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**BENCH-SCALE CO-PROCESSING
TOPICAL REPORT 1**

CONTRACT DE-AC22-87PC79812

~~CONFIDENTIAL~~

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Pittsburgh Energy Technology Center
United States Department of Energy
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Prepared by
Carol A. Piasecki, John G. Gatsis, and Howard E. Fullerton
UOP
Des Plaines, Illinois

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BENCH-SCALE CO-PROCESSING TOPICAL REPORT 1

1.0 INTRODUCTION

This topical report is the first for the UOP Bench-Scale Co-processing contract, which is sponsored by the U.S. Department of Energy under contract number DE-AC22-87PC79818. The objective of this contract is to extend and optimize the UOP single-stage, slurry-catalyzed co-processing scheme that was developed under a previous contract, DE-AC22-84PC70002. The technical feasibility of the co-processing concept using a proprietary vanadium-based slurry catalyst was demonstrated under this previous contract. This demonstration was accomplished by screening a variety of coal and resid combinations under varying conditions of temperature, pressure, residence time, resid/coal ratio, and catalyst concentration,¹ optimizing these conditions in a continuous pilot plant and demonstrating the long-term operability of the bench-scale unit,² and by the design of a conceptual commercial co-processing unit based on the pilot plant results.³

UOP co-processing uses a single-stage, slurry-catalyzed scheme in which petroleum vacuum resid and coal are simultaneously upgraded to a high-quality synthetic oil. The conceptual flow diagram of a commercial unit is shown in Figure 1. A highly active, well-dispersed catalyst permits operations at moderate- and high-severity reaction conditions with minimum detrimental thermal reactions. In this process, finely ground coal, petroleum resid, and catalyst are mixed, combined with hydrogen, and then directed to a single-stage reactor, where the simultaneous upgrading of the petroleum resid and coal occurs. The reactor effluent is directed to a series of separators, where a hydrogen-rich gas is recovered and recycled back to the reactor inlet. The balance of the material is sent to a series of separators, where the light gasses, light oil, vacuum gas oil (VGO), catalyst, unconverted coal, ash, and residues are recovered. The catalyst is recycled back to the

Figure 1

UOP Co-Processing Flow Scheme

reactor. The UOP co-processing scheme is designed to be integrated into a conventional petroleum refinery. The hydrocarbon products from the co-processing unit will be sent to the refinery for final upgrading to finished products.

The economics of co-processing are strongly dependent on the cost of the catalyst. There are two basic philosophies regarding the operations of slurry catalyst systems. The first approach is to use a metal, such as molybdenum or vanadium, that has an inherent hydrogenation function but in most cases is too expensive to simply throw away. These catalysts can improve the yields and product quality significantly, but catalyst recovery is usually essential to justify the overall economics of the process. The alternative is throwaway once-through systems that are designed to operate with a less expensive catalyst (iron oxide, for example) or a catalyst containing a low concentration of an expensive metal. With the iron system, the recovery of the metals from the unconverted coal and ash solids is not attempted. The less expensive catalysts generally have poor hydrogenation activity and in UOP studies to date, have shown poor plant operability and a propensity for coking. Even though some catalyst costs are incurred, they avoid the rather substantial capital investment associated with metals recovery.

A major focus of this contract is to investigate ways to reduce the catalyst and catalyst recovery costs and improve the overall economics of the process. To accomplish the objectives of this contract, the co-processing project was divided into the following four tasks:

- Task 1: Project Management Plan
- Task 2: Laboratory Support
- Task 3: Continuous Bench-Scale Operations
- Task 4: Process Assessment

This report documents the work completed under Task 2.0, Laboratory Support. The overall objective of Task 2.0 was to obtain and characterize the feedstocks for the contract and to provide a screening mechanism to test new catalyst systems prior to testing in the continuous pilot plant. The main elements of the experimental program for Task 2.0 include:

- Feedstock procurement and analysis
- Catalyst improvements
- Catalyst recycle screening

2.0 FEED PROCUREMENT AND ANALYSIS

The main criteria used to select the feedstocks for this study were:

- Reference feedstocks from the prior UOP contract
- Commercial importance and availability
- Physical and chemical properties

2.1 Coal Feedstocks

2.1.1 Reference Coals

Two coal feedstocks used in UOP's previous contract were chosen for this study. They included the reference coal, Illinois Coal No. 6 from Burning Star Mine (bituminous), and Wyodak Coal from Clovis Pt. Mine (subbituminous). New batches of each of these coals were obtained for this project. The new coals are designated C1.4 and C4.4 for Illinois Coal No. 6 and Wyodak Coal, respectively. The grinding and drying of the coals was done by Empire Coke Company of Holt, Alabama. The preparation procedure and equipment used for grinding and drying the coals was described in the first topical report of the previous contract.¹ Analysis of the latest batches are compared to the coals used in the previous programs in Table 1 for Illinois Coal No. 6 and Table 2 for Wyodak Coal. The new coals are almost equivalent to the previous reference coals.

A sample of "clean" Illinois Coal No. 6 was also prepared to study the effects of a low ash coal, as discussed in the next section.

Table 1
Reference Illinois Coal No. 6

	Batch C1.1	Batch C1.2	Batch C1.3	Batch C1.4
Proximate Analysis (As Received Basis), wt-%:				
Volatile Matter	39.9	39.9	39.7	38.8
Fixed Carbon ^a	47.2	45.4	45.3	45.8
Moisture	3.2	4.1	4.4	4.1
Ash	9.7	10.6	10.5	11.3
Ultimate Analysis (Moisture Free Basis), wt-%:				
Carbon	70.8	71.7	73.0	69.6
Hydrogen ^b	4.66	5.05	5.22	4.86
Sulfur	3.14	3.48	3.48	3.03
Nitrogen	1.42	1.43	1.43	1.40
Oxygen ^a	9.97	7.33	5.87	9.36
Ash	10.0	11.0	11.0	11.8
^a By difference ^b Corrected for moisture content Notes: C1.1 used for autoclave testing under DE-AC22-84PC70002 C1.2 used for bench-scale testing under DE-AC22-84PC70002 C1.3 used for autoclave testing under DE-AC22-87PC79818 C1.4 used for bench-scale testing under DE-AC22-87PC79818				

Table 2
Wyodak Coal

	Batch C4.1	Batch C4.3	Batch C4.4
Proximate Analysis (As Received Basis), wt-%:			
Volatile Matter	37.0	34.7	39.8
Fixed Carbon ^a	38.0	44.5	36.7
Moisture	14.7	12.9	16.4
Ash	10.3	7.89	7.08
Ultimate Analysis (Moisture Free Basis), wt-%:			
Carbon	64.1	67.3	65.0
Hydrogen ^b	4.49	5.06	5.06
Sulfur	1.16	0.96	0.90
Nitrogen	0.81	0.92	0.84
Oxygen ^a	17.3	16.7	19.7
Ash	12.1	9.1	8.5
^a By difference ^b Corrected for moisture content Notes: C4.1 used for autoclave testing under DE-AC22-84PC70002 C4.3 used for bench-scale testing under DE-AC22-84PC70002 C4.4 used for contract DE-AC22-87PC79818			

2.1.2 Coal Beneficiation Work

One of the objectives of this contract is to reduce the cost of recovering slurry catalyst. The recovery cost is directly related to the amount of solids (coal ash and unconverted carbonaceous material) that must be separated from the catalytic metals downstream of the co-processing unit. Reducing the amount of ash processed through the unit should have a positive impact on the cost of catalyst recovery.

