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TWO-STAGE, CLOSED COUPLED CATALYTIC LIQUEFACTION OF COAL

SEVENTEENTH QUARTERLY REPORT FOR THE PERIOD

1 OCTOBER 1992 - 31 DECEMBER 1992

A.G. Comolli
E.S. Johanson
W.F. Karolkiewicz
L.K. Lee
R.H. Stalzer

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ABSTRACT

This quarterly report covers activities of the Two-Stage, Close-Coupled Catalytic Liquefaction of Coal Program during the period October 1 - December 31, 1992, at Hydrocarbon Research, Inc. in Lawrenceville and Princeton, New Jersey. This DOE contract period is from October 1, 1998 to March 31, 1992.

The overall purpose of the program is to achieve higher yields of better quality transportation and turbine fuels and to lower the capital and production costs in order to make the products from direct coal liquefaction competitive with other fossil fuel products.

This quarterly report covers work on Laboratory Testing and Bench Scale Studies with Black Thunder and Illinois No. 6 coals.

SUMMARY

The major activities during this period were preparation and testing of FeOOH-impregnated Black Thunder coal in Bench Scale Run (CC-15) and evaluation of A060 (AKZO) NiMo extrudates with Illinois #6 coal (CC-16).

Using a procedure developed by Pittsburgh Energy Technology Center approximately 1100 lbs. of iron-impregnated coal was prepared. This FeOOH impregnated coal was evaluated in a 14 day Bench Run (CC-15) with and without FeOOH. Results were promising with distillate yields of 60-66 Wt% MAF coal versus 57.4 Wt% without iron catalyst. The process consisted of FeOOH impregnated coal preparation and use of a pretreatment reactor plus a back-mixed first stage followed by a supported catalyst second stage.

Since Shell 317 bimodal NiMo catalyst is no longer manufactured, Bench run CC-16 was conducted to evaluate A060 AKZO experimental catalyst. This catalyst was prepared in quantity and successfully tested in ebullated beds at Wilsonville. Results show the overall performance to be as good as Shell 317 and that A060 is a good substitute catalyst for future experimentation.

INTRODUCTION

The studies conducted in this quarterly report are presented by task and in sequence.

Task 1 is the Management Plan. *Task 2* is for Laboratory Studies and includes microautoclave and micro-reactor work. *Task 3* is for Bench-Scale studies. *Task 4* is for Mini PDU Scale-up. *Task 5* is the Technical Assessment, including Modelling, Design and Economics. *Task 6* is Program Administration.

The contract period was October 1, 1998 to September 30, 1992 and has been extended to March 31, 1993.

TASK 2 - LABORATORY SCALE STUDIES

COAL AND SOLVENT EVALUATION

In preparation for run CC-16 (Evaluation of AO60 Akzo Catalyst) with a new lot of Illinois #6 coal a microautoclave comparison was conducted. A standard baseline solvent obtained from a heavy distillate from a Wilsonville Illinois No. 6 Bituminous Coal Run (HRI 5198) and a Sub-Bituminous derived solvent from HRI PDU Run 260-03 (Tank #4, L-769) were used to determine the convertability of a new lot of Illinois No. 6 coal, HRI 6081. The coal basis for comparison was an Illinois No. 6 coal used in previous Bench-Scale catalyst studies of the Low Severity CTSL program, Contract #85PC80002 as reported in Topical Report DOE-80002-T-2. These catalyst evaluation studies of Davison Amocat 1C, UOP RCM-4 and Shell S-317 were used to judge the performance of a new Amocat 1C type NiMo catalyst prepared by Akzo. Results are shown in *Table 1*. Note that catalytic coal conversion is equivalent with lower catalytic resid conversion indicated with standard solvent. Also shown is that the Wyoming coal solvent is of lower quality than the Wilsonville Bituminous derived solvent.

