared independent of feed at each temperature.

Denitrogenation increased with increasing coal-liquids. However, as discussed above, this could have simply been caused by the lower boiling points of these feeds.

Ramscarbon and sulfur conversions were slightly higher at each temperature with the blends than with Feed A, but the differences probably are not statistically significant.

Hydrogen uptake increased with increasing coal liquids at each temperature and hydrogen uptake increased with increasing temperature. This result is expected because the coal liquids are more aromatic than petroleum resid (Feed A) and more hydrogen would go into ring saturation.

#### Product Quality

Each boiling range fraction got more aromatic and had a lower sulfur content with increasing coal-liquids content at each temperature. These results are illustrated in Figures 8 and 9 which show percent aromatics and percent sulfur in the 650-1000°F cuts, respectively.

The nitrogen contents of the cuts did not show a consistent pattern. The 360-°F cut showed increasing nitrogen with increasing coal-liquids. The 360-650°F fraction showed increasing nitrogen with increasing coal-liquids only at "base". The nitrogen content within the 650-1000°F fraction was the same with each feed at each reaction temperature.

#### SUMMARY

The purpose of these experiments was to answer the question: "How would the addition of coal-liquids affect resid hydroprocessing?", specifically addressing the

topics of unit operability, conversion and hydrogen consumption, catalyst activity maintenance, and product quality.

Our conclusions are:

1. Unit Operability: BETTER
2. Conversions: EQUAL OR HIGHER
3. Hydrogen Consumption: HIGHER
4. Unexpected Effect on Catalyst Activity: NONE
5. Product Quality: MORE AROMATIC, LOWER SULFUR.

#### REFERENCES

1. Brooks, J. A., R. J. Bertolacini, L. C. Gutberlet, and D. K. Kim, "Catalyst Development for Coal Liquefaction," EPRI Final Report for RP #408-1, -2, November 1979.
2. Mahoney, J. A., J. J. Helstrom, and R. J. Pellet, "Coal Liquefaction Catalyst Development," DOE Final Report for Contract #DE AC 22-79ET-14803, August 1982.
3. Tait, A. M., M. M. Schwartz, and M. A. Pacheco, "Advanced Coal Liquefaction Catalyst Development, DOE Contract Number DE-AC22-81PC40009: Final Report," April 29, 1986.

TABLE I  
FEEDSTOCK INSPECTIONS

Percent Coal Liquids:	0	15	40	100
Feedstock Identification:	<u>A</u>	<u>C (a)</u>	<u>D (b)</u>	<u>B (c)</u>
Elemental Analyses				
C, %	84.85	85.38	86.22	88.40
H, %	10.39	10.06	9.55	8.48
S, %	4.04	3.38	2.56	0.26
O, %	1.48	0.83	2.01	1.57
N, %	0.49	0.54	0.59	0.78
Ni, ppm	56	46	34	<2
V, ppm	246	201	152	<2
Ramscarbon, %	18.5	20.1	20.6	22.4
Oil, %	29.3	29.2	29.2	24.8
Resin, %	58.5	56.9	56.5	56.1
Asphaltene, %	12.0	11.5	9.4	4.3
°API	6.8	6.0	4.0	-1.5
% 1000+°P (d)	92	85.6	75	49.5

(a) C = 85% A + 15% B.

(b) D = 60% A + 40% B.

(c) Blend of Wilsonville liquids derived from Illinois No. 6 coal.

(d) By distillation.

TABLE II  
 RUN 17-258  
AVERAGE TOTAL LIQUID PRODUCT INSPECTIONS\*

Reaction Temperature	Base			Base + 20°F					
	A	C	D	A	A	C	D	A	B
Feedstock Identification	A	C	D	A	A	C	D	A	B
% Coal Liquids in Feed	0	15	40	0	0	15	40	0	100
Sample Days	62-69	72-77	80-84	87-96	99-105	110-119	123-132	136-142	146-152
°API	21.9 (.43)	19.0 (.1)	16.6 (.2)	21.2 (.5)	25.5 (.6)	23.2 (.5)	20.2 (1.0)	25.6 (.5)	10.3 (.4)
S, wt%	0.62 (.03)	0.47 (.05)	0.27 (.01)	0.60 (.03)	0.40 (.04)	0.34 (.02)	0.25 (.04)	0.52 (.04)	0.080 (.027)
N, wt%	0.323 (.025)	0.348 (.031)	0.331 (.015)	0.321 (.016)	0.266 (.023)	0.294 (.013)	0.288 (.025)	0.285 (.010)	0.304 (.014)
Ramscarbon, wt%	7.05 (.04)	7.26 (.30)	6.78 (.18)	7.15 (.15)	3.20 (1.37)	3.02 (1.26)	3.56 (1.11)	4.34 (1.04)	4.66 (.13)
SHFT	1.07 (.52)	0.80 (.35)	0.61 (.30)	1.30 (.31)	0.97 <sup>(a)</sup> (.46)	0.83 (.23)	0.48 (.13)	0.78 <sup>(a)</sup> (.22)	0.15 (.05)
Hexane Insoluble, wt%	3.94 (.35)	4.18 (.55)	3.26 (.14)	4.18 (.27)	2.60 (.61)	2.61 (.24)	2.16 (.21)	2.63 (.12)	1.67 (.2)

\*Mean (Standard Deviation)

(a) Sample from high-pressure receiver.

TABLE III  
 RUN 17-258  
MASS BALANCE DATA

Reaction Temperature	Base			Base + 20°F						
	A	C	D	A	A	C	D	A	B	
Feedstock Identification	A	C	D	A	A	C	D	A	B	
% Coal Liquids in Feed	0	15	40	0	0	15	40	0	100	
Sample Days	68	72 77	83	92	104	117	131 139	142	147 152	
C <sub>1</sub> -C <sub>4</sub> , %	3.1	3.7 3.8	3.8	4.0	10.0	6.2	5.0 6.0	6.0	7.5 7.5	
Hydrogen Consumption, SCF/B	1078	1139 1226	1456	1105	1858	1620	1660 1338	1468	1837 1754	
Wt% Product Recovered	100	90 100	97	86	114	101	96 96	100	99 99	

TABLE IV  
 RUN 17-258  
CONVERSIONS

Reaction Temperature	Base			Base + 20°F					
	A	C	D	A	A	C	D	A	B
Feedstock Identification	A	C	D	A	A	C	D	A	B
% Coal Liquids in Feed	0	15	40	0	0	15	40	0	100
Sample Days	62-69	72-77	80-84	87-96	99-105	110-119	123-132	136-142	146-152
% Desulfurization	85	86	89	85	90	90	90	88	69
% Denitrogenation	32	35	44	32	44	46	51	42	62
% Ramsarbon Conv.	62	64	67	62	83	85	82	77	79
% 1000°+ Conv. by Distillation	—	70.0	71.1	67.5	82.7	88.8	88.9	82.4	77.4