Removing the ash from the coal before the coal comes in contact with the catalyst may be economically attractive because the separation can be carried out at that point without losing any of the catalyst with the waste solids. A number of new "clean coal" processes have been developed that might be used to clean the coal being fed into the co-processing unit. The driving force for the development of clean coal technology has been to reduce the sulfur content of the coal and lower SO₂ emissions from coal consumers. However, in most cases, the quantity of ash in the coal is significantly reduced. The ash reduction was of primary interest to UOP because the co-processing unit will carry out desulfurization.

For this contract, UOP tested a cleaned coal that has been deashed mechanically by gravity separation techniques. A number of commercially proven processes rely on the density difference between coal and ash to make a crude separation. UOP sent a batch of Illinois No. 6 reference coal to Bituminous Coal Research (BCR) Laboratories for separation in their double-cone, heavy media separation pilot plant.

The 666 lb sample of mine-washed 2 ¼ inch by 0 mesh coal was divided into two portions. One part was a control sample that underwent all of the same crushing, sizing, and drying operations as the remaining sample, but not the heavy media cleaning step. Figure 2 shows a schematic of the coal preparation process. The mine-washed coal was air-dried to equilibrium and then screened at 1 ¼ inch by 10 mesh (~0.7 inch openings). The coal retained on the 1 ¼ inch screen was broken using a jaw

Figure 2
Coal Preparation Schematic

crusher and mixed with the minus- 1 ¼ inch material. Approximately 160 lb of the 1 ¼ inch by 10 mesh working fraction was riffled from the 468 lb available and held as the control portion for later comparison with the beneficiated float.

Small representative samples of the 1 ¼ inch by 10 mesh were also riffled from the working sample. These samples were used to check the performance of the BCR double-cone separator at levels approximating 1.25 and 1.26 specific gravity. The double cone separator system pumps a preset magnetite and water slurry up through the feed sample, which is held in a fine-mesh screen basket (30 mesh openings). The float material is lifted from the basket placed in the upper cone, flows over a weir, and is collected in a similar basket situated in the lower cone. The sink material is retained in the upper cone feed basket. The magnetite slurry is recovered from the bottom cone and recirculated. Gravity levels are set and closely monitored from pycnometer readings taken in the separation area of the upper cone. The results of the first two test samples are summarized in Table 3. At a gravity of 1.26, the yield of float material was about 54%, which corresponds to a 52% reduction in the ash content. Bulk washing of the working coal was initiated at the 1.26 gravity level. Periodically, the accumulated coal was sampled and tested for ash content. These results are also summarized in Table 3 as Bulk Tests Nos. 1-4. The gravity of the heavy medium was adjusted gradually upward over the course of the work to improve the float yield and maintain the ash content of the product at less than 6.0 wt-% (50% reduction in ash from the feed). A maximum yield of about 70% was achieved at a gravity of 1.31. All of the test float samples were combined to make a composite sample. The float product and control coal were each pulverized in a Mikromill under an inert nitrogen atmosphere using a screen with 0.020 inch openings to give more than 95% of the finished product that is less than 100 mesh.

Table 3
Coal Cleaning Test Results from BCR National Labs

Sample	Gravity	lb	Float Fraction		Sink Fraction	
			Yield, wt-%	Ash, wt-%	Yield, wt-%	Ash, wt-%
Test 1	1.25	5	35	5.41	65	13.5
Test 2	1.26	5	54	5.73	46	15.4
Bulk Test 1	1.26	38	52	5.27	48	16.7
Bulk Test 2	1.28	29	57	5.60	43	17.5
Bulk Test 3	1.30	39	63	5.60	37	17.5
Bulk Test 4	1.31	49	70	5.89	30	20.2
Test Composite		165	61	5.60	39	17.3
Estimated Commercial Yield: ~ 70% for 50% reduction in ash from 12.0 to 6.0 wt-%.						

Analysis of the four composite fractions from the coal beneficiation work are summarized in Table 4. The control sample has been designated C1.5; the beneficiated float, C1.6; the fines from the initial screening, C1.7; and the high-ash sink sample, C1.8.

Table 4
Cleaned Coal Sample

	Illinois Coal No. 6 Fraction			
	Control	Cleaned Float	Fines	Reject Sink
Designation	Batch C1.5	Batch C1.6	Batch C1.7	Batch C1.8
Proximate Analysis (As Received Basis), wt-%:				
Volatile Matter	36.0	37.5	32.1	33.7
Fixed Carbon ^a	45.4	48.6	42.6	45.3
Moisture	8.2	8.7	14.3	12.9
Ash	10.4	5.1	11.1	7.0
Ultimate Analysis (Moisture Free Basis) wt-%:				
Carbon	69.3	75.0	68.4	67.3
Hydrogen ^b	5.22	6.06	5.15	5.07
Sulfur	3.33	2.78	3.42	0.96
Nitrogen	1.43	1.51	1.38	0.92
Oxygen ^a	9.40	9.07	8.70	17.77
Ash	11.3	5.6	12.9	8.0
^a By difference ^b Corrected for Moisture Content				

2.2 Petroleum Resid Feedstocks

2.2.1 Reference Resid

The reference petroleum resid for this contract is Lloydminster vacuum resid, which was chosen from the six vacuum resids tested in the earlier program. Lloydminster vacuum resid was chosen because it appeared to be average based on its properties (API, distillation, % asphaltenes, and heteroatom content). The latest batch of Lloydminster Resid, designated R10 was commercially vacuum fractionated by Husky Oil at their Lloydminster Refinery and sold as 120-150 Pen Asphalt. The new feedstock is compared to the previous reference resid, R8, in Table 5. The two reference feeds are virtually identical.

2.2.2 Alternative Resids

One objective of this contract is to expand the feedstock data base for the continuous co-processing bench-scale unit. Two resids have been chosen based on current commercial interests. The first of these, an Athabasca Tar Sand Bitumen (R11), was provided by Syncrude Canada, Ltd. Properties of the bitumen are shown in Table 6. The other, Hondo Vacuum Resid, is of interest because of its typically high level of asphaltenes. However, this batch of Hondo resid had significantly lower asphaltenes at 14.7 wt-% heptane insolubles as compared to the ~22 wt-% that was expected based on past results. The properties of the Hondo Vacuum Resid are shown in Table 6.

