

SINGLE-STAGE SLURRY CATALYZED CO-PROCESSING

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INTRODUCTION

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

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

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

PROPOSED PROCESS CONCEPT

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

FEEDSTOCK SELECTION

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

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

The chemical and physical properties are shown in Table 1. Figure 1 shows the relationship of API gravity with respect to hydrogen, C₇ insolubles and carbon residue content. The contaminants (C₇ insolubles and carbon residue) increase and hydrogen content decreases with decreasing API gravity.

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

CATALYST COMPARISON STUDY

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

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

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

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

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

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

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

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

COAL/RESID REACTIVITY EVALUATION

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

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

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

CONTINUOUS BENCH-SCALE OPERATIONS

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

A simplified block diagram of the pilot plant is shown in Figure 5. The slurry feed (finely ground coal, petroleum resid and catalyst) is combined with hydrogen-rich recycle gas and is then preheated before it enters the bottom of the upflow reactor. The products from the reactor are then separated into a gas and oil stream at the high pressure separator. The gas stream from the high pressure separator is combined with make-up hydrogen before being recycled back to the incoming fresh feed. The oil stream from the high pressure separator is sent to a stripper where the lighter hydrocarbons are separated from the heavier fraction. The lighter hydrocarbon stream is separated further in the debutanizer into C₄ minus and C₄ plus products. The heavier hydrocarbon stream from the stripper is sent to a vacuum fractionator to obtain appropriate fractions.

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

Operating Conditions

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

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

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

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

CONCLUSIONS

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

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

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TABLE 1

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

TABLE 2

Coal Analyses

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

*Difference

TABLE 3

Catalyst Comparison Study

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

TABLE 4

Catalyst Comparison Study
Total Liquid Product Properties

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

*Estimated

TABLE 5

Continuous Bench-Scale Operations

Effect of Temperature

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

TABLE 6

Continuous Bench-Scale Operations

Effect of Residence Time

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

FIGURE 1
VACUUM RESID FEEDSTOCKS
COMPOSITION

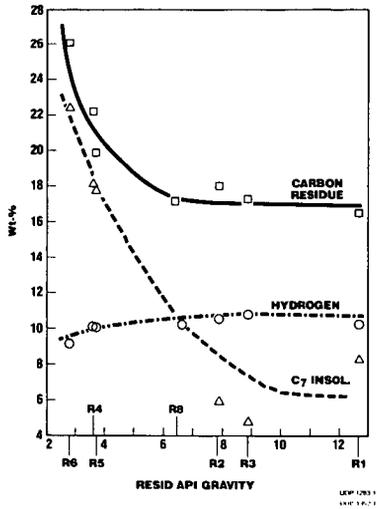


FIGURE 2
RESID REACTIVITY SCREENING
(ILLINOIS COAL NO. 6)

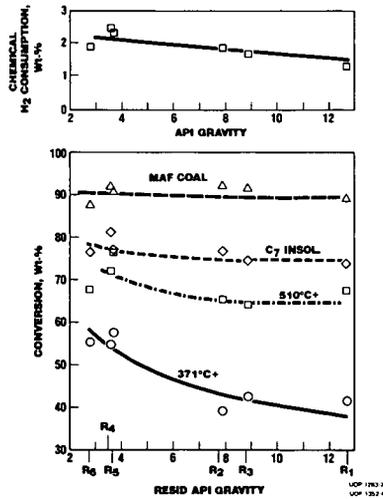
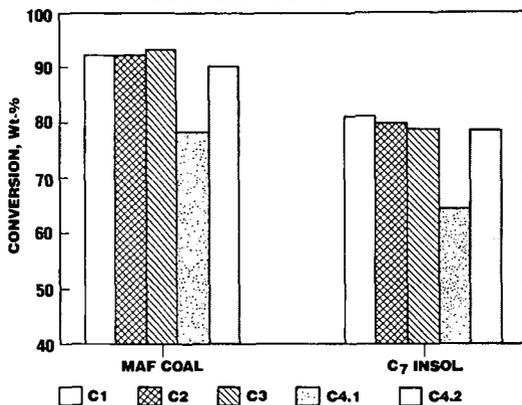
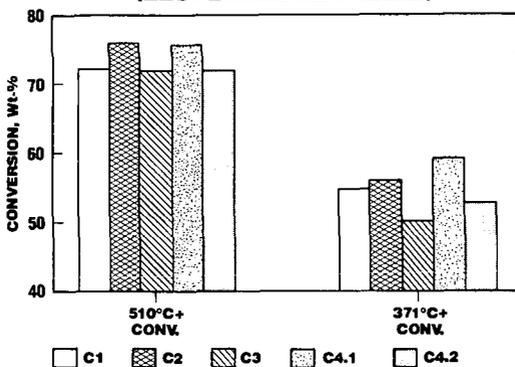


FIGURE 3
COAL REACTIVITY SCREENING
(LLOYDMINSTER RESID)



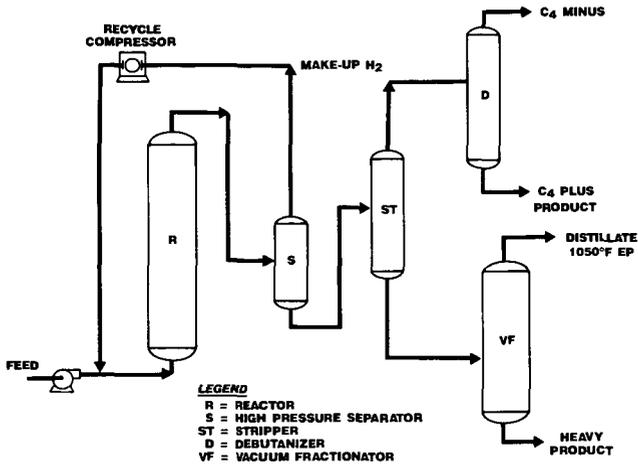
UOP 1283-27
 UOP 1352-5

FIGURE 4
COAL REACTIVITY SCREENING
(LLOYDMINSTER RESID)



UOP 1283-31
 UOP 1352-6

**FIGURE 5
PILOT PLANT FLOW SCHEME**



UGP 1327