TABLE V  
INSPECTIONS OF PRODUCTS AFTER "BASE" HYDROTREATING

Coal Liquids in Feed, %	0	15	40
Feedstock Identification	A	C	D
Run Identification, 17-258-	94	77	84
<u>360°F-, wt%</u>	4.8	4.1	3.9
C, %	82.61	86.04	86.26
H, %	13.95	14.17	14.01
N, ppm	20	212	241
S, %	0.079	0.049	0.022
Paraffins, wt%	54.8	48.0	44.2
Cycloparaffins, wt%	29.0	31.6	34.4
Aromatics, wt%	16.3	20.4	21.4
<u>360-650°F, wt%</u>	24.9	27.7	30.7
C, %	87.25	87.65	87.84
H, %	12.97	12.56	12.07
N, ppm	832	1220	1310
S, %	0.74	0.056	0.034
°API	31.0	30.3	26.6
Paraffins, wt% (a)	30.6	25.3	18.1
Cycloparaffins, wt% (a)	30.5	31.0	31.1
Aromatics, wt% (a)	38.9	43.7	50.8
C-sub-A, wt% (a)	17.2	17.5	23.1
<u>650-1000°F, wt%</u>	37.9	41.5	43.1
C, %	87.48	87.74	88.85
H, %	11.81	11.23	10.87
N, ppm	0.30	0.28	0.32
S, %	0.51	0.41	0.22
°API	19.68	16.53	13.30
Ramscarbon, %	7.30	7.61	5.75
Paraffins, wt% (a)	14.5	12.5	7.8
Cycloparaffins, wt% (a)	31.2	29.5	22.0
Aromatics, wt% (a)	54.3	58.0	70.2
C-sub-A, wt% (a)	25.8	30.6	35.8
Oils, %	70.3	65.1	58.3
Resins, %	28.7	33.0	39.8
Asphaltenes, %	0	0	0
<u>1000°F+, wt%</u>	29.9	25.7	21.7
C, %	87.89	88.38	89.13
H, %	9.96	9.61	9.08
N, ppm	0.61	0.65	0.64
Ni, ppm	22	25	20
V, ppm	6	5	2
S, %	1.18	1.00	0.66
°API	5.24	2.79	0.12
Ramscarbon, %	23.7	29.1	31.6

(a) By Robinson-type mass spectral analysis.

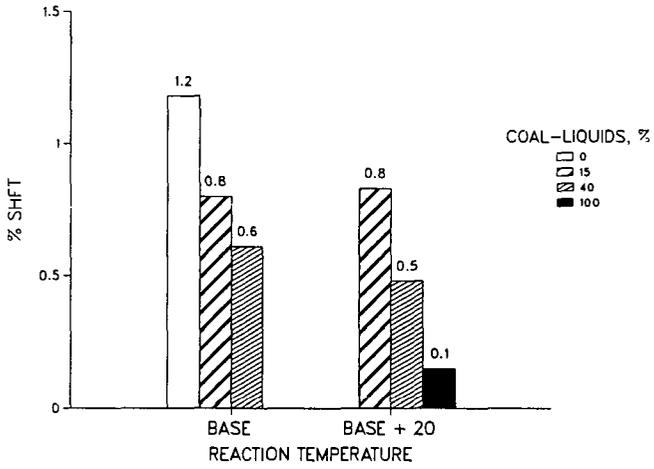
TABLE VI  
DISTILLED PRODUCT INSPECTIONS FROM  
HYDROTREATING AT "BASE + 20°F"

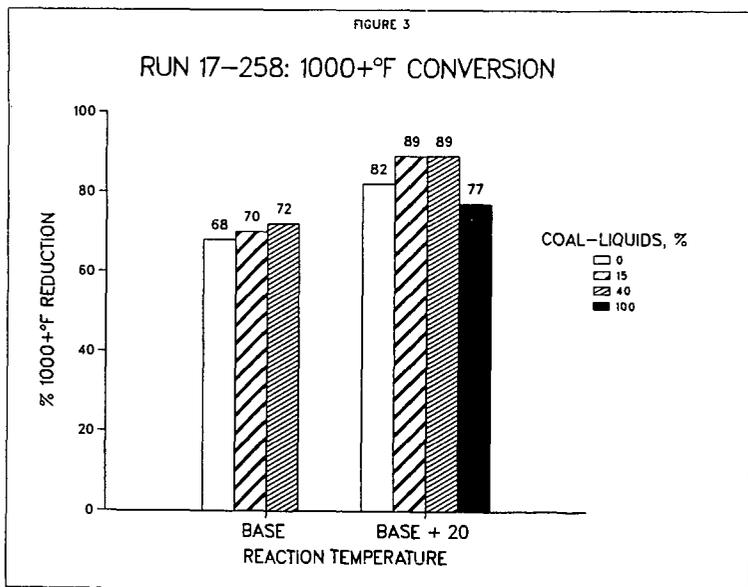
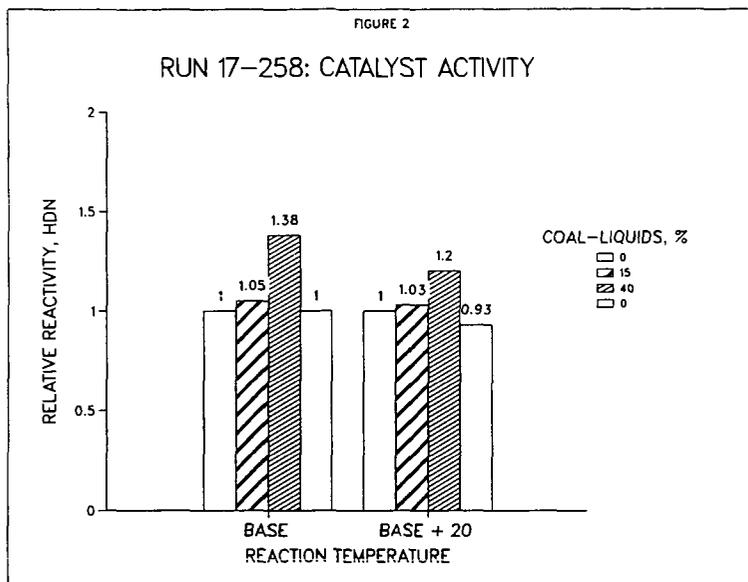
Feed Identification: Run 17-258-	A 135-139	C 111-116	D 122-126	B 148-151
Coal Liquids in Feed %:	0	15	40	100
<u>360°F-Wt%</u>	9.08	9.0	8.5	5.1
C, %	85.07	81.73	85.32	86.87
H, %	14.41	13.35	14.09	13.17
N, ppm	136	158	222	348
S, ppm	480	238	300	279
<u>360-650°F Wt%</u>	39.51	37.7	38.2	46.0
C, %	86.94	87.19	87.89	88.89
H, %	12.64	12.47	12.11	10.86
N, %	0.132	0.124	0.115	0.137
S, ppm	1250	440	240	50
°API	32.7	32.6	28.4	19.0
Paraffins, wt% <sup>(a)</sup>	30.2	27.7	21.7	4.8
Cycloparaffins, wt% <sup>(a)</sup>	30.7	30.4	30.9	28.8
Aromatics, wt% <sup>(a)</sup>	39.1	41.9	47.4	66.4
C-sub-A, wt% <sup>(a)</sup>	18.0	17.2	20.1	32.4
<u>650-1000°F, Wt%</u>	33.77	43.4	43.9	36.2
C, %	87.33	88.26	88.90	91.14
H, %	11.28	10.65	10.35	8.00
N, %	0.349	0.394	.337	.440
S, %	0.56	0.44	0.276	0.011
API	19.1	13.2	10.7	-1.2
Ramscarbon, %	1.2	2.5	1.8	1.1
Paraffins, wt% <sup>(a)</sup>	15.5	10.8	7.0	--
Cycloparaffins, wt% <sup>(a)</sup>	27.5	22.6	16.7	--
Aromatics, wt% <sup>(a)</sup>	57.0	66.6	76.3	100
C-sub-A, wt% <sup>(a)</sup>	28.8	33.8	41.7	63.1
Oils, %	68.0	61.3	55.9	35.1
Resins, %	31.1	35.7	41.1	62.6
Asphaltenes, %	0.4	0.8	0.4	0.8
<u>1000°F+, Wt%</u>	16.24	9.6	8.3	11.21
C, %	88.23	90.32	89.11	92.25
H, %	8.63	7.91	7.81	6.36
N, %	0.793	0.814	0.592	.206 <sup>(?)</sup>
S, %	1.39	.98	.63	.044
Ni, ppm	31	29	26	16
V, ppm	16	7	4	5
°API	-1.5	-5.6	-9.4	-11.4
Ramscarbon, %	34.7	42.5	52.5	49.9