Table 5
Reference Lloydminster Vacuum Bottoms

	R8	R10
API Gravity @ 15.6°C	6.5	6.6
Specific Gravity @ 15.6°C	1.0254	1.0246
D1160 Distillation:		
IBP, °C	369	379
5 vol-% over, °C	432	455
10, °C	463	473
20, °C	505	509
EP, °C	523	512
Vol-% over @ EP	26.5	22.0
371°C+, wt.-%	98.4	98.9
510°C+, wt.-%	79.4	82.4
Analysis:		
Carbon, wt-%	83.7	83.6
Hydrogen, wt-%	10.0	10.3
Sulfur, wt-%	5.1	4.77
Nitrogen, wt-%	0.48	0.59
Oxygen (by Neut. Act.), wt-%	NA	0.54
Carbon Residue (MRCT), wt-%	17.30	17.39
Toluene Insolubles, wt-%	0	0.012
Heptane Insolubles, wt-%	13.91	13.56
Petroleum Ash, wt-%	0.05	0.041
Nickel, ppm	83	82
Vanadium, ppm	165	163
Iron, ppm	3.6	34
Molecular Weight	755	912
Pour Point, °C	49	54

Table 6
Athabasca Tar Sand Bitumen and Hondo Vacuum Resid

	Athabasca Bitumen	Hondo Vacuum Resid
	R11	R12
API Gravity @ 15.6°C	7.4	5.9
Specific Gravity @ 15.6°C	1.019	1.0298
D1160 Distillation:		
IBP, °C	243	398
5 vol-% over, °C	329	465
10, °C	354	492
20, °C	410	—
30, °C	453	—
EP, °C	514	509
Vol-% over @ EP	40	14.0
371°C, wt-%	84.5	99.7
510°C, wt-%	63.0	92.3
Analysis:		
Carbon, wt-%	82.4	82.2
Hydrogen, wt-%	10.4	9.6
Sulfur, wt-%	5.32	5.5
Nitrogen, wt-%	0.42	1.37
Oxygen (by Neut. Act.), wt-%	1.14	0.74
Carbon Residue (MRCT), wt-%	14.4	17.2
Toluene Insolubles, wt-%	0.794	0.23
Heptane Insolubles, wt-%	10.6	14.7
Petroleum Ash, wt-%	0.797	0.087
Nickel, ppm	69	126
Vanadium, ppm	201	295
Iron, ppm	518	14
Molecular Weight	600	815
Pour Point, °C	23	61
BS&W, LV-%	1.4	NA

3.0 CATALYST SCREENING TESTS

The reactivity screening task was designed to evaluate new catalyst systems for co-processing and to establish which catalysts should be tested in the bench-scale plant. Various vanadium and molybdenum catalyst formulations were studied. The objectives and test results for each of these subtasks are discussed in the following sections. A detailed summary of the operating conditions, analytical results, and product distributions from each run are in Sections 3.1 and 3.2.

3.1 Description of Autoclave Testing

Batch experimentation during Task 3.0 was conducted in an 1800 cc rocking autoclave. The system consists of a double-pedestal shaking mechanism, connecting spirals for inlets and outlets to the reactor vessel, and an electric heating jacket for temperature control. Mixing of the reactor contents is provided by tilting the autoclave through an angle of 30 degrees at 36 cycles per minute. Autoclave pressure is automatically controlled by adding makeup hydrogen. To accurately determine hydrogen consumption, the makeup hydrogen feed rate is measured by a positive displacement metering system. Throughout the test run, the pressure and temperature are measured and recorded on a continuous basis. A schematic of the test equipment and product workup is shown in Figure 3.

The following section describes the test procedure used during the autoclave testing conducted in Task 2. The same test equipment was used throughout this program and the prior contract DE-AC22-84AC70002 to ensure comparable test results.

The autoclave test procedure includes a pressure test, drying step, heat up, cool down, and product workup. Weighed amounts of resid, coal, and catalyst are added to the autoclave. The

Figure 3
Autoclave Schematic

WCC: Water Cooled Condenser
DIC: Dry Ice Condenser

feed is dried to simulate the drying step that takes place in the continuous pilot plant feed tank. The drying step is done at 150°C under a vacuum. The system is purged with nitrogen to remove any oxygen and then pressure tested at 440 psia. After being depressured, the system is repressured to 1470 psia with a gas consisting of 90 vol-% H₂ and 10 vol-% H₂S. Autoclave mixing begins, and the temperature is systematically raised to the desired set point over the next two hours. At this point, pure hydrogen is added automatically to maintain the desired pressure. After the system has been at the desired conditions for the required time, the heat and makeup hydrogen are shut off.

Based on previous UOP studies, the following conditions were selected as the base operating conditions:

- Temperature of 420°C
- Residence Time of 2 hr
- Pressure of 3,000 psig
- Resid/coal ratio of 2:1 wt/wt

The rocking of the autoclave is continued until the reactor has cooled to 300°C (~ 2 hr). At this point, the entire system is shut off and allowed to cool overnight.

After the system has cooled, workup of the various product streams begins. First the autoclave is depressured through a foam trap, and the gas is caustic scrubbed, sampled, and metered. To remove any additional gas from the reactant mixture, the material is stripped insitu with nitrogen. This effluent gas is scrubbed, sampled, and metered. The slurry product from the autoclave is poured off. The material remaining in the autoclave is removed by rinsing the vessel with toluene until the autoclave is clean.

The slurry product poured from the autoclave is centrifuged to remove the solids. The centrate liquid is collected in a separatory funnel to remove water. The centrate solids are removed from the centrifuge cup with toluene and added to the toluene rinse solution. The toluene rinse solution is then centrifuged to remove the solids. The centrate liquid (toluene-soluble fraction) is filtered and flashed on a rotary flash evaporator. Toluene is removed overhead together with small amounts of water, which is collected in a dry-ice trap. The recovered toluene-soluble product is combined with the separated centrate liquid to give the total liquid product, which immediately analyzed for heptane-insoluble and toluene-insoluble content. The toluene-insoluble material (catalyst, coal minerals, and unconverted coal) is dried in a vacuum oven at 100°C, and water is recovered in a dry-ice trap.

The results of these tests may best be characterized by the amount of coal conversion, nondistillable conversion, and heptane-insoluble conversion achieved. For this study, the coal conversion has been calculated as the disappearance of moisture and ash-free (MAF) coal, the nondistillable conversions have been based on the disappearance of MAF coal plus 510°C+ resid, and the heptane-insoluble conversions have been based on the disappearance of MAF coal plus heptane insolubles in the resid. Also, a distillate conversion has been reported. This conversion is defined in the same manner as the nondistillable conversion but uses 371°C instead of 510°C as the cutpoint. Because the feed to the co-processing unit contains a solid, each of these conversions may reasonably be reported on a wt-% basis.

3.2 Discussion of Results

3.2.1 Modified Vanadium Catalyst

A modified vanadium catalyst was prepared using a slightly different method of preparation than that used during Contract DE-AC22-84PC70002. This new catalyst preparation offers a potential cost savings. A catalyst concentration survey was completed with modified vanadium catalyst, K2.0, over a range of concentrations from 100 ppm to 1.0 wt-% metal by weight in the moisture and ash free feed (MAFF). The Lloydminster resid contained about 165 ppm vanadium (~110 ppm vanadium on MAFF basis with coal), which represents an autocatalytic minimum catalyst concentration. Unless otherwise specified, concentrations reported are the actual amount of metal added as catalyst and excludes any metals from the resid.

The results from the concentration survey are reported in Appendix A. As illustrated in Figures 4-8, the conversions and liquid product properties fall right in line with those for reference vanadium catalyst, K1.0. Maximum MAF coal conversion of about 94 wt-% was achieved at a concentration of about 0.5 wt.-% vanadium. At higher catalyst concentrations, the equilibrium coke laid down on the catalyst increases and the overall coal conversion, which is defined as the disappearance of MAF solids, begins to decline. However, nondistillable conversion, heptane-insoluble conversion, and liquid product properties continue to improve with increased catalyst concentration over the range tested.

