

## HIGH-SEVERITY CO-PROCESSING

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### INTRODUCTION

UOP is continuing bench-scale research and development of coal and petroleum resid co-processing technology under the sponsorship of U.S. Department of Energy. Earlier work, under completed contract DE-AC22-84PC70002, has been reported in a series of papers and reports (1-7). The overall objectives, to evaluate the technical feasibility of the co-processing concept and to establish a co-processing data base, were met. The concept of single-stage, slurry-catalyzed co-processing was successfully demonstrated in laboratory batch experiments (1) and in continuous bench-scale operations (2). Good long-term operability with the UOP vanadium-based catalyst was demonstrated for nearly 2,000 hours on-stream (3). A method of recovering the catalyst was developed and demonstrated on a laboratory scale. Based on the long-term operability and catalyst recovery studies, a conceptual commercial design was completed for a co-processing unit integrated into a 100,000 BPSD conventional refinery (3,4).

The primary objective of the current contract, DE-AC22-87PC79818, is to extend and optimize the single-stage, slurry-catalyzed co-processing scheme. Catalyst economics plays a major role in determining the overall profitability of slurry-phase co-processing. Consequently, much work has been devoted to exploring new catalyst systems and improving catalyst activity, dispersion, and recovery techniques. Most of the early development work was done using a vanadium-based slurry catalyst. A newer molybdenum-based slurry catalyst has been developed. In autoclave testing, the molybdenum-based catalyst gave equivalent conversions and yields as the vanadium-based catalyst at one-tenth the metal concentration (8). This molybdenum-based catalyst has been evaluated in the continuous bench-scale unit. Plant modifications, including the addition of a recycle loop, have made bench-scale operations possible at much higher severities than were previously possible. Good plant operations have been achieved at temperatures up to 470°C and with catalyst concentrations as low as 500 ppm molybdenum (9). Processing at high severities for short durations has demonstrated high nondistillable conversion without excessive carbon loss to retrograde reactions and light-ends yield. This important advancement in co-processing should significantly improve the process economics. A long-term operability study at high-severity conditions was needed to demonstrate that high-severity co-processing is feasible and can be run for extended periods without major operational problems. This paper reviews the results of a recent long-term operability study at high severity.

### Continuous Bench-Scale Operations

A simplified block diagram of the pilot plant is shown in Figure 1. The unit contains many of the essential features of the commercial flow scheme and is equipped to quantitatively measure the hydrogen consumption in the operations. The slurry feed (finely ground coal, petroleum vacuum resid, and catalyst) is combined with a hydrogen-rich recycle gas and is preheated before it enters the bottom of an upflow reactor. The products from the reactor are separated into gas and oil streams in the high-pressure separator (HPS). The gas stream from the HPS is combined with makeup hydrogen before being recycled back to the incoming fresh feed. A portion of the oil stream

from the HPS is recycled back to the incoming fresh feed, and the remainder is sent to a stripper. The lighter hydrocarbon stream from the stripper is sent to a debutanizer, where it is separated into  $C_4$  and  $C_5$  products. The heavier hydrocarbon stream from the stripper is sent to a vacuum fractionator to recover an overhead stream (light oil and vacuum gas oil) and a bottoms stream containing catalyst, coal minerals, insoluble carbonaceous material, and nondistillable hydrocarbons.

The addition of a recycle loop to the plant, i.e., the recycle of a portion of the HPS liquid back to the fresh feed, has greatly improved plant operability, especially at temperatures greater than 440°C. A recycle ratio of greater than 5:1 (based on recycle to fresh feed) is typically used. The space velocity of the fresh feed is maintained constant. The recycle results in increased liquid velocities and backmixing in the reactor. The improved mixing may help to eliminate the wall effect associated with a small bench-scale reactor. The liquid recycle also has a "flywheel" effect that helps to better withstand upsets in the fresh feed rate.

Prior to the introduction of liquid recycle, the reactor temperature in the bench-scale unit was limited to a maximum of about 425°C. As the operating temperature was increased beyond 425°C, a rapid decrease in heptane insolubles followed by coking and plugging problems made the plant increasingly difficult to operate (2).