(a) By Robinson-type mass spectral analysis

FIGURE 1

RUN 17-258: SHELL SOLIDS





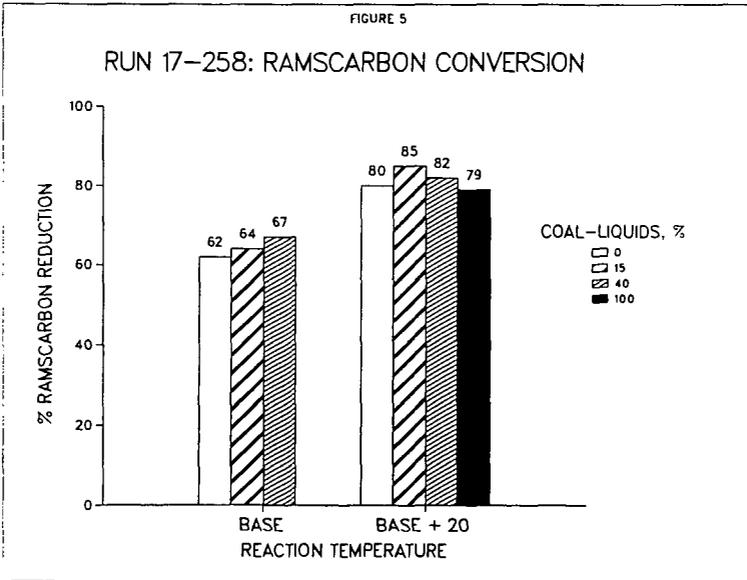
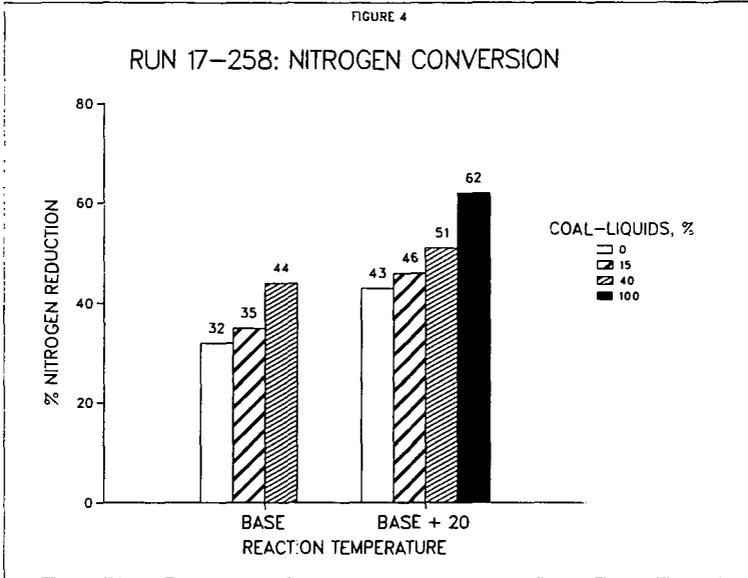