The K2.0 catalyst formulation appears to have better dispersion than reference K1.0 catalyst (Table 7). A detail summary of the runs is given in Appendix B. When K1.0 was originally tested at 0.2 wt.-%, it showed about 10% lower MAF coal conversion and almost 15% lower heptane-insoluble conversion than the new K2.0 at 0.2 wt.-%. Subsequent tests using more highly dispersed

Figure 4

*Coal and Nondistillable Conversions vs.
Catalyst Concentration for UOP Vanadium Catalyst*

Figure 5

*Heptane Insoluble Conversion vs.
Catalyst Concentration for UOP Vanadium Catalyst*

Figure 6

*Effect of Catalyst Concentration
on API for Vanadium Catalyst*

Figure 7

*Effect of Catalyst Concentration
on MCRT*

UOP 2007-7

Figure 8

*Effect of Catalyst Concentration
on Sulfur for Vanadium Catalyst*

Table 7
Vanadium Catalyst Dispersion Study (0.2 wt-% V)

	Catalyst Type			
	K2.0	K1.0	K1.0'	K1.0"
Conversions, wt-%:				
MAF Coal	92.2	79.1	82.6	89.9
Heptane Insoluble	61.3	61.9	60.5	74.1
510°C+	64.3	64.6	63.9	69.1
C ₅ -510°C Liquid Yield, wt. %	86.7	84.2	83.3	87.0

K1.0 eliminate this offset (Table 7). The dispersed catalysts were designated K1.0' and K1.0" to represent increasing dispersion. This improvement with the dispersed system illustrates that not only is the gross catalyst concentration important, but of equal importance is how well the catalyst is dispersed and can be used for stabilizing reactive coal and asphaltene fragments before they polymerize to coke.

3.2.2 Molybdenum Catalyst Testing

Two UOP molybdenum catalyst formulations were prepared and tested. The molybdenum catalyst was anticipated to be more active than the UOP reference vanadium catalyst. The results of the two formulations are summarized Appendix C, and compared with the standard UOP vanadium catalyst at a similar 1 wt-% metals level. Little difference was observed between the two molybdenum formulations, and so subsequent testing was completed with the first formulation (designated K6.2). This formulation involves a much less costly preparation technique. The molybdenum catalyst was tested in triplicate to establish a baseline for this new molybdenum-based catalyst. The results of these tests are summarized in Appendix D.

As expected, the dispersed molybdenum catalysts were more active than the vanadium catalyst at similar metal concentrations. The molybdenum catalysts showed equivalent coal conversion but improved heptane-insoluble and nondistillable conversions as well as better denitrification.

Because the K6.2 molybdenum catalyst was more active, a temperature survey was conducted to determine if a temperature adjustment would be needed from 420°C reference temperature to achieve optimum conversion. Tests were conducted with 1.0 wt-% molybdenum over a temperature range of 390°C to 450°C. Results are summarized in Appendix E. The effects of temperature on conversion is illustrated in Figure 9. As with the reference vanadium catalyst, the optimum temperature for the molybdenum system appears to be about 420°C. As temperature is increased further, cracking and thermal retrograde reactions begin to dominate over catalytic reactions, and the result is the production of light gases, larger asphaltene molecules, polyaromatics, and coke. As temperature is increased to about 430°C, nondistillable conversion also reaches a peak and begins to decline.

Figures 10-13 show the effect of temperature on liquid product properties. The same type of optimum behavior is observed at the reference temperature of 420°C. The API goes through a maximum of about 18.5. Condensation reactions at higher temperatures, as well as removal of some of the lighter hydrocarbons by cracking to gases, account for an eventual decline in API at high temperatures. The heptane-insoluble content, Conradson carbon content(measured as wt-% MCRT), and sulfur content all go through a minimum at about 420°C. As some of the light "cleaner" portions of the product are cracked out, the undesirable, more contaminated heavy portions of the product are concentrated. Based on this temperature survey, 420°C was chosen as the operating temperature for all subsequent autoclave tests with the molybdenum systems.

Figure 9

*Conversion vs. Temperature
for UOP Molybdenum Catalyst*

Figure 10

*Effect of Temperature
on API for Molybdenum Catalyst*

Figure 12

*Effect of Temperature
on MCRT for Molybdenum Catalyst*

Figure 13

Effect of Temperature on Heptane Insolubles for Molybdenum Catalyst

The next series of tests conducted with the K6.2 catalyst was a catalyst concentration survey covering a range from 50 ppm to 2.0 wt-% molybdenum. The results of these autoclave experiments are summarized in Appendix F. Figure 14 shows the effect of catalyst concentration on coal and nondistillable conversions. Nondistillable conversion increases linearly with the log of concentration. The coal conversion goes through a maximum of about 94 wt-% at 0.2 wt-% molybdenum. This curve is similar to that of the vanadium-based catalysts, except that the maximum is shifted to a lower catalyst concentration for the molybdenum. The molybdenum catalyst appears to be 5 to 10 times more active than an equivalent amount of vanadium. This result is easily seen in Figure 15, where the vanadium results are superimposed on those from the molybdenum study but with the log-scale shifted one full cycle. With this factor of 10 adjustment, all of the points fall on the same curve. The same trend is observed with the liquid product properties in Figures 16-18. Thus, equivalent yields and conversions can be achieved using either the vanadium or about one-tenth the concentration, by weight, of molybdenum.

Figure 14

*Coal and Nondistillable Conversions vs.
Catalyst Concentration for Molybdenum Catalyst*

Figure 15

*Coal and Nondistillable Conversions
for Vanadium and Molybdenum Catalyst*

Figure 16

*Comparison of API
for Molybdenum and Vanadium Catalyst*

Figure 18

*Comparison of MCRT
for Molybdenum and Vanadium Catalyst*

Figure 17

*Comparison of Sulfur
for Molybdenum and Vanadium Catalyst*

4.0 CATALYST RECYCLE STUDY

Catalyst recovery, though expensive, offers several potential benefits over throwaway systems. Because most of the metals are recovered and reused, the amount of waste metal that must be disposed of is less than in a once-through system. Environmental concerns over the safe disposal of the waste metals from the process are minimized. In today's increasingly strict regulatory climate, metal recovery may be legislated purely for environmental reasons.

The objective of the catalyst recycle study is to demonstrate the activity and stability of the UOP molybdenum catalyst after it has been processed through four cycles of use and recovery. The data generated will help quantify the steady-state activity as well as the efficiency of the catalyst recovery scheme. Both of these factors contribute to determining the catalyst makeup rate.

4.1 Catalyst Recovery Procedure

Proprietary chemical separation techniques were successfully demonstrated for both the UOP vanadium catalyst^{1,2} and the UOP molybdenum catalyst from the coal-derived solids, as reported in this section. The recovered catalytic metals were then converted to the catalyst precursor and recycled. The advantage of this catalyst recovery technique is that fresh catalyst is always used in the process and consequently no catalyst deactivation should occur. The recovery scheme used involves the following steps:

1. Separation of the catalyst and coal solids from the vacuum fractionator bottoms
2. Calcination (oxidation) of the catalyst
3. Extraction of the calcined catalyst
4. Filtration of the extracted solids at extraction conditions

5. Recovery of the catalyst from the extract

6. Preparation of the catalyst precursor

The separation of the solids (coal minerals, insoluble carbonaceous material, and catalyst) from the slurry product is the key step. Under the conditions used in co-processing, the solids become finely dispersed in the liquid product, and so physical separation is difficult. A successful separation yields a liquid product with a low solids content and minimizes the liquid loss. The removal of solids is necessary for downstream processing in any fixed-bed catalytic process.