With the addition of liquid recycle, the bench-scale unit can be run at much higher temperatures without developing coking problems (9). Temperatures of up to 470°C were achieved. The increased severity had little effect on the maximum coal conversion, which was still about 92%, but did result in about 20% increase in maximum asphaltene conversion (as measured by heptane insolubles) and an almost 30% increase in the 510°C+ nondistillable conversion.

The mechanism for improved high-temperature plant operability and conversions with liquid recycle may be due to better contacting of the reactive coal fragments with hydrogen and catalyst as a result of improved reactor backmixing or to the decrease in the relative contact between the coke precursors and the hot reactor walls as a result of greater superficial liquid velocities in the reactor. Hydrodynamic differences resulting from recycle may have also affected the flow regime, heat transfer characteristics, or gas void volume in the reactor. Further reactor modeling studies are needed to thoroughly understand these phenomena.

### **Feedstocks**

The feedstocks used for this study were reference feedstocks Lloydminster vacuum resid, designated as R10, and Illinois No. 6 coal, designated as Cl.4. Feed properties are given in Tables 1 and 2. Lloydminster vacuum resid (950°F<sup>+</sup>, 120-150 Pen.) was obtained from a commercial refinery in Canada. Illinois Coal No. 6 was obtained by the Kentucky Center for Energy Research Laboratory from the Burning Star Mine. Grinding (thru 200 mesh) and drying were done by Empire Coke Company of Holt, Alabama. The preparation procedure and equipment have been previously described (5).

### **TEMPERATURE SURVEY STUDY**

An important part of the single-stage, slurry-catalyzed processing program is to determine the optimum conversion level that produces high liquid yields by selective catalytic conversion as opposed to thermal conversion. A temperature survey study was conducted to determine the highest processing temperature attainable without excessive carbon loss to retrograde reactions and light ends (9). Standard operating conditions were used: 3000 psig, 5:1 minimum liquid recycle ratio, base WHSV, 2:1 mixture of petroleum resid to coal, and 0.12% molybdenum catalyst concentration.

The run was started at 427°C, and the temperature was increased in a stepwise manner. Six test conditions (427, 432, 438, 446, 451, and 459°C) were run. The plant operated well, even at the higher processing temperatures, and showed no evidence of either thermal degradation or reactor fouling. The conversion showed a steady increase with temperature and no sign of decrease even at 459°C. The unconverted coal showed a steady decrease with temperature (Figure 2), and the heptane-insoluble conversion increased with temperature (Figure 3). The greatest impact of the higher temperature was the 30 wt-% increase in nondistillable conversion (Figure 4) without significant carbon loss to retrograde reactions and only about 6% increase in light-ends yields (Figure 5). Table 3 compares the yields and product properties at 427, 446, and 459°C. The product distribution shows the expected trends when temperature was increased: an increase of lighter fractions (C<sub>1</sub>-C<sub>4</sub>, C<sub>5</sub>-177°C, and 177-343°C) and a decrease of heavier fractions (343-510°C and 510+°C). The quality of the liquid product improved with increasing temperature. The API gravity and hydrogen content of the product increased; and heptane insolubles, sulfur, and nitrogen levels decreased.

#### LONG-TERM OPERABILITY STUDY

A long-term operability study at high-severity conditions was undertaken to determine if high-severity co-processing could be run continuously for extended periods without major operational problems or the gradual buildup of coke in the reactor. The run was conducted at standard operating conditions: 3,000 psig, 5:1 minimum liquid recycle ratio, base WHSV, 2:1 mixture of petroleum resid to coal, and 0.090% molybdenum catalyst concentration. The reactor temperature was held at 455°C during the initial three weeks of operation, then increased to 465°C, and maintained for 17 days. During the operation, daily weight balances were conducted to ensure the integrity of the operation.