FIGURE 6

RUN 17-258: SULFUR CONVERSION

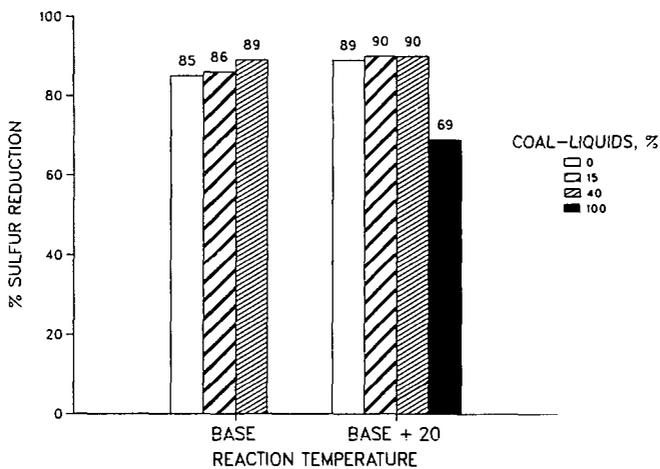
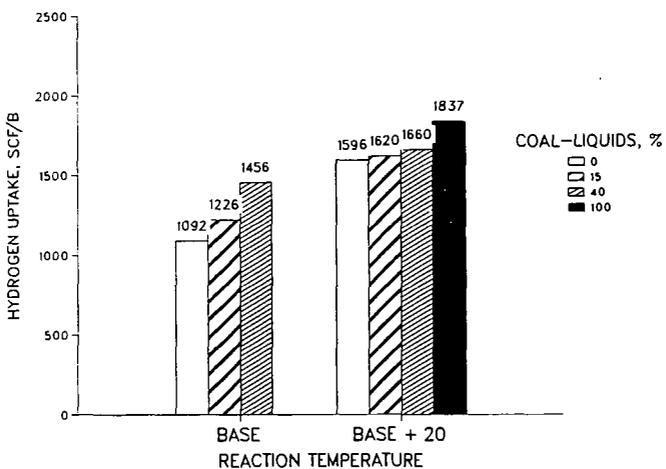
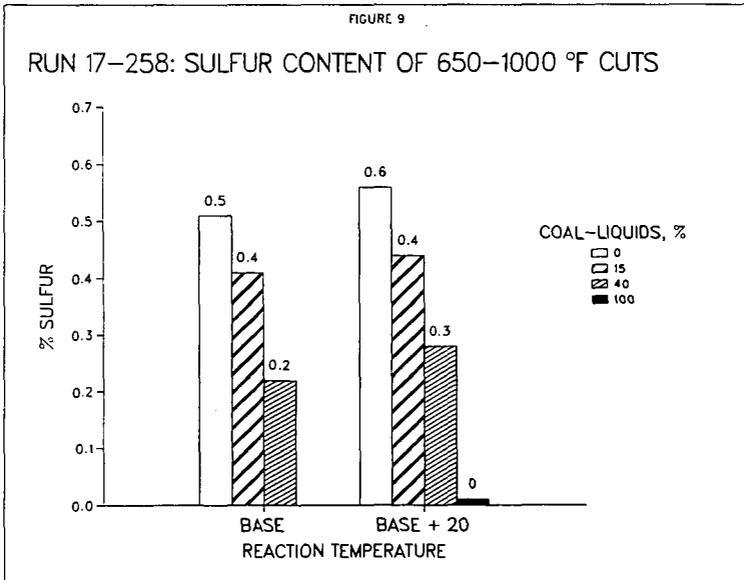
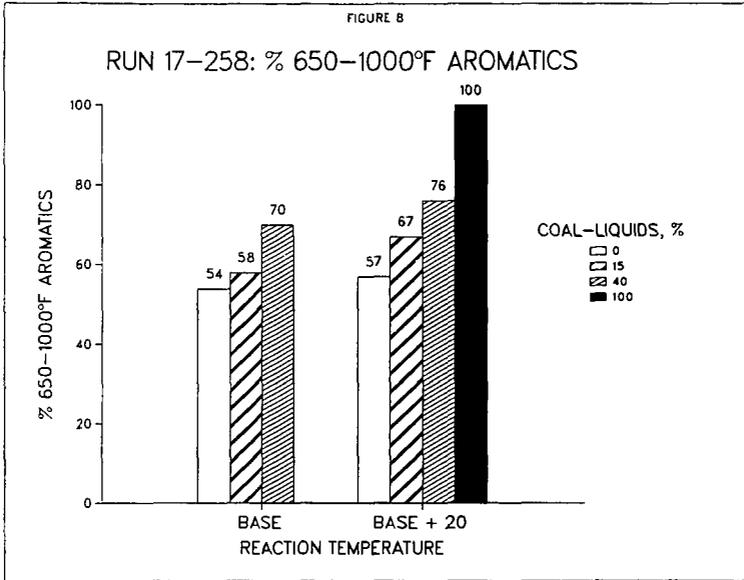


FIGURE 7

RUN 17-258: HYDROGEN UPTAKE





## Effect of Coal Concentration on Coprocessing Performance

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### Introduction

Coprocessing represents an attractive combination of heavy oil upgrading and coal liquefaction technology. Compared with coal liquefaction, coprocessing eliminates or reduces the use of a recycle oil solvent. This results in a greater proportion of the reactor volume being occupied by upgradable feedstock rather than recycle solvent. The net result is higher effective reactor throughput and lower capital and operating costs. Compared with heavy oil upgrading, coprocessing offers the ability to increase operating margins by replacing expensive oil with lower cost coal. There are also other benefits related to the ability of the added coal to act as an adsorbent for coke formed during the reaction and for heavy metals present in most feedstocks. For some processes and under certain operating conditions there is also the possibility of synergistic effects which results in better process yields (1-2).

In the final analysis the real challenge is to make coprocessing more economically attractive than heavy oil upgrading and this requires a better understanding of the effects that adding more coal to the feed can have on fundamental process behaviour. This paper describes the effects of increasing coal concentration on the coprocessing performance of the CANMET process operating with an Alberta subbituminous coal and Cold Lake vacuum bottoms (CLVB).

### Experimental

All experiments were performed with Forestburg subbituminous C coal (from Luscar Ltd.) in minus 200 mesh size (75  $\mu$ m). The same coal was used to prepare an iron based disposable additive for the process by impregnation with iron sulphate using a water slurry. Coal characteristics are given in Table 1 and those of the oil feed (CLVB, from Imperial Oil Ltd.) in Table 2. Slurry feeds with coal concentrations up to 39.5 wt. % maf coal were prepared by mixing the coal, the additive and the oil to keep the total iron concentration constant at approximately 0.50 wt. % on a maf slurry feed basis.

Coprocessing experiments were carried out in a single stage bench-scale unit which is described elsewhere (3). For comparison purposes, all experiments were performed at 450°C, 13.9 MPa total pressure, 1.0 kg/h·L nominal space velocity and 71.4 g H<sub>2</sub>/kg slurry feed (4500 SCF/B). Details of the product workup procedures are also described elsewhere (3).

## Results and Discussion

There was a marked difference in process operability in the absence of coal versus its presence in small concentrations even though the same amount of iron based catalyst was used in both cases. Without coal, reactor outlet plugging was experienced and long term operation was not possible. When coal was used, no operational problems were encountered at up to about 40 wt.% maf coal in the slurry feed. This indicates a potential benefit of coprocessing where the coal is used as a carrier or support for a disposable catalyst.

### Process Yields

Gross process yields are shown as a function of coal concentration in Figure 1. The addition of about 2-4 wt.% maf coal results in a significant increase in distillate yield. Similar results have also been reported based on isotopic mass balance measurements for an Athabasca atmospheric resid and Vesta subbituminous coal without the use of a catalyst (4). At coal concentrations over the range of most operational interest for coprocessing, the distillate yield is constant and equal to that for the no coal case until a slight drop is observed starting at about 30 wt.% maf coal. These results indicate a potential synergism at lower coal concentrations for a disposable iron based catalyst process of this type. More experimental work needs to be done to determine how this effect is influenced by different catalyst concentrations and other operating parameters such as temperature and space velocity.

Residue yield is almost a mirror image of the distillate yield as would be expected if gas yield is relatively constant as shown in Figure 1. About 30 to 50% of this residue is pentane soluble oil which with a proper solid separation scheme might be extracted for further upgrading to distillate. With more severe operation, residue yields can be lowered to the 20 wt.% range including pentane soluble oils.

### Coal and Pitch Conversion

The effect of coal concentration on coal and pitch conversion is shown in Figure 2. The coal conversion data suggests that two different mechanisms are prevalent; one for low coal concentrations and one for higher concentrations starting at about 10 wt.% maf coal. Similar results have been reported when coal-derived liquids replaced a portion of a heavy oil feed (5). This would explain the higher coal conversion values at higher coal concentrations where more coal derived liquids would be available to enhance hydrogen transfer reactions compared with lower coal concentrations where the predominant effect is due to the oil solvent only. For this reacting system, a coal concentration of about 10 wt.% on a maf slurry feed basis is required to observe an enhancement in coal conversion.

Pitch conversion values are directly proportional to residue yields and this accounts for the similar shapes of these curves which are shown in Figures 1 and 2.