In the UOP separation process, the coal slurry product was solubilized and blended with water to form an aqueous phase containing the solids. The solvent phase is then separated from the aqueous slurry phase. The advantageous of this separation are that the process:

- Yields a liquid product containing low solids, which can be processed in fixed-bed catalytic processes without plugging.
- Yields a solids containing stream that is pumpable.
- Maximizes recovery of solid-free liquid product.
- Minimizes solvent losses.

The solids were then calcined in a muffle oven, where the temperature was carefully stepped. During the calcination, the unconverted carbon was burned off and, the catalytic metals were converted to a oxidized state. The calcined catalyst-in topcoal solids were then extracted in a batch autoclave pilot plant. The catalyst was solubilized and separated from the insoluble coal solid impurities by filtration. The filtrate was then evaporated to recovery the catalyst. The recovered catalyst metals were converted to the catalyst precursor and tested for activity in the autoclave test at base conditions. The procedure for the extraction and filtration is described in Reference 2.

Four complete cycles of catalyst use in autoclave testing and recovery in batch laboratory processing were completed. For the first cycle, six identical autoclave tests were conducted with 1 wt-% molybdenum-based catalyst at reference conditions to provide the starting material for the study. A composite sample was prepared from the six products to provide enough material for feed to the next cycle as well as for product and catalyst analysis at each step in the catalyst recovery process. The number of test runs for each of the subsequent cycles was reduced to compensate for catalyst losses as a result of sample analysis and recovery losses. For the second and third cycles, four and three autoclave tests, respectively, were completed. The products from each run were combined after the extraction step and stored under nitrogen.

4.2 Discussion of Results

Little or no loss of the catalyst occurred in the solid/resid separation or calcination steps. An excess of 85 % of the catalytic metals was recovered using this chemical separation technique. The majority of the losses occurred in the extraction step. A summary of the results is presented in Appendix G.

The activity test results for the four passes are compared to the fresh catalyst results in Table 8. The coal conversion was essentially equivalent: no loss in activity resulted from the catalyst recovery process. The recovered catalyst had a slightly lower cracking activity, as indicated by the lower nondistillable conversion, and a slightly higher hydrogenation activity, as shown by the higher heptane-insoluble conversion. However, these variations are believed to be within the experimental error.

Table 8
Molybdenum Catalyst Recycle

	Reference	1st Pass	2nd Pass	3rd Pass	4th Pass
Conversions, wt-%:					
MAF Coal	92.0	90.9	92.5	92.5	92.5
Heptane-Insoluble	89.4	89.7	90.6	91.6	91.3
510°C+	76.5	72.7	71.2	72.3	72.1
C ₅ -510°C Liquid Yield, wt-%	68.4	67.3	63.3	66.7	66.5

The liquid product properties for composite tests are not directly comparable to the product properties reported for previous autoclave tests. Because of the differences in the way the products are worked up for recovering the catalyst, the light ends boiling below toluene boiling point are not included in the total liquid product for the composite tests, and so the product properties generally look heavier. Normally, the light product is poured out of the autoclave, and the residual material is removed with toluene. The result is that C₅+ liquids boiling below toluene were subsequently lost when the toluene was fractionated. All weight recovery losses are assumed to be from the C₅-371°C fraction, and an appropriate correction to the data has been made. Although caution must be used in comparing these data to other autoclave tests worked up with normal procedure, the data in Table A-7 of Appendix A are all on a comparable basis.

5.0 CONCLUSIONS

Autoclave experiments to improve catalyst activity, dispersion, and recovery techniques were conducted during Task 2.0. A new molybdenum-based catalyst was demonstrated for co-processing. This catalyst resulted in conversions and yields that are equivalent to the reference vanadium catalyst used for DE-AC22-84PC70002 but at one-tenth the metal concentration. The optimum molybdenum concentration determined in the autoclave testing was 0.1 wt-%. The optimum autoclave operating temperature of 420°C for the molybdenum catalyst was the same as that for the vanadium catalyst. All other standard operating conditions remained constant.

New vanadium preparation techniques were tested. Both a more dispersed vanadium catalyst and a less costly preparation technique were successfully demonstrated. The work demonstrated that a well-dispersed catalyst was equally as important as the gross catalyst concentration. Despite the improvements in the vanadium catalyst, the new molybdenum catalyst was still significantly more active.

Catalyst recovery and reuse over four complete cycles was demonstrated. An excess of 85 wt-% metals recovery was consistently achieved. The catalyst activity and conversions remained essentially the same over the four passes.

APPENDIX A

Autoclave Run Summary: Catalyst Concentration Series With Modified UOP Vanadium Catalyst

Catalyst Concentration Series with Modified UOP V Catalyst

Autoclave Test:	S860-85	S860-91	S860-95	S860-107	S860-117	S860-121
Coal Type	AR C1.3	AR C1.3	AR C1.3	AR C1.3	AR C1.3	AR C1.3
Resid Type	R8	R8	R8	R8	R8	R8
Catalyst Type	K2.0	K2.0	K2.0	K2.0	K2.0	K2.0
Resid/Coal, wt/vt	1.92	1.98	1.99	2.07	2.05	2.08
Catalyst, wt% NAF	0.53	0.20	0.10	0.05	0.02	0.01
Temp., Deg C.	420	420	420	420	420	420
Pressure, atm.	200	200	200	200	200	200
Res. Time, hrs.	2	2	2	2	2	2
Weight Recovery, %	96.50	95.13	98.79	91.62	92.72	88.05
NAF Wt. Rec., %	97.88	95.66	99.42	91.57	93.07	88.62
Ash Balance, %	90.33	94.77	102.22	100.42	95.06	82.70
Conversions, wt% *						
NAF Coal	94.11	92.15	85.40	84.01	73.09	69.35
Heptane Ins.	80.43	61.28	55.85	67.89	58.20	55.83
S10C+	66.24	64.30	65.47	66.31	64.99	64.83
371C+	45.92	44.22	44.77	48.03	48.63	49.49
Prod. Dist., wt%						
NH3	0.1	0.3	0.3	0.2	0.2	0.2
H2O	3.6	2.2	1.7	2.1	2.3	1.8
H2S	3.1	2.7	2.8	2.8	2.7	2.7
CO2	0.9	1.0	0.9	0.9	0.9	0.8
C1-C4	5.8	6.6	5.6	5.1	5.9	5.5
C5-371C**	35.3	34.1	35.6	39.2	38.0	39.3
371-510C	24.3	24.4	24.9	22.4	20.7	19.7
S10C+	27.2	28.2	24.9	23.8	21.3	20.3
NAF Coal*	2.1	2.8	4.9	5.2	9.4	11.0
H2 Consumption***	-2.33	-2.24	-1.63	-1.62	-1.49	-1.41
Total	100.0	100.0	100.0	100.0	100.0	100.0
Total Liquid Product Properties						
API	13.2	11.3	13.8	13.3	13.4	13.3
wt% carbon	85.30	86.10	85.50	85.65	85.00	85.10
wt% hydrogen	10.80	10.65	10.45	10.80	10.50	10.75
wt% sulfur	1.99	2.17	2.00	2.12	2.22	2.24
wt% nitrogen	0.85	0.70	0.55	0.75	0.56	0.55
wt% oxygen						
wt% tol. insol.	0.836	1.497	1.049	1.094	1.271	1.12
wt% heptane ins.	7.748	17.116	16.568	10.846	11.947	12.183
NCRT	11.64	13.145	12.9	16.19	18.655	15.025
D1160:						
IBP, Deg C	65	64	59	60	63	70
50t, Deg C	421	445	418	425	399	404
EP, Deg C	560	542	556	543	559	559
vol% @ EP	75	72	77	75	77	76