Catalyst and coal ash balances were followed to monitor fouling or deposition in the pilot plant. Product recoveries, H<sub>2</sub> consumption, and catalyst and ash balances indicated stable operation. The weight recoveries versus hours on-stream are shown in Figure 6 and can be compared with the average value, shown as a solid line. The weight recoveries were good and averaged 100.3 wt-%. The average reactor bed temperature for the 455 and 465°C operation versus hours on-stream is shown in Figure 7: the solid line on the figure represents the average temperature of 455.5°C and 464.7°C. The run was ended by a planned shutdown after 38 days on-stream without any significant operational problem. Upon disassembling the reactor, the walls were found to be free of coke or any deposits.

Conversions, product distribution, and total liquid product properties are shown in Tables 4 and 5 for the 455°C operations and in Tables 6 and 7 for the 465°C operation. The average coal, heptane-insoluble, and nondistillable conversions were 90.5, 74.6, and 78.9 wt-%, respectively, for the 455°C temperature and 91.9, 86.3, and 84.2 wt-%, respectively, for the 465°C temperature. As shown in Figures 8, 9, 10, and 11 the conversions and yields are comparable to those obtained at the same temperature in the temperature survey study.

#### CONCLUSIONS

Long-term operability of co-processing at high-severity conditions was demonstrated. Plant operations and performance were extremely good, and no major operational problems were encountered. High nondistillable conversion was obtained without excessive carbon loss to retrograde reactions and light-end yields. The operability of co-processing at high severity represents an important advance that may significantly improve the process economics.

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**Table 1**  
**Analysis of Lloydminster Vacuum Resid (R10)**

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

**Table 2**  
**Analysis of Illinois No. 6 (CL4)**

Proximate Analysis: (AR Basis), wt-%	
Volatile Matter	38.84
Fixed Carbon <sup>a</sup>	45.80
Moisture	4.08
Ash	11.28
Ultimate Analysis (AR Basis), wt-%	
Carbon	66.75
Hydrogen <sup>b</sup>	4.66
Sulfur	2.91
Nitrogen	1.34
Oxygen <sup>a</sup>	8.98
Ash	11.28
Moisture	4.08

<sup>a</sup> By difference

<sup>b</sup> Corrected for Moisture

**Table 3**  
**Effect of Severity on Yields and Product Properties**

Temperature, °C	427	446	459
<b>Yields, wt-% MAFF:</b>			
H <sub>2</sub> O + CO <sub>2</sub>	6.7	4.0	4.3
H <sub>2</sub> S	1.6	3.3	3.5
NH <sub>3</sub>	0.2	0.4	0.8
C <sub>1</sub> -C <sub>4</sub> (Light Ends)	2.5	5.5	9.1
C <sub>5</sub> -177°C (Naphtha)	5.4	12.0	14.5
177-343°C (Distillate)	17.6	24.0	36.0
343-510°C (VGO)	29.3	26.1	22.9
510+°C (Resid)	34.0	24.2	10.3
Unc. MAF Coal	5.6	3.6	2.3
H <sub>2</sub> Consumption	(2.8)	(2.9)	(3.6)
Total	100.0	100.0	100.0
<b>C<sub>5+</sub> Total Liquid Product:</b>			
MAFF, wt-%	86.2	86.3	83.7
API Gravity	12.9	17.0	19.9
Carbon, wt-%	84.7	84.0	84.4
Hydrogen, wt-%	10.0	10.3	11.0
Sulfur, wt-%	2.1	1.4	1.1
Nitrogen, wt-%	0.9	0.8	0.4
Heptane Insolubles, wt-%	9.8	9.1	3.1
MCRT, wt-%	12.7	11.2	6.2

**Table 4**  
**Conversion and Product Distribution**  
**of 455°C High-Severity Co-Processing**

Normalized Conversion	Wt-%
Coal	90.5
Heptane Insolubles	74.6
Nondistillable, 510+ °C	78.9
Product Distribution	Wt-% MAFF
H <sub>2</sub> O, CO <sub>2</sub> , CO	3.2
H <sub>2</sub> S	4.7
C <sub>1</sub> -C <sub>4</sub>	7.5
C <sub>5</sub> -177°C	13.8
177-343°C	25.8
343-510°C	24.0
510+ °C	17.7
Unc. MAF Coal	3.3
H <sub>2</sub> Consumption	(1.6)
Total	100.0