### Distillate Characteristics

Gross distillate characteristics as a function of coal concentration are shown in Figure 3. It is apparent that increasing coal concentration in the slurry feed does not decrease the specific gravity or H/C atomic ratio of the overall distillate product. Although the H/C ratio of the product is essentially constant with increasing coal concentration the difference in H/C ratio between slurry feed and distillate product results in a monotonic increase with increasing coal concentration indicating that hydrogen addition reactions are enhanced. This advantage is offset somewhat since with increasing coal concentration the aromaticity of the distillate as determined from  $^1\text{H}$  NMR and the Brown-Ladner equation is also increasing as shown in Figure 3. However, an increase in aromaticity of the naphtha fraction, would be an advantage for high octane gasoline production obtained by reforming the naphtha.

### Metals Removal

The effect of coal concentration on vanadium and nickel removal is shown in Figure 4. Based on these results, which show a considerable amount of scatter, nickel seems to be preferentially removed at lower coal concentrations even though its concentration in the slurry feed is less than half that of vanadium. As the coal concentration increased, the vanadium and nickel concentration in the slurry feed decreased but as shown in Figure 4 removal of both nickel and vanadium increased. Similar results have been reported for other coals and oil feedstocks (2,6) and this highlights an advantage of coprocessing over other upgrading technologies.

### Conclusions

Process operability is improved by the addition of coal. At low coal concentrations in the CANMET process a synergism exists in terms of distillate yields. However, more research needs to be undertaken to determine how other operating parameters affect the degree of potential improvement and if it can be maintained for higher coal concentrations of more interest for commercial operations. The present results indicate that replacing oil with increasing amounts of coal in the feed does not lower the amount of distillate produced up to a coal concentration of about 30 wt.% maf on a slurry feed basis.

Two different mechanisms seem to be operating in terms of coal conversion. For low coal concentrations where the effect of coal derived liquids is negligible, coal conversion decreases with increasing coal concentration. At higher coal concentrations, the presence of coal derived liquids is suggested to result in an increase in coal conversion. Hydrogen addition and metals removal are enhanced with increasing coal concentration but the resulting distillate product becomes more aromatic. This could have significant influence on the type and nature of downstream upgrading to produce marketable products.

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Table 1 - Characteristics of Forestburg Subbituminous C Coal

<u>Proximate Analysis</u> (wt.% as received)		<u>Ultimate Analysis</u> (wt.% dry basis)	
Moisture	19.17	Carbon	64.04
Ash	7.68	Hydrogen	3.87
Volatile matter	34.00	Sulphur	0.53
Fixed carbon	39.15	Nitrogen	1.65
		Ash	9.50
		Oxygen (by diff.)	20.41
<u>Metal Content, ppm</u>		<u>Calorific Value</u>	
Fe	2379	cal/g	4933
Ni	18	btu/lb	8879
V	trace		
<u>Petrographic analysis, vol.% as received on -200 mesh size</u>			
Vitrinite	92.2		
Liptinite	2.6		
Inertinite	3.1		
Mean reflectance	0.42		

Table 2 - Characteristics of Cold Lake Vacuum Bottoms

<u>General</u>	
Specific Gravity, 15/15°C	1.038
Conradson Carbon Residue, wt.%	17.1
Pentane Insolubles, wt.%	23.48
Benzene Insolubles, wt.%	0.20
Aromaticity ( <sup>1</sup> H NMR)	34.5
Viscosity, at 80°C, poise	249.12
at 110°C, poise	21.59
<u>Distillation (Spinning Band)</u>	
IBP, °C	420
Distillate (-525°C), wt.%	16.8
Residue (+525°C), wt.%	83.25
<u>Elemental Analysis, wt.%</u>	
Carbon	78.6
Hydrogen	9.3
Sulphur	5.5
Nitrogen	0.6
Ash	0.0
Oxygen (by difference)	5.9
<u>Metal content, ppm</u>	
Fe	18
Ni	93
V	235