* Adjusted for Ash Balance, if Ash Balance < 100%

** Adjusted for 100% NAF Recovery

*** Adjusted for catalyst reduction

APPENDIX B

Autoclave Run Summary: Catalyst Dispersion Study With UOP Reference Vanadium Catalyst

Catalyst Dispersion Study with UOP Reference V Catalyst

Autoclave Test:	S860-91	S860-127	S860-163	S860-191
Coal Type	AR C1.3	AR C1.3	AR C1.3	AR C1.3
Resid Type	R8	R8	R8	R8
Catalyst Type	K2.0	K1.0	K1.0'	K1.0"
Resid/Coal, wt/wt	1.98	2.06	2.03	2.03
Catalyst, wt% MAF	0.20	0.20	0.20	0.20
		--increasing dispersion--		
Temp., Deg C.	420	420	420	420
Pressure, atm.	200	200	200	200
Res. Time, hrs.	2	2	2	2
Weight Recovery, %	95.13	98.71	93.72	95.22
MAF Wt. Rec., %	95.56	99.39	94.14	95.86
Ash Balance, %	94.77	102.50	95.86	98.58
Conversions, wt% *				
MAF Coal	92.15	79.09	82.63	89.88
Heptane Ins.	61.28	61.90	60.49	74.14
510C+	64.30	64.56	63.93	69.09
371C+	44.22	46.14	46.70	56.23
Prod. Dist., wt%				
NH3	0.3	0.0	0.3	0.3
H2O	2.2	1.7	3.3	1.9
H2S	2.7	2.6	3.0	2.9
CO2	1.0	0.7	0.7	0.7
C1-C4	6.6	5.4	4.9	5.6
C5-371C**	34.1	37.7	36.3	47.0
371-510C	24.4	22.8	21.7	16.7
510C+	28.2	23.7	25.3	23.3
MAF Coal*	2.8	6.8	6.1	3.5
H2 Consumption***	-2.24	-1.54	-1.51	-1.96
Total	100.0	100.0	100.0	100.0
Total Liquid Product Properties				
API	11.3	12.7	11.6	12
wt% carbon	86.10	85.40	85.90	84.50
wt% hydrogen	10.65	10.30	10.35	11.00
wt% sulfur	2.17	2.18	2.08	2.01
wt% nitrogen	0.70	0.67	0.59	0.65
wt% oxygen				
wt% tol. insol.	1.497	0.579	0.898	1.133
wt% heptane ins.	17.116	11.044	14.17	9.218
MCRT	13.145	14.465	14.025	14.4
D1160:				
IBP, Deg C	64	65	77	30
50%, Deg C	445	396	407	422
EP, Deg C	542	559	538	544
vol% @ EP	72	80	74	74

* Adjusted for Ash Balance, if Ash Balance < 100%

** Adjusted for 100% MAF Recovery

*** Adjusted for catalyst reduction

Autoclave Run Summary: Molybdenum Versus Vanadium Catalyst

APPENDIX C

Autoclave Test Results

Test No.	5771-155	5771-165	5392-059
Catalyst	Mo (K6.2)	Mo	V
wt-% Catalyst (MAF feed basis)	0.97	0.99	1.00
<u>Conversions*, wt-%</u>			
Coal	93.31	93.54	93.09
Heptane Insolubles	90.55	89.67	83.46
510°C+ Non-distillables	77.31	76.55	72.35
371°C+	59.34	55.38	49.61
<u>Product Yields (MAF basis), wt-%</u>			
H ₂ , CO _x , H ₂ S, NH ₃	8.32	8.88	3.2
C ₁ -C ₄	4.94	11.88	3.0
C ₅ -371°C*	48.50	37.87	45.9
371-510°C	20.64	23.88	26.0
510+°C	17.33	18.05	21.5
MAF Coal*	2.82	2.29	2.5
Hydrogen Consumption	(2.55)	(2.85)	(2.1)
Total	100.00	100.00	100.00
<u>Total Liquid Product Properties</u>			
°API	18.5	18.0	15.7
wt-% C	86.95	86.85	85.55
wt-% H	11.0	10.9	11.5
wt-% S	0.74	1.03	1.9
wt-% N	0.25	<0.10	0.65
wt-% O	0.2	0.1	0.4
IBP/50%/EP, °C	64/390/521	61/387/531	72/391/572

All tests at base conditions (420°C, 200 atm., 2 hrs. res. time)

* corrected for ash balance

APPENDIX D

Autoclave Run Summary: Molybdenum Catalyst Comparison At 1 wt-% Metal

Mo Catalyst Comparison At 1 wt-% Metal

Autoclave Test:	6438-31	5771-155	6438-143
Coal Type	AR C1.3	AR C1.3	AR C1.3
Resid Type	R8	R8	R8
Catalyst Type	K6.2	K6.2	K6.7
Resid/Coal, wt/wt	2.14	2.06	2.01
Catalyst, wt% MAF	1.03	0.98	1.00
	10%inH2O	10%inH2O	10%inH2O
Temp., Deg C.	420	420	420
Pressure, atm.	200	200	200
Res. Time, hrs.	2	2	2

Weight Recovery, %	91.85	80.53	94.28
MAF Wt. Rec., %	93.76	81.51	95.80
Ash Balance, %	84.42	86.62	95.18

Conversions, wt% *

MAF Coal	91.08	91.96	91.21
Heptane Ins.	89.44	89.40	90.32
MCRT	76.77	82.75	77.05
510C+	69.20	76.51	67.15
371C+	48.84	58.38	45.50

Prod. Dist., wt%

H2O + COx	2.6	4.3	4.3
H2S	3.9	4.3	3.7
NH3	0.5	0.7	0.3
C1-C4	3.9	4.7	3.2
C5-177C **	12.8	24.8	10.7
177-343C	23.1	18.4	21.6
343-510C	29.4	25.2	30.7
510C+	23.6	17.6	25.4
Unc MAF Coal *	2.8	2.6	2.9
H2 Consumption	-2.6	-2.7	-2.7
Total	100.0	100.0	100.0

Total Liquid Product Properties

API	18.2	18.5	17.4
wt% carbon	86.89	86.95	86.70
wt% hydrogen	10.67	11.00	10.66
wt% sulfur	0.88	0.74	1.17
wt% nitrogen	0.41	0.25	0.63
wt% heptane ins.	1.84	2.72	1.42
wt% MCRT	9.47	8.03	8.75