TABLE 1
MICROAUTOCLAVE EVALUATION OF ILLINOIS NO. 6 COAL (HRI-6081)
FOR RUN CC-16

Test at 800°F for 30 Minutes
4/1/(1) Solvent/Coal/ (Catalyst) Ratio
2000 psig Hydrogen Atmosphere

Therm/Cat	Solvent	Coal Conversion, Wt%	
		HRI-5174 ⁽¹⁾	HRI-6081 ⁽²⁾
Thermal	HRI-5198 ⁽³⁾	79.9	86.5
Catalytic	HRI-5198 ⁽³⁾	91.0	91.7
Thermal	L-769 ⁽⁴⁾		52.0
Catalytic	L-769 ⁽⁴⁾		89.2

Therm/Cat	Solvent	TGA ⁽⁵⁾ RESID CONVERSION, Wt%	
		HRI-5174	HRI-6081
Thermal	HRI-5198 ⁽³⁾	38.5	34.1
Catalytic	HRI-5198 ⁽³⁾	70.9	57.5
Thermal	L-769 ⁽⁴⁾		28.3
Catalytic	L-769 ⁽⁴⁾		47.3

NOTES:

- ⁽¹⁾ HRI-5174 was an Illinois No. 6 Coal used in Catalyst Evaluation Runs 227-35, -36, and -37.
- ⁽²⁾ HRI-6081 will be used in Run 227-76 (CC-16). The sample was a composite of the undried, pulverized coal just received.
- ⁽³⁾ Standard microautoclave solvent (Wilsonville heavy distillate) from Illinois No. 6 coal.
- ⁽⁴⁾ Filtered Tank #4 oil derived from Black Thunder coal sampled post-July 1992 infusion from PDU Run 260-03.
- ⁽⁵⁾ TGA Thermo Gravimetric Analysis method for determination of 975°F+ conversion.

TASK 3 - BENCH SCALE STUDIES

Bench Runs CC-15 "The Evaluation of Iron Impregnated Sub-Bituminous Coal" and CC-16 "The Evaluation of Bi Modal, NiMo, A060 AKZO Catalyst" were conducted in this period.

RUN CC-15

OBJECTIVE

The objective this run was to evaluate the performance of dispersed iron-based catalyst on the Liquefaction of Black Thunder Mine Coal in a thermal-catalytic mode in the bench scale continuous flow unit.

OPERATIONS

The iron catalyst precursor was impregnated on the coal matrix using an incipient wetness technique developed by Pittsburgh Energy Technology Center and described in U.S. Patent No. 5,096,570, March 17, 1992, "Method for Dispersing Catalyst onto Particulate Material" by A. Cugini and B. Utz, and scaled up by HRI for this Bench-Run. Black Thunder Mine coal was impregnated with hydrated iron oxide (FeOOH) at 5000 ppm of iron using this technique and was liquefied in a thermal catalytic mode. The iron catalyst precursor was first activated in a pretreating stage (at 527 or 570°F) prior to the thermal (dispersed catalyst) stage. The catalytic stage was an ebullated bed reactor consisting of Shell S-317 NiMo catalyst. The performance of this system was compared with that obtained without the use of a dispersed iron catalyst using the same lot of Black Thunder coal.

The iron catalyst precursor (FeOOH) was activated with H₂S at 522°F (Condition 1) and 565°F (Conditions 2 to 4). The test was conducted using constant conditions of space velocity of about 42.5 lb coal/h/ft³ (supported catalyst), and temperatures of 800°F and 775°F for the thermal (dispersed catalyst) and the catalytic reactors, respectively. The run conditions and results are given in *Tables 2 and 3*, attached.

The yield of C₁-C₃ gas remained constant around 10.5 W% maf coal reflecting the relatively stable operation. Although the results were masked by the continuous deactivation of the supported catalyst throughout the course of the run, the process performance in term of coal conversion, 975°F⁺ conversion, and C₄-975°F distillate yield were higher in tests with iron impregnated coal as compared with the untreated coal (Condition 3). *Figure 1* shows the distillate yield, coal and residual oil conversion at each condition. *Figure 2* illustrates the distillate selectivity at each condition.

In the presence of iron additive, coal conversions varied slightly between 92.7 and 93.1 W% maf coal (Conditions 1, 2 and 4). In Condition 3, no dispersed catalyst was used. The coal conversion dropped by 2.7 W% to 90.0 W%. The decrease in residuum conversion (3.7 W%) and distillate yield (7.7 W%) were more noticeable because these performances were more sensitive to catalyst activity. *Figure 3* attached shows the effect of catalyst deactivation on distillate yield, resid conversion and denitrogenation. Iron additive was reintroduced in Condition 4, repeat of Condition 2. The coal conversion increased back up to 92.7 W%, while the residuum conversion and distillate yield rebound to a level as projected assuming linear deactivation in catalyst activity. Interstage samples show that all coal conversion occurred in the thermal stage (at 800°F). Similar trend was

observed on the effect of iron additive on coal conversion in the interstage sample, i.e. 3.7 to 4.1 W% lower when no additive was used.