Figure 1  
Effect of Coal Concentration on Yields

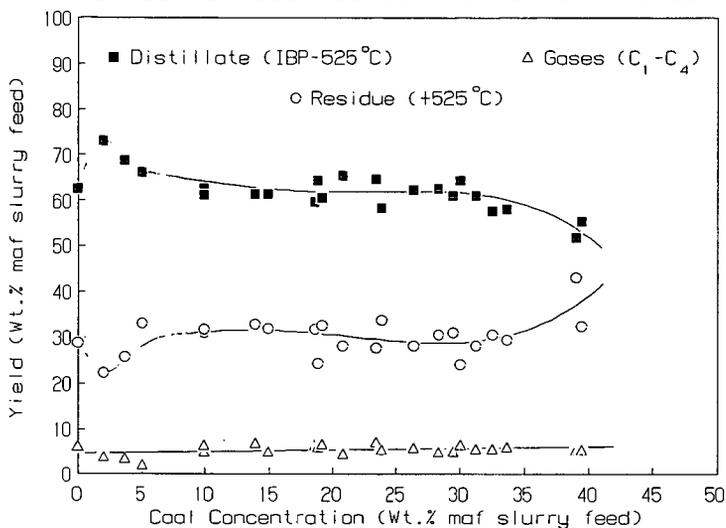


Figure 2  
Effect of Coal Concentration on Conversion

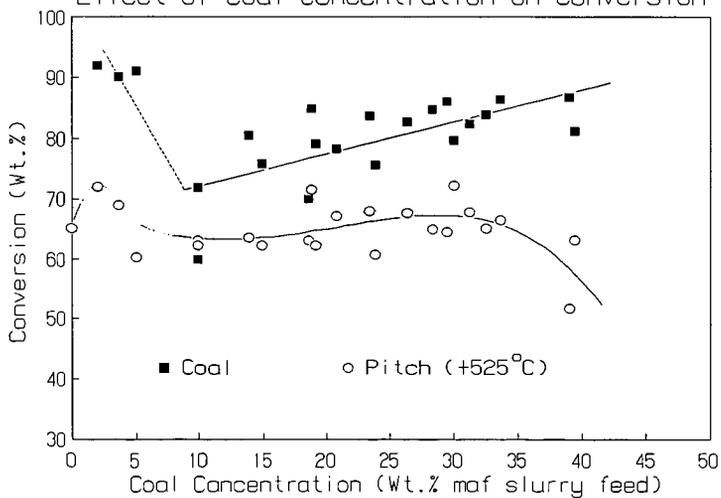


Figure 3  
Effect of Coal Concentration on  
Distillate Characteristics

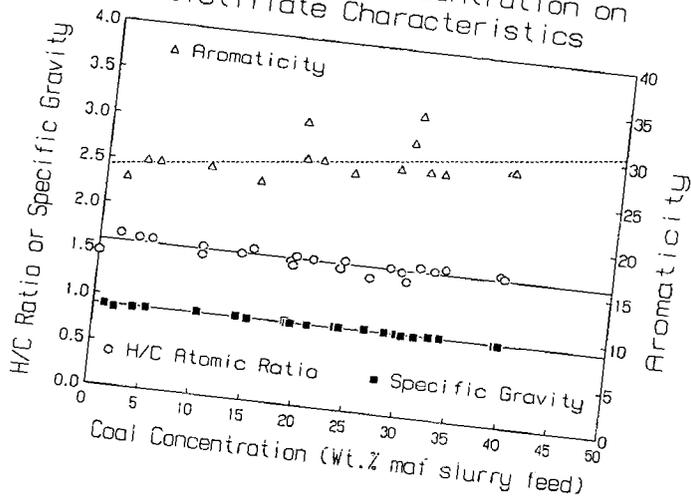
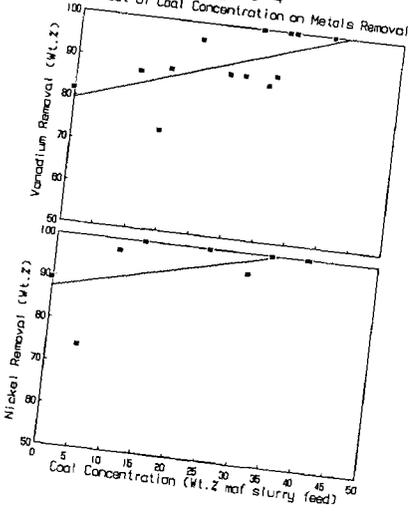


Figure 4  
Effect of Coal Concentration on Metals Removal



PARAMETER EVALUATION FOR COPROCESSING OF BROWN COAL AND VACUUM RESIDUE FROM  
PETROLEUM

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INTRODUCTION

An increasing share of petroleum short - or vacuum residue (VR) from refining confronted with more heavy crudes is hard to be marketed or upgraded. Coprocessing is the attempt to coreact VR in a hydrogenative and preferable once-through operation together with an appropriate share of a suitable coal especially lignite. A report on this covering the literature till end of 1986 will be published by the European Commission (EC) in 1988 titled "coprocessing".

If the aimed for technology is once-through a limited preevaluation is possible by batch type autoclave experiments especially with respect to parameter influences. This report covers autoclave experiments for one "Rheinische" brown coal and different petroleum refining products including a light vacuum distillate (LSP); a very heavy vacuum distillate (ZYL); the vacuum residue (VR) from one single crude oil and another vacuum residue (VRW) very high in molecular weight.

EXPERIMENTAL

The coal (as reacted) is characterized by analytical data:

moisture 5.9%; ash (wf) 3.6%; volatile matter (dmf) 48.8%; xylene extract 5.8%  
And the ultimate analysis (dmf): 68.3% C; 5.6% H; 1.3% S (total); 0.7% N; 24.1% O  
(diff)

The petroleum derived reactands (solvents) are characterized by basic analytical data:

	LSP	ZYL	VR	VRW
Conradson carbon (%)	0.04	0.27	21.7	
Asphaltenes (%)	-	-	1.6	2.1
Aromaticity (%)	16	18	50	23
Average molecular weight (VPO)	249	433	897	1410
Ultimate analysis % C	86.0	86.2	85.4	86.5
% H	11.6	11.2	9.7	11.4
% S	1.6	2.4	3.3	1.5
% N	0.1	0.1	0.4	0.4
% O (diff)	0.7	0.1	1.2	0.3

For an experiment a coal was slurried in a solvent at a ratio of 1:1.7 and 3.8% red mud and 0.6% Na<sub>2</sub>S (referring to coal dmf) were added as catalyst. All experiments were conducted batchwise in a rocking autoclave prepressurized with hydrogen at a set initial pressure. The reactions were controlled for temperature and pressure recorded versus time. Heating and cooling rates were 0.3 K/s. After cooling back to normal temperature products gases (G) were released and analysed by TC-gaschromatography and the hydrogen uptake of the experiment was calculated from gas analysis, water produced (W) and pressure difference before and after the experiment. Non gaseous products were separated and evaluated as raw naphtha (N), medium and heavy oils (O), asphaltenes (A) (precipitated in hexane), and residue (R) (benzene insoluble) all based on feed coal (dmf). For some experiments water was not determined separately and then is contained in the figure for gases. For all solvents forgoing experiments under the same conditions provided the base of correlations for yields of products from only coal.

TEMPERATURE DEPENDENCE

For each feed combination the temperature was screened from 380 to 460°C at set conditions of 9 MPa initial hydrogen pressure and 60 min. residence time. The results are given in Table 1.

The hot system pressure decreases over the residence time for all petroleum derived solvents up to 435°C but already increases at 455°C from stronger cracking reactions in the solvent. Accordingly the hydrogen uptake does not differ or decreases from 435 to 460°C. In total the system pressure is not very much dependent

on the nature of the solvent. The hydrogen uptake in general increases with temperature and no clear dependence on the nature of the solvent exists. The conversion of coal at 380°C is independent of the nature of solvents at a constant 49 to 50%. At higher temperatures conversion is always highest in the coal derived solvent but heavy vacuum distillates from petroleum provide an almost equal conversion in the range of 410 to 435°C whereas the vacuum residue gives a low conversion independent of the temperature. Heavy solvents obviously do not prevent coking at 460°C under the conditions given. The share of asphaltene in the products in general decreases at higher temperatures but this then is dependent strongly on the nature of the solvent. In light vacuum distillate the share of coal derived asphaltene stays below 10% but in heavy distillates it is as high as 17% but then strongly reduced again at temperatures above 430°C. For the vacuum residue at 380°C almost 30% of coal derived asphaltene exist but then decrease strongly to only 2% at 460°C. It should be noticed, however, that these figures are calculated by difference and that this vacuum residue reacted alone results up to 11% asphaltene at 410°C decreased to 6% at 460°C. Reacted alone these solvents give less than 3% of asphaltene at 460°C with the already quoted exception of vacuum residue.

From experiments in petroleum derived solvents the share of product gases in the range of 10 to 13% is almost independent of the nature of solvent and on temperature. Reacted alone these solvents give 5% of gases to the most at 460°C. The higher the temperature the higher is the share of methane in all product gases. There also is a considerable content of carbon dioxide from the destruction of coal but not much influenced anymore by temperature above 380°C.

The share of naphtha in the products for petroleum derived solvents has a maximum at 410°C for vacuum distillates, increases with the boiling range of the solvent, reaches 16% for ZYL-solvent, is much lower for vacuum residue but then increasing with temperature to 11% at 460°C. The total naphtha yield combined from coal and solvent is 40% for ZYL-solvent and 33% for VR-solvent at 460°C.

The total oil yield from coal increases with the boiling range of a petroleum derived distillate solvent to a maximum at 435°C but still increasing to 460°C for the vacuum residue as a solvent. Since no true separation of product oils in shares stemming from coal or solvent is possible a characterization refers to the total product oil. In general an increase in reaction temperature decreases the atomic H/C-ratio of the product oil but still reflects the quality of each feed solvent whereas aromaticity increases with temperature rather independent of the nature of the solvent. At 435°C aromaticities of the total product oil are about 0.35 but are above 0.50 at 460°C. The average molweight of the total product oil at lower reaction temperatures are strongly dependent on the nature of the feed solvent but are equalized at 435°C for distillate solvents to an average of 250 as well as for vacuum residue but then down to 250 only at 460°C.