- * Adjusted for Ash Balance, if Ash Balance < 100%
- ** Adjusted for 100% MAF Recovery (losses assumed to be C5-177C cut)

APPENDIX E

Autoclave Run Summary: Temperature Series With UOP Molybdenum Catalyst

Temperature Series with UOP Mo Catalyst

Autoclave Test:	S771-181	S771-185	S771-188	S771-189	S771-191
Coal Type	AR C1.3	AR C1.3	AR C1.3	AR C1.3	AR C1.3
Resid Type	R8	R8	R8	R8	R8
Catalyst Type	K6.2	K6.2	K6.2	K6.2	K6.2
Resid/Coal, wt/wt	2.00	2.00	2.06	2.03	2.04
Catalyst, wt% MAF	1.00	1.00	0.98	0.99	0.99
Temp., Deg C.	390	405	420	435	450
Pressure, atm.	200	200	200	200	200
Res. Time, hrs.	2	2	2	2	2
Weight Recovery, %	99.62	92.53	83.48	85.13	91.45
MAF Wt. Rec., %	95.18	91.84	81.49	81.02	90.71
Ash Balance, %	109.08	95.75	86.62	94.75	99.11
Conversions, wt% *					
MAF Coal	87.18	92.25	91.79	87.29	71.93
Heptane Ins.	77.37	86.56	89.26	84.10	66.52
S10C+	40.71	56.90	76.45	84.42	82.12
371C+	23.95	36.70	58.32	70.57	75.31
Prod. Dist., wt%					
NH3	0.5	0.3	0.7	0.6	0.6
H2O	0.0	2.2	3.2	0.3	2.9
H2S	2.8	3.5	4.2	4.0	3.8
CO2	0.6	0.6	1.0	0.7	0.7
C1-C4	1.4	2.8	4.7	9.3	20.0
C5-371C**	21.1	29.5	46.9	57.6	49.4
371-S10C	24.1	25.5	21.0	15.7	9.0
S10C+	46.9	34.6	17.6	9.2	6.2
MAF Coal*	4.3	2.8	3.3	5.2	10.2
H2 Consumption***	-1.60	-1.85	-2.63	-2.64	-2.81
Total	100.0	100.0	100.0	100.0	100.0
Total Liquid Product Properties					
API	10.6	13.2	18.8	17	17.6
wt% carbon	85.85	85.75	86.95	86.90	86.00
wt% hydrogen	11.40	11.30	11.00	10.80	10.35
wt% sulfur	1.64	1.39	0.74	0.80	1.00
wt% nitrogen	0.30	0.60	0.35	0.45	0.35
wt% oxygen	0.96	1.06	0.30	0.66	0.74
wt% tot. insol.	0.17	0.099	0.46	0.499	0.87
wt% heptane ins.	6.17	3.87	2.72	4.00	9.13
NCRT	13.7	11.62	8.03	11.92	11.7
D1160:					
ISP, Deg C	113	72	64	72	48
50%, Deg C	487	434	390	320	270
EP, Deg C	520	529	552	428	398
volt @ EP	88.4	70	85.5	80	80

* Adjusted for Ash Balance, if Ash Balance < 100%

** Adjusted for 100% MAF Recovery

*** Adjusted for catalyst reduction

APPENDIX F

Autoclave Run Summary: Catalyst Concentration Series With UOP Molybdenum Catalyst

Catalyst Concentration Series with UOP Mo Catalyst

Autoclave Test:	S860-73	S771-188	S860-48	S860-167	S860-33	S771-201
Coal Type	AR C1.3	AR C1.3	AR C1.3	AR C1.3	AR C1.3	AR C1.3
Resid Type	28	28	28	28	28	28
Catalyst Type	K6.2	K6.2	K6.2	K6.2	K6.2	K6.2
Resid/Coal, wt/wt	3.03	3.06	3.04	3.04	3.98	3.04
Catalyst, wt HAF	1.98	0.98	0.49	0.51	0.20	0.20
Temp., Deg C.	420	420	420	420	420	420
Pressure, atm.	300	300	300	300	300	300
Res. Time, hrs.	2	2	2	2	2	2
Weight Recovery, %	93.96	83.48	86.76	97.03	93.99	96.73
HAF Wt. Rec., %	91.47	81.49	87.96	98.98	93.31	97.43
Ash Balance, %	93.92	86.62	87.80	93.96	96.82	102.09
Conversions, wt %						
HAF Coal	84.53	91.79	93.61	92.94	93.30	93.76
Heptane Ins.	85.89	89.26	88.29	89.93	77.98	80.38
S10C+	74.69	76.45	71.63	69.14	70.40	70.00
371C+	53.84	58.32	54.18	47.07	50.68	48.31
Prod. Dist., wt %						
H2	0.4	0.7	0.4	0.2	0.4	0.7
H2O	0.7	3.2	5.3	3.4	2.7	3.3
H2S	4.3	4.2	3.8	3.7	3.3	3.1
CO2	0.7	1.0	1.0	0.8	0.9	0.7
C1-C4	5.0	4.7	4.8	5.6	4.9	4.0
C5-371C**	45.8	46.9	41.5	36.3	40.8	38.9
371-S10C	23.9	21.0	20.9	25.8	23.3	25.3
S10C+	16.7	17.6	22.3	24.3	23.3	23.8
HAF Coal*	5.6	3.3	3.4	2.3	2.4	2.1
H2 Consumption***	-3.00	-2.63	-2.42	-2.17	-1.97	-1.86
Total	100.0	100.0	100.0	100.0	100.0	100.0
Total Liquid Product Properties						
API	20.3	19.5	15.4	17.4	14.4	15.2
wt% carbon	86.50	86.93	85.93	86.40	84.70	84.70
wt% hydrogen	11.40	11.00	10.75	10.75	10.85	10.85
wt% sulfur	0.57	0.74	1.14	1.17	1.49	1.62
wt% nitrogen	0.50	0.25	0.60	0.70	0.55	0.25
wt% oxygen		0.20				1.18
wt% tol. insol.	0.076	0.46	0.51	NA	1.55	0.85
wt% heptane ins.	1.125	2.72	3.911	2.258	0.9	7.32
HCMT	5.77	8.83	12.33	9.405	12.73	11.3
D1160:						
IBP, Deg C	60	64	49	48	33	50
SBP, Deg C	390	390	427	434	412	411
EP, Deg C	560	552	514	566	546	551
wt% @ EP	85	85.5	70	78	77.2	78