The iron impregnated coal contained substantially higher nitrogen content (L-780, 2.64 W%) than the untreated coal (HRI-5828, 0.95 W%). This was probably due to the sorption of ammonium nitrate on the coal matrix during the precipitation procedure. As a result, both the interstage and the two-stage product liquids exhibited higher nitrogen content with iron impregnated coal was used, as shown in *Figure 4* versus when iron oxide was used on Black Thunder coal and with supported NiMo catalyst in runs CC-4 and CC-7.

SUMMARY

Run CC-15 (227-75) was successfully completed with three conditions on FeOOH impregnated coals and one condition with the same lot of untreated Black Thunder coal.

At relatively low concentration of 0.5 W%, the dispersed iron additive improved distillate yield, coal and 975°F+ conversions. The highest distillate yield of 66.1 and coal conversion of 93.1 W% were obtained in Condition 1, a decrease in distillate yield and resid conversion of about 6% occurs without the iron additive when considering results from Conditions 2, 3 and 4.

The impregnated procedure may have introduced some additional nitrogen to the coal matrix and resulted in a higher nitrogen product.

The economics of the improved process performance should be evaluated against the costs for impregnating the iron catalyst precursor as well as the additional hydrotreating requirements.

TABLE 2

EVALUATION OF FEOOH IMPREGNATED COAL (CC-15)

Catalyst: Shell 317 Ni/Mo Coal: Black Thunder Mine

Condition	1	2	3	4
MODE				
1st Stage	Dispersed	Dispersed	Therm.	Dispersed
2nd Stage	Supported Cat.	Supported Cat.	Supported Cat.	Supported Cat.
TEMPERATURE °F				
Pretreating	522	568	566	566
1st Stage	799	801	801	800
2nd Stage	775	774	775	773
Catalyst Age, Lb coal/lb cat.				
2nd Stage	147	228	316	403
SPACE VELOCITY				
Lb coal/h/ft ³ , cat.	42.3	41.7	43.7	42.7
Additive Rate, W% mf coal	0.4	0.4	None	0.4
H ₂ S Rate, W% mf coal	3.5	3.6	3.2	3.0
PERFORMANCE, W% MAF COAL				
C ₁ -C ₃	10.6	10.8	10.4	10.5
H ₂ Used	9.3	9.0	8.1	8.3
C ₄ -975°F	66.1	64.1	56.4	60.2
Coal Conversion				
1st Stage	91.1	91.1	87.0	90.7
2nd Stage	93.1	92.7	90.0	92.7
975°F+ Conv.	89.1	87.7	84.0	85.3

TABLE 3**EVALUATION OF FEOOH IMPREGNATED COAL (CC-15)****Catalyst: Shell 317 Ni/Mo Coal: Black Thunder Mine**

Condition	1	2	3	4
NORMALIZED YIELDS, W% DRY FRESH FEED				
C ₁ -C ₃ in Gas	9.94	10.13	9.94	9.86
C ₄ -C ₇ in Gas	2.80	2.91	3.00	2.57
IBP-390°F	16.26	16.36	15.61	14.69
390-500°F	13.67	13.30	12.22	11.12
500-650°F	14.55	17.59	14.98	15.70
650-850°F	10.04	7.99	6.66	10.08
850-925°F	1.81	2.07	1.66	2.43
925°F+ Resid	3.79	4.67	5.66	6.98
Unconverted Coal	6.50	6.87	9.40	6.85
Ash	6.03	6.03	5.71	6.03
Water	15.52	16.41	19.33	17.43
CO _x	2.11	1.58	2.68	1.71
NH ₃	2.71	2.62	0.73	2.49
H ₂ S	-0.02	-0.07	0.25	-0.10
Total	108.72	108.46	107.82	107.84

Run CC-15 Process Performance FeOOH Impregnated Black Thunder Coal

FIGURE 1

Run CC-15
Distillate Yield

FIGURE 2

Run CC-15 Process Performance

Effect of Catalyst Deactivation [W% maf Coal]

■ HDN ♦ Distillate * Resid Conv.

FIGURE 4

* Run CC-4 and CC-7 used Magnetite Fe_2O_3 plus supported NiMo Catalyst.