**Table 5**  
**Total Liquid Product Properties**  
**of 455°C High-Severity Co-Processing**

API Gravity	17.2
Carbon, wt-%	85.1
Hydrogen wt-%	10.4
Sulfur, wt-%	1.3
Nitrogen, wt-%	0.4
Heptane Insolubles, wt-%	9.9
MCRT, wt-%	9.3

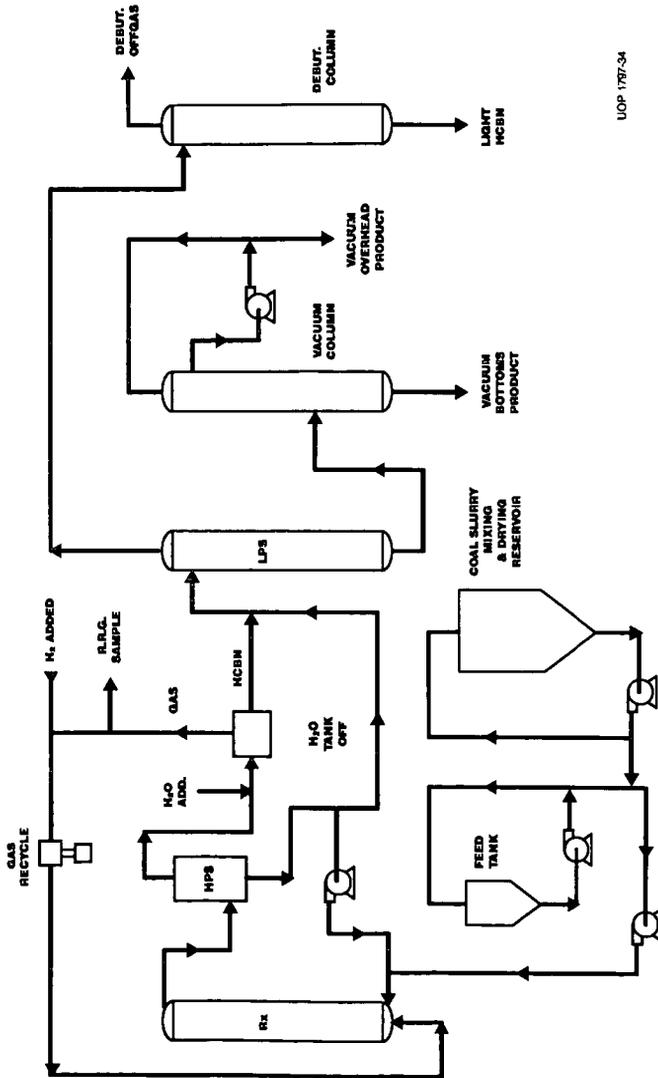
**Table 6**  
**Conversion and Product Distribution**  
**of 465°C High-Severity Co-Processing**

Normalized Conversion	Wt-%
Coal	91.9
Heptane Insolubles	86.3
Nondistillable, 510+ °C	84.2
Product Distribution	Wt-% MAFF
H <sub>2</sub> O, CO <sub>2</sub> , CO	5.0
H <sub>2</sub> S	5.9
C <sub>1</sub> -C <sub>4</sub>	9.9
C <sub>5</sub> -177°C	19.5
177-343°C	28.2
343-510°C	17.9
510+ °C	12.8
Unc. MAF Coal	2.9
H <sub>2</sub> Consumption	(2.1)
<b>Total</b>	<b>100.0</b>

**Table 7**  
**Total Liquid-Product Properties**  
**of 465°C High-Severity Co-Processing**

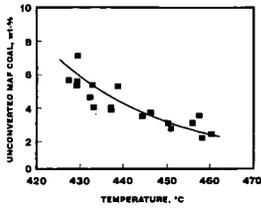
API Gravity	20.3
Carbon, wt-%	83.7
Hydrogen, wt-%	10.5
Sulfur, wt-%	1.0
Nitrogen, wt-%	0.4
Heptane Insolubles, wt-%	4.4
MCRT, wt-%	8.4