* Adjusted for Ash Balance, if Ash Balance < 100%

** Adjusted for 100% HAF Recovery

*** Adjusted for catalyst reduction

Catalyst Concentration Series with UOP Mo Catalyst

Autoclave Test:	S860-7	S860-147	S860-15	S860-39	S860-159	S860-139
Coal Type	AR C1.3	AR C1.3	AR C1.3	AR C1.3	AR C1.3	AR C1.3
Resid Type	28	28	28	28	28	28
Catalyst Type	K6.2	K6.2	K6.2	K6.2	K6.2	K6.2
Resid/Coal, wt/wt	2.05	1.97	2.03	2.02	2.06	2.00
Catalyst, wt MAFF	0.10	0.10	0.05	0.02	0.02	0.01
Temp., Deg C.	420	420	420	420	420	420
Pressure, atm.	200	200	200	200	200	200
Res. Time, hrs.	2	2	2	2	2	2
Weight Recovery, %	95.49	97.11	94.67	97.28	98.03	96.88
MAF Wt. Rec., %	96.36	91.32	94.47	95.93	97.38	96.77
Ash Balance, %	103.34	94.66	104.89	96.55	95.68	130.58
Conversions, wt %						
MAF Coal	92.58	93.31	91.28	91.49	91.97	82.15
Heptane Ins.	77.40	80.10	79.52	82.87	76.63	62.07
S10C+	67.91	69.74	67.33	71.85	64.09	61.89
371C+	47.02	50.22	46.13	52.31	45.53	43.04
Prod. Dist., wt %						
NH3	0.5	0.3	0.4	0.3	0.3	0.2
H2O	2.9	-0.3	2.4	1.8	0.7	2.5
H2S	3.1	2.8	2.9	3.3	3.0	2.6
CO2	1.0	0.7	1.1	0.8	0.8	0.8
C1-C4	4.8	4.7	4.5	5.4	7.6	6.7
C5-371C+	37.0	42.9	37.1	43.8	36.1	33.4
371-S10C	24.8	23.1	25.2	23.9	23.0	23.2
S10C+	25.2	23.9	25.3	21.4	28.3	27.2
MAF Coal+	2.4	2.5	2.9	3.3	2.7	6.0
H2 Consumption***	-1.82	-2.62	-1.73	-2.03	-2.42	-2.40
Total	100.0	100.0	100.0	100.0	100.0	100.0
Total Liquid Prod.						
API	13.5	14.1	12.3	12.7	12	9.8
wt % carbon	84.10	85.50	84.90	83.90	87.05	84.75
wt % hydrogen	11.30	12.20	10.90	10.85	10.60	10.30
wt % sulfur	1.76	2.10	1.99	1.71	1.82	2.12
wt % nitrogen	0.40	0.65	0.55	0.65	0.66	0.68
wt % oxygen						
wt % tot. insol.	0.49	1.441	1.52	1.48	1.108	1.87
wt % heptane ins.	8.57	7.788	7.11	6.1	8.511	12.801
HCRT	11.25	12.24	11.18	10.64	12.575	16.51
D1160:						
IBP, Deg C	66	32	68	46	81	68
SBP, Deg C	417	403	418	422	434	431
EP, Deg C	533	544	533	551	516	540
wt % 0.5	75.1	77	75	85.5	70	72

Catalyst Concentration Series with UOP Mo Catalyst

Autoclave Test:	S860-173	S860-143	S860-03
Coal Type	AR C1.3	AR C1.3	AR C1.3
Resid Type	R8	R8	R8
Catalyst Type	K6.2	K6.2	K6.2
Resid/Coal, wt/vt	2.01	2.07	2.04
Catalyst, wt% HAF	0.01	0.005	0.00
Temp., Deg C.	420	420	420
Pressure, atm.	200	200	200
Res. Time, hrs.	2	2	2
Weight Recovery, %	89.65	90.68	94.01
HAF Wt. Rec., %	89.69	89.68	94.13
Ash Balance, %	98.73	98.11	113.24
Conversions, wt% *			
HAF Coal	80.58	85.68	63.80
Heptane Ins.	68.69	67.42	83.45
S10C+	64.16	66.66	68.88
371C+	47.49	48.86	52.46
Prod. Dist., wt%			
NH3	0.3	0.4	0.4
H2O	1.9	0.8	2.4
H2S	2.9	2.9	2.8
CO2	0.7	0.6	1.3
C1-C4	5.6	5.4	6.4
C5-371C++	37.7	40.8	40.8
371-S10C	21.1	21.9	20.2
S10C+	24.4	24.0	14.8
HAF Coal*	7.2	5.2	12.0
H2 Consumption***	-1.78	-1.78	-1.14
Total	100.0	100.0	100.0
Total Liquid Prod.			
API	11.8	11.8	13.6
wt% carbon	85.80	84.30	84.90
wt% hydrogen	10.25	11.40	11.35
wt% sulfur	2.07	2.05	2.10
wt% nitrogen	0.65	0.62	0.40
wt% oxygen			
wt% tol. insol.	NA	1.469	0.35
wt% heptane ins.	9.349	11.874	11.04
MCRT	NA	14.895	10.05
D1160:			
IRP, Deg C	73	63	65
808, Deg C	434	421	377
EP, Deg C	541	542	532
volt @ EP	71	74	80

APPENDIX G

Autoclave Run Summary: Molybdenum Catalyst Recycle Study

Mo Catalyst Recycle Study

	1 ST PASS	2 ND PASS	3 RD PASS	4 TH PASS	
Autoclave Test:	S771-155	S860-193	6430-55	6430-105	6430-165
Coal Type	RR C1.3	RR C1.3	RR C1.4	RR C1.3	RR C1.3
Resid Type	RR	RR	RR	RR	RR
Catalyst Type	K6.2	K6.2	K6.3	K6.4	K6.5
Resid/Coal, wt/wt	2.06	2.03	1.99	1.95	1.97
Catalyst, wt% MAF	0.90	0.99	1.01	1.02	1.01
	ERR	ERR	ERR	ERR	ERR
Temp., Deg C.	420	420	420	420	420
Pressure, atm.	200	200	200	200	200
Res. Time, hrs.	2	2	2	2	2

Weight Recovery, %	80.53	77.75	85.16	87.83	85.15
MAF Wt. Rec., %	81.51	78.73	86.03	88.05	85.97
Ash Balance, %	86.62	82.98	92.67	91.57	91.79

Conversions, wt%

MAF Coal	91.96	90.90	92.50	92.49	92.49
Heptane Ins.	89.40	89.72	90.64	91.56	91.29
MCRI	81.88	79.98	79.56	81.03	81.48
S10C+	76.51	72.70	71.19	72.25	72.06
371C+	58.38	52.78	49.50	49.38	50.63

Prod. Dist., wt%

H ₂ O + CO ₂	4.3	4.0	5.8	4.1	4.4
H ₂ S	4.3	4.2	4.3	4.1	4.1
NH ₃	0.7	0.5	0.9	0.4	0.3
C1-C4	4.7	3.8	3.4	3.3	3.3
C5-177C	24.8	22.0	15.9	16.6	16.5
177-343C	18.4	17.3	17.4	18.9	20.3
343-510C	25.2	26.0	30.0	31.2	29.7
510C+	17.6	20.5	22.3	21.4	21.6
Unc MAF Coal *	2.6	3.0	2.5	2.5	2.5
H ₂ Consumption	-2.7	-3.2	-2.5	-2.5	-2.6
Total	100.0	100.0	100.0	100.0	100.0

Total Liquid Product Properties

API	18.5	13.5	13.3	15	15.1
wt% carbon	86.95	87.20	86.62	86.91	86.88
wt% hydrogen	11.00	10.70	10.32	10.92	10.91
wt% sulfur	0.74	0.94	0.99	0.97	0.98
wt% nitrogen	0.25	0.59	0.05	0.59	0.73
wt% heptane ins.	2.72	2.037	2.89	1.44	1.64
wt% MCRI	8.03	8.955	9.37	8	7.93

* Adjusted for Ash Balance, if Ash Balance < 100%

** Adjusted for 100% MAF Recovery (losses assumed to be C5-177C)

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