** Run CC-15 used FeOOH plus supported catalyst.

*** C₂, C₃, C₄, and C₅ refer to comparable run conditions.

RUN CC-16

OBJECTIVE

Evaluate the performance of AO60, AKZO, $\frac{1}{16}$ " NiMo extrudates at standard conditions with Illinois #6 coal to qualify this catalyst in place of obsolete Shell 317 NiMo.

SCOPE OF WORK

The coal for this run was an Illinois No. 6 coal, and the catalyst was AKZO, AO-60, $\frac{1}{16}$ " extrudates for both stages. The start-up oil was a blend of pressure filter liquids derived from previous runs using Illinois No. 6 coal or Black Thunder Mine coal.

The operating conditions for this run were chosen so as to duplicate the operating conditions used in previous catalyst evaluation runs 227-35, 36, 37 (I-16, I-17, I-18). These were a series of runs performed for catalyst evaluation using Amocat 1C $\frac{1}{32}$ " extrudates, UOP RCM4 $\frac{1}{20}$ " spheres, and Shell S-317 $\frac{1}{32}$ " extrudates on Illinois No. 6 coal. This allows a direct comparison of the results of this run with the results of the previous runs so as to evaluate the AO-60 catalyst in the CTSL process.

The operating conditions are given in *Table 4*. The run consisted of only two conditions, the first lasting nine days and the second lasting 4 days. The first and second stage reactor temperatures were 750°F and 800°F in Condition 1 and 775°F and 810°F in Condition 2. The dry coal space velocity was 46 lbs/hr/ft³ catalyst (per stage) throughout the run.

The yield of distillate obtained from the use of AO60 catalyst is compared with the yield from Amocat 1C (an earlier version of AO60 prepared by Davison) UOP NiMo spheres RCM 4 and Shell 317 nickel moly the standard catalyst used for Bench-Scale Studies and now no longer manufactured. Results are shown in *Table 5* and catalyst properties in *Table 6*.

Coal and resid conversion are illustrated in *Figures 5 and 6* and C₁-C₃ and C₄-975°F yield in *Figures 7 and 8* attached. Note the yields are on a dry coal basis and that the Illinois #6 feed coal contained 10.6 Wt% ash. Residual oil conversion and distillate yields were very favorable for the AO60 when compared with the other extrudates.

SUMMARY

Run 227-76 (CC-16) completed, as scheduled, 13 days of operation with Illinois No. 6 coal, testing the activity of AKZO AO-60 $\frac{1}{16}$ " nickel molybdate extrudate catalyst in the CTSL process. The conditions for the run duplicated the conditions of three previous catalyst evaluation runs, which had tested $\frac{1}{32}$ " Amocat 1C extrudates, $\frac{1}{20}$ " UOP RCM4 spheres, and Shell S-317 extrudates. These three catalysts had performed similarly and very well in Runs 227-35, -36, and -37 (I-16, -17, and -18).

The resid conversions and distillate yields for the AO-60 and the other catalysts were very similar. In Condition 1 (750°F first stage 800°F second stage, and 46 lb/hr/ft³ catalyst/stage), resid conversion decreased from 88.4 to 82.9 W% of maf coal, and the C₄-975°F distillate yield decreased from 73.7 to 68.6 W% between periods 4 and 9. In the higher severity Condition 2 (775°F first stage, 810°F second stage, and increased feed coal concentration) the resid conversion averaged 90.0 W%, and the distillate yield averaged 72.7 W%. The AO-60 catalyst did selectively produce slightly more naphtha and less vacuum gas oil and residuum than the other three catalysts.

Overall, the AO-60 catalyst performed very well in the CTSL process. There was no apparent excessive physical degradation of the catalyst in this 13-day operation. Based on the information from this run and operations at Wilsonville the AO-60 catalyst would be an appropriate catalyst for the future CTSL operations.

TABLE 4
OPERATING CONDITIONS
RUN 227-76

CONDITION PERIODS	1 1-9	2 10-13
<hr/>		
NOMINAL CONDITIONS		
Coal Space Velocity (Lbs/hr/ft ³ Cat.)	46	46
Slurry Oil/Coal Ratio	1.5	1.1
Solvent/Coal Ratio **	1.8	1.4
Unit pressure (PSIG)	2500	2500
TEMPERATURES °F		
Reactor 1	750	775
Reactor 2	800	810
Atmospheric Still Reboiler	610	625
Hot Separator Liquid	560	600
RECYCLES (WT% DRY COAL)		
Coal	680	680
Pressure Filt. Liq. to Slurry	150	110
Buffer 1st Stage	15	15
Buffer 2nd Stage	15	15
Topped Separator Bottoms	0	0