From recalculations and estimations for a once-through operation for the coal derived solvent the total liquid yield is 73% (M=300) at 460°C, for the vacuum residue as a solvent it is 58% (M=265) at 435°C, and for the most effective petroleum derived solvent it is 78% (M=225) at again 435°C.

#### RESIDENCE TIME DEPENDENCE

Since 435°C is not the temperature for a maximum gain of total products but obviously significant for the degradation of the brown coal in the mixture residence time variations in between heating-up only and 120 min. are made as presented in Tab. II). The apparent initial system pressure is dependent on the boiling range as well as on the crackability of the solvent but then much higher than from experiments with these solvents alone without addition of coal. This is due to the hydrocarbon gases and the carbon dioxide produced from coal and only compensated to some degree from the hydrogen consumption.

The hydrogen uptake shortly after heating up is low and little dependent on the nature of the solvent. After 60 min. residence time it is completely independent of the nature of the solvent. The hydrogen uptake increases for 10 min. only but thereafter is obviously in equilibrium. These results are calculated by difference. For these solvents reacted without coal under the same conditions the hydrogen uptake increases four- to sixfold from 0 to 60 min. residence time and thus the data calculated for coal are limited in their evaluation.

For product gases the major component is carbon dioxide produced rather spontaneously, thus explaining the small increase of gases with residence time in the range of 10 to 14%. From experiments with only solvents the share of product

gases under the same conditions stays below 2% even at 60 min. residence time. More significant are the differences in produced or retransformed asphaltenes. For short contact times they directly reflect the nature of the solvent. For the light LSP-solvent the asphaltenes derived from coal are rather independent of residence time whereas for the other distillate reach a maximum after 10 min. but then are transferred into oils by about 2% after 60 min. For vacuum residue which reacted without coal gives less than 2% asphaltenes at short contact time the coal derived asphaltenes immediately reach 33% but are transferred into oils by 25% after 30 min. From the solvents alone reacted without coal under the same conditions the product share of naphtha strongly increases with residence time reaching about 20% after 60 min. The coal derived naphtha is lower, reaches a maximum in distillate solvents after 10-30 min. but is much more dependent on the nature of the solvent. Recalculated for a once through operation this feed combination at 435°C and 30 min. residence time results to a total of 17% naphtha. For vacuum residue only 8% are gained from coal after 30 min. and a recalculated total for the feed combination would be little more than 10%. More important for the feed combinations are the yields of oil boiling above 200°C as derived from coal. In general it can be stated that the lighter the solvent the higher is the oil yield from coal. The oil yield increases almost steadily with residence time but then data are dependent on the nature of the solvent. The total liquid yield containing naphtha and heavy oils again is the higher the lighter the solvent and is in general increasing with residence time. For the light vacuum distillate as a solvent the total liquid yield from coal of 40% and of 35% for heavy vacuum distillate as a solvent are reached after 60 min. residence time. For vacuum residue as a solvent the influence of time on the total liquid yield from coal is most pronounced. From 3% occurring immediately after heating up it is increased to 26% after 30 min. residence time. Since no true separation of product oil boiling above 200°C from either coal or solvent is possible, any characterization of oil refers to the total product oil. After heating up only the H/C-ratio of the total product oil is dominated from the solvent with 1.61 for product from LSP-experiments to 1.39 for products from VR-experiments but after 60 min. it is equalized to 1.40 almost independent of the solvent. In accordance the aromaticity of the product oil almost independent of the nature of solvent increases from about 0.26 at heating up to about 0.37 after 60 min. and then is markedly higher than in the solvents themselves. The average molweight (M) of the product oil for each residence time is determined from the nature of solvent but overproportionally decreased in the experiments with the vacuum residue (initial molweight 900) with M=390 at only heating up but M=250 after 60 min. Recalculated for a once-through operation the total oil yield would be 61% with M=305 for 30 min. residence time from vacuum residue as a solvent and 74% with M=270 for 30 min. residence time from the heaviest vacuum distillate as a solvent.

#### PRESSURE DEPENDENCE

For comparison set conditions of 435°C and 60 min. residence time were chosen for a variation of initial hydrogen pressure of 6 to 15 MPa. This in the case of 15 MPa initial leads to unrealistic system pressures of up to 42 MPa but are tolerated here for parameter evaluation only. The experiments are limited to two petroleum derived solvents only. The results are presented in Tab. III]. The hydrogen uptake increases with initial pressure but rather independent on the nature of solvent and the gas formation is slightly reduced by pressure. For this coal in all solvents conversion increases with increasing initial pressure. For the range of 9-12 MPa initial pressure the coal conversion is the lower the heavier the nature of the solvent applied. For 15 MPa initial pressure the coal conversion might be suppressed if the hot system pressure is too high. Asphaltenes also increase with an increase of the initial pressure but for a given pressure are almost independent of the nature of the solvent. Naphtha formation is improved by a high initial pressure but not very much dependent on the nature of the solvent. For solvent (VR) the oil yield from coal scatters for initial pressures of 9-15 MPa but again is rather independent of the nature of the solvent. About 27% oil yield are gained at maximum in VR. Since no true separation of product oils from coal or solvent is possible an analytical evaluation refers to the total product oil boiling above 200°C. For coal BKR from all solvents the aromaticity of the total product oils is almost constant in a range of 0.35-0.40 against

a solvent aromaticity of about 0.2 and not systematically influenced by pressure or by the nature of the solvent. The strong destruction of coal as well as of heavy residual solvents is reflected from the average molweight (M). In LSP (M=249) the molweight of the total product oil is almost independent of the initial pressure with M=224 for 6 MPa and M=218 for 15 MPa. VR (M=897) comparable data are M=313 at 9 MPa and M=268 at 15 MPa. Based on a once-through approach recalculated total liquid yields including naphtha under the conditions given and at 12 MPa initial pressure (hot system pressure in the autoclave already above 30 MPa) and is 66% including 18% naphtha and 48% heavy product oil with M=285 in VR.

#### FEED MIXTURE DEPENDENCE

These experiments are based on a variation of mixtures of the same coal but a different VR-W residue described in the experimental section. The results are presented in Tab. IV) for set conditions of RMPaH, 430°C and 30 min. residence time. The system pressure is strongly influenced from the share of coal increasing by 13MPa from 0 to 67% of coal and dominated by CO<sub>2</sub>,CO and much lesser CH<sub>4</sub> originating from coal. With two exceptions the pressure drops during 30 min. on temperature, however, is almost constant. Hydrogen consumption by reacting VRW is 0.48%. For coal up to about 30% the hydrogen consumption is lower than for VRW. Coal might in part provide hydrogen for radical capping of fragments from VRW. Above 30% coals' hydrogen consumption is increasing from about 0.5% to 0.67% about proportional. The coal conversion is highest at 69% for about 10% of coal, then decreasing but almost constant at about 50% for 30 to 67% of coal. Product gas formation is strongly increasing with the share of coal and is mainly CO<sub>2</sub> and CO. The total residue increases with the share of coal but the ratio of total residue versus coal share in the feed is about constant. A certain part of the coal does not react under the conditions given, or a part of asphaltenes are included in the residue because the total asphaltene content decreases strongly with an increasing share of coal. The naphtha formation is increasing with the share of coal but then almost constant above 30% of coal in the feed. The high boiling oils are decreasing from more coal in the feed but still above 50% for 30% of coal in the feed. The quality of these high boiling oils are improved from a higher share of coal in the feed. Only VRW or mixed with little coal results to more than 80% of total liquid yield but the quality of the product oil is insufficient with a molecular weight of or above 500. Shares of 30-40% of coal in the feed provide a total liquid yield of 70% with a molecular weight of heavy product oil at or below 400.