**FIGURE 1  
CO-PROCESSING PILOT PLANT**

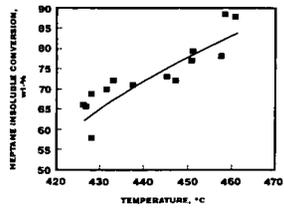


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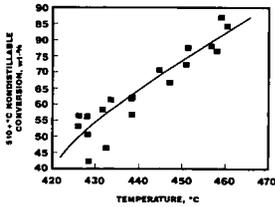
**FIGURE 2**  
**UNCONVERTED COAL YIELD**  
**vs. TEMPERATURE OF 0.12% Mo**



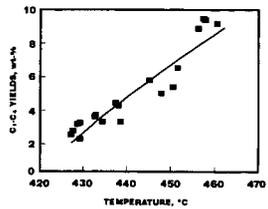
**FIGURE 3**  
**HEPTANE INSOLUBLE CONVERSION**  
**vs. TEMPERATURE OF 0.12% Mo**



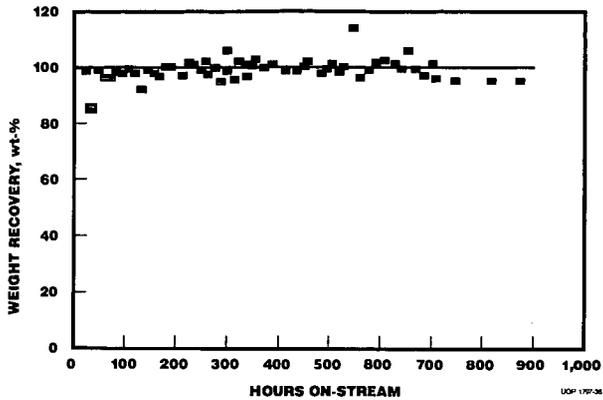
**FIGURE 4**  
**NONDISTILLABLE CONVERSION**  
**vs. TEMPERATURE OF 0.12% Mo**



**FIGURE 5**  
**LIGHT-ENDS YIELDS**  
**vs. TEMPERATURE OF 0.12% Mo**



**FIGURE 6**  
**HIGH-SEVERITY CO-PROCESSING**  
**WEIGHT RECOVERIES**



**FIGURE 7**  
**HIGH-SEVERITY CO-PROCESSING**  
**OPERATING TEMPERATURE**

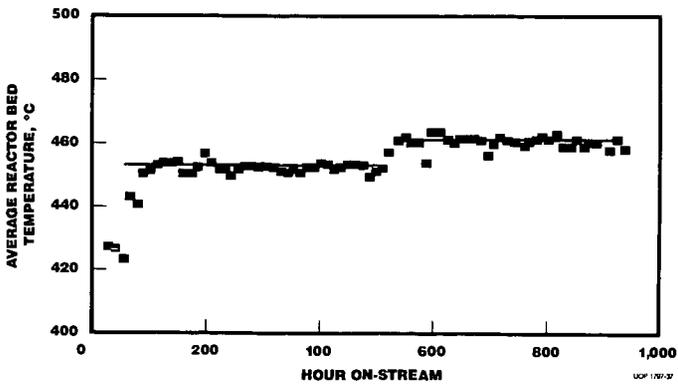


FIGURE 8  
UNCONVERTED COAL YIELD  
COMPARISON

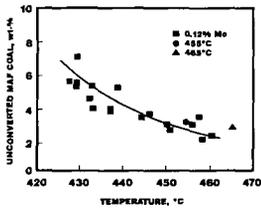


FIGURE 9  
HEPTANE INSOLUBLE CONVERSION  
COMPARISON

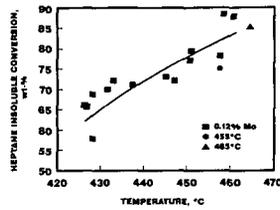


FIGURE 10  
NONDISTILLABLE CONVERSION  
COMPARISON

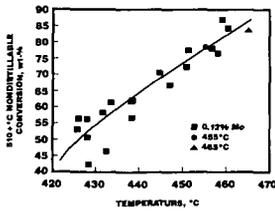


FIGURE 11  
LIGHT-ENDS YIELDS  
COMPARISON