** Includes buffer oil to first and second stages.

TABLE 5**COMPARISON OF A0-60, AMOCAT 1C, UOP RCM4, SHELL 317****PERIOD 9**

	A060	AMOCAT 1C	RCM4	S-317
Coal Conversion (W% MAF)	92.5	93.41	93.67	93.73
975°F+ Conversion (W% MAF)	84.4	84.97	84.91	84.38
H ₂ Consumption (W% Dry)	6.46	6.47	6.26	6.26
YIELDS (W% DRY BASIS)				
C ₁ -C ₃ Gases	5.76	5.00	5.28	5.15
C ₄ -390°F	17.18	15.01	15.51	15.17
390-650°F	28.03	30.06	28.75	28.06
650-975°F	16.13	17.91	18.37	18.26
975°F+	7.28	7.55	7.84	8.36q
C ₄ -975°F	61.34	62.99	62.62	61.48

PERIOD 13

	A060	AMOCAT 1C	RCM4	S-317
Coal Conversion (W% MAF)	94.1	94.6	95.07	94.91
975°F+ Conversion (W% MAF)	89.7	89.42	90.97	87.72
H ₂ Consumption (W% Dry)	7.02	6.99	7.20	6.77
YIELDS (W% DRY BASIS)				
C ₁ -C ₃ Gases	7.71	7.04	8.42	6.13
C ₄ -390°F	21.68	20.13	21.73	18.13
390-650°F	33.21	33.11	32.55	32.66
650-975°F	11.46	12.95	12.04	14.05
975°F+	3.98	4.64	3.66	6.43
C ₄ -975°F	66.35	66.18	66.32	64.85

TABLE 6
FRESH CATALYST PROPERTIES

HRI NUMBER Run Number	5337 I-16	5339 I-17	5359 I-18	6043 CC-16
Catalyst	Amocat 1C	UOP RCM4	S-317	AO-60
Nominal Size	$\frac{1}{32}$ "	$\frac{1}{20}$ " sphere	$\frac{1}{32}$ "	$\frac{1}{16}$ "
CHEMICAL ANALYSIS				
Molybdenum	10.95	9.60	10.76	12.25
Nickel	1.91	1.79	2.86	2.6
PHYSICAL PROPERTIES				
Bulk Density, (gm/cc)	0.646	0.602	0.638	0.557
Particle Density, 10psi Hg (gm/cc)	0.811	0.866	0.990	0.872
Skeletal Density, 60,000 psi Hg (gm/cc)	1.776	2.164	3.031	3.547
Surface Area (Calc.), (M_2 /gm)	273	260	263	286
M_2 /cc particle	221	225	260	249
Pore Volume, (cc/gm)	0.670	0.772	0.681	0.874
cc/cc particle	0.543	0.668	0.674	0.762
Average Crush Strength, (Lb/mm)	2.17	6.70	1.78	2.67
Average Diameter (mm)	0.90	1.55	1.00	1.59
Length, Average (mm)	3.3		3.8	3.8
< 2.5 mm (W%)	18.7		2.8	6.0
2.5 to 6.3 mm (W%)	78.8		70.0	74.1
> 6.3 mm (W%)	2.4		27.2	19.9
PORE SIZE DISTRIBUTION, CC/GM				
Diameter > 30 A	0.67	0.77	0.68	0.873
Diameter > 100 A	0.41	0.69	0.37	0.54
Diameter > 250 A	0.12	0.04	0.17	0.24
Diameter > 500 A	0.10	0.015	0.16	0.12
Diameter > 1500 A	0.06	0.005	0.04	0.008
Diameter > 4000 A	0.00	0.00	0.04	0.008
PORE DIAMETER (A)				
At Median Pore Volume	110	156	105	125
4 [Pore Vol./Calc Surf Area]	98	119	104	122

FIGURE 5

975F + CONVERSION

FIGURE 6

FIGURE 7

C1-C3 GAS YIELD

FIGURE 8

TASK 4 - TECHNICAL ASSESSMENT

No activity in this period.

TASK 5 - ADMINISTRATION

The following topical reports are being prepared:

1. Bench Scale Studies - Sub-Bituminous Coal
2. Bench Scale Studies - Bituminous Cal
3. Laboratory Scale Studies and Technical Assessment
4. Final Topical Report - "Close Coupled Two Stage Catalytic Coal Liquefaction"

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