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Table I) Dependence on temperature  
(9 MPa initial hydrogen pressure; 60 min. residence time)

	Feed		Reaction parameters			
	Solvent	Temperature (°C)	hot pressure beginning	(bar) end	H-up- take %	Conver- sion
1	LSP	380	243	243	0.9	48
2	LSP	410	255	247	1.1	57
3	LSP	435	265	259	1.2	62
4	LSP	460	303	346	1.2	53
5	ZYL	380	230	231	0.7	49
6	ZYL	410	240	230	1.4	63
7	ZYL	435	274	263	1.1	62
8	ZYL	460	279	332	1.1	48
9	VR	380	256	253	0.7	50
10	VR	410	276	255	1.2	50
11	VR	435	291	276	1.1	51
12	VR	460	306	335	1.3	48

continued

	Product distribution (% of feed coal)					
	G	R	A	W	N	O
1	12.1	52.3	8.7	2.1	11.3	14.4
2	12.1	42.9	11.3	3.1	14.9	16.8
3	11.0	37.8	9.1	2.5	9.8	31.0
4	12.6	47.3	4.7	3.0	7.0	26.6
5	10.9	51.1	14.6	3.1	11.4	9.6
6	12.5	37.3	17.3	5.3	15.8	12.9
7	13.8	38.0	13.0	3.8	7.9	24.6
8	13.2	52.0	3.0	4.0	10.5	18.4
9	11.0	50.3	29.2	-	5.0	5.2
10	12.7	49.7	23.7	1.9	6.4	6.8
11	13.4	48.7	8.6	4.0	5.4	21.0
12	12.4	51.6	2.3	4.0	10.6	20.4

All %-results are referring to coal daf. G = gases; R = residue (benzene insoluble); A = asphaltenes (hexane insoluble); W = water; N = naphtha (boiling below 200°C); O = oil

Tab II) Dependence on residence time  
(9 MPa initial hydrogen pressure; 435°C)

	Feed	Reaction parameters				H-up- take %	Conver- sion %
		Solvent	Residence time (min)	hot pressure begin.	pressure (bar) end		
1	LSP	0	276			0.5	42
2	LSP	10	274	274		1.1	54
3	LSP	30	275	274		1.1	57
4	LSP	60	265	259		1.2	63
5	ZYL	0	282			0.3	44
6	ZYL	10	277	275		0.8	56
7	ZYL	30	276	265		1.1	59
8	ZYL	60	274	263		1.1	62
9	ZYL	120	275	263		1.2	59
10	VR	0	287			0.5	46
11	VR	10	289	281		0.8	49
12	VR	30	284	281		1.1	51
13	VR	60	291	276		1.1	51

continued

	Product distribution (% of feed coal)					
	G	R	A	W	N	O
1	11.0	58.4	8.6	2.7	10.5	9.3
2	14.1	46.0	8.1		14.5	18.4
3	12.0	43.4	7.3	3.1	11.6	23.7
4	11.0	37.8	9.1	2.5	9.8	31.0
5	10.6	56.0	13.7	2.9	8.0	9.1
6	11.6	44.4	14.0	4.4	8.5	17.9
7	12.5	40.7	12.2	4.9	8.2	22.6
8	13.8	38.0	13.0	3.8	7.9	24.6
9	12.7	41.0	10.6	2.1	5.2	29.6
10	10.2	54.4	32.9		2.0	1.0
11	11.2	50.7	17.6	4.3	2.5	14.5
12	13.5	48.7	7.6	5.1	8.2	17.7
13	13.4	48.7	8.6	4.0	5.4	21.0

All %-results are referring to coal daf: G=gases; R=residue (benzene insoluble); A=asphaltenes (hexane insoluble); W=water; N=naphtha (boiling below 200°C); O=oil

Tab III) Dependence on hydrogen pressure  
(435°C, 60 min residence time)

Feed		Reaction parameters				
Solvent		initial H <sub>2</sub> -pressure (bar)	hot pressure beginning	(bar) end	H-up take %	Con- version %
1	LSP	60	213	251	0.8	47
2	LSP	90	265	259	1.2	62
3	LSP	120	327	315	1.8	63
4	LSP	150	408	375	1.8	66
5	VR	90	291	276	1.1	51
6	VR	120	361	319	1.5	61
7	VR	150	420	371	1.8	64

continued

Product distribution (% of feed coal)						
	G	R	A	W	N	O
1	14.9	52.6	4.2	4.4	8.4	16.3
2	11.0	37.8	9.1	2.5	9.8	31.0
3	14.1	36.9	7.9	3.5	10.0	29.4
4	13.8	33.9	8.7	3.6	10.4	31.4
5	13.4	48.7	8.6	3.1	6.3	21.0
6	11.4	39.1	9.3	3.6	11.2	26.9
7	11.4	36.1	9.0	5.4	14.8	25.1

All %-results are referring to coal daf: G=gases; R=residue (benzene insoluble);  
A=asphaltenes (hexane insoluble); W=water; N=naphtha (boiling below 200°C);  
O=oil

Tab IV) Dependence on feed mixture  
 mixtures of coal and residue VRW without catalyst addition  
 (conditions 430°C; 12 MPa initial hydrogen pressure; 30 min.  
 residence time)

No	Feed %			Reaction parameters			
	VRW	coal	dmf	hot pressure (bar) beginning	end	H-up- take % (of coal)	Conver- sion of coal %
1	100	0		301	289	0.48	-
2	91	9		312	299	0.35	69
3	83	17		330	317	0.46	55
4	71.5	28.5		360	340	0.56	53
5	61.5	38.5		372	359	0.59	50
6	50	50		389	373	0.64	47
7	33	67		430	392	0.67	50

Product distribution (% of feed)

	G	R	A	W	N	O	M (average mol weight of total heavy oil)
1	0.5	4.5	9.3	-	12.1	74.1	471
2	2.4	3.8	6.9	-	11.3	76.0	520
3	2.6	11.8	7.3	0.9	13.0	64.9	448
4	3.2	17.7	5.8	0.9	21.3	51.7	409
5	4.3	20.7	5.9	2.5	19.2	48.0	373
6	6.3	26.9	2.5	6.7	19.0	39.2	363
7	9.0	33.1	2.1	8.3	19.4	28.7	360

All %-results are referring to total feed (dmf): G=gases; R=residue (benzene insoluble); A=asphaltenes (hexane insoluble); W=water; N=naphtha (boiling below 200°C); O=oil