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CATALYTIC MULTI-STAGE LIQUEFACTION OF COAL

FIFTH QUARTERLY REPORT FOR THE PERIOD

1 OCTOBER 1993 - 31 DECEMBER 1993

A.G. Comolli
E.S. Johanson
L.K. Lee
V.R. Pradhan
R.H. Stalzer

FINAL ✓

WORK PERFORMED UNDER CONTRACT

DE-AC22-93PC92147

HYDROCARBON RESEARCH, INC.
100 OVERLOOK CENTER, SUITE 400
PRINCETON, NJ 08540

JANUARY 1994

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ABSTRACT

This quarterly report covers the activities of Catalytic Multi-Stage Liquefaction of Coal during the Period October 1 - December 31, 1993, at Hydrocarbon Research, Inc. in Lawrenceville and Princeton, New Jersey. This DOE Contract Period is from December 8, 1992 to December 7, 1994.

The overall objective of this program is to produce liquid fuels from coal by direct liquefaction at a cost that is competitive with conventional fuels. Specifically, this continuous bench-scale program contains provisions to examine new ideas in areas such as: low temperature pretreatments, more effective catalysts, on-line hydrotreating, new coal feedstocks, other hydrogen sources, more concentrated coal feeds and other highly responsive process improvements while assessing the design and economics of the bench-scale results.

This quarterly report covers work on Laboratory Scale Studies, Continuous Bench-Scale Operations, Technical Assessment and Project Management.

SUMMARY

This report describes preliminary results obtained from the residual oil microautoclave reactivity tests and the future tests in this series planned ahead. It also covers the Laboratory Support work in terms of microautoclave testing for screening proper first-stage ebullated bed reactor supported catalyst to be used in the upcoming bench Run CMSL-04. This bench Run, CMSL-04, is planned to be carried out under similar mode/configuration as the Run CMSL-03, except that it will incorporate three main differences from CMSL-03: (i) CO/H₂ composition of 90/10 V/V%, (ii) supported Co-Mo/Alumina or Ni-Mo/Alumina extrudate catalyst in the first stage reactor, and (iii) on-line hydrotreater.

The main objective of Bench Run CMSL-04 is to evaluate the impact of using synthesis gas as reducing gas in the first stage of a two-stage liquefaction scheme. In combination with water, synthesis gas is known to be effective in dissolution of coal and removal of oxygen at relatively low thermal severity conditions. The use of synthesis gas, rather than high purity hydrogen, may lead to potential savings in both capital and operating costs through possible elimination of the external water-gas shift reactor and a smaller first stage reactor.

Economic studies, as a part of the technical assessment, have been continued in this quarter. Detailed economics of the impact of lowering solvent/coal ratio in coal liquefaction are being addressed (based on results obtained during the bench Run CMSL-02).

CMSL Program planning/review meeting was conducted with the DOE during December 1993. The plans for upcoming bench Runs were discussed during this meeting.

TASK 2 - LABORATORY SCALE STUDIES

RESIDUAL OIL ACTIVITY EVALUATION

The last quarterly report discussed scoping tests in the Residual Oil Activity Program. A Detailed Plan of the first 24 microautoclave tests is shown in Table 1. During this reporting Period, additional tests, RE-07 through RE-10, were completed.

Results of Microautoclave Runs RE-07 to RE-10 : Residual Oil Activity Evaluation For Run 227-70 Products

Runs RE-07 to RE-10 of the Microautoclave Residual Oil Activity Program have been completed. These runs evaluated the residual oil reactivity for the residual oil components produced in Periods 5 and 12 of Run 227-70, which tested Black Thunder Mine Coal.

Figure 1 compares the residual oils conversion for the products from these two operating periods and includes the results, previously reported for the product of Period 23 of Run 227-55. The residual oils conversion is based on the following definition:

Residual Oils Conversion = 100 {1 - (Wt% 975°F Resid in Product Oil / Wt% of 975°F Resid in the Feed Oil)}

Where, the 975°F resid contents are determined from the TGA analyses of the feed and the product oils.

Both the Bench Runs 227-55 (CC-1) and 227-70 (CC-12) were carried out with the Wyoming Black Thunder Mine subbituminous coal. CC-1 was carried out with two catalytic ebullated bed reactors in the CTSL Mode, while CC-12 was carried out in the same CTSL Mode but with a rejuvenated Shell-317 catalyst in the first reactor stage.

Nominally, the Run 227-70 residual oils were more reactive than the Run 227-55-23 oil. The conversions obtained with the 227-70-5 sample was equivalent to a reactivity 1.6-1.9 times that of the 227-55-23 sample. The conversion obtained with the 227-70-12 sample was slightly lower than that of the 227-70-5 sample in an equivalent test, but about 1.75 times that of run 227-55-23 sample (the product sample from a second test with the 227-70-12 sample was contaminated during product recovery).

However, there are two anomalies qualifying this interpretation of these results. Reanalysis of the feeds and products from these four tests is planned to clarify the significance of the reported difference of the blended feed compositions from that obtained in the earlier tests with the 227-55-23 feed blend. Also, the failed test with the 227-70-12 sample will be repeated, along with replicate of a test with the 227-70-5 sample with the object to clarify the very high liquid recovery (1.16%) obtained in the first test.

These results indicate that this test method can determine significant differences in residual oil activity, and it is planned to complete the entire program of 14 additional runs. This program includes tests on three more products from Black Thunder Mine coal operations (including a first stage sample), four samples from Illinois coal operations, and two samples from New Mexico operations (including an interstage sample).

Summary of Test Conditions

Catalyst	Presulfided Criterion C-317 Catalyst
Blends	30 W% of the subject residuum blended with 70% coal liquefaction distillate
Temperature	825 F
Pressure	2,000 psig hydrogen
Time	30 minutes for the current tests
Catalyst/oil	0.25 and 1.00 grams/gram
Analyses	TGA residual oil content of feed and products

The Table 2 summarizes the conditions and results for Runs RE-01 through RE-10, and the Figure 1 summarizes the conversions for the various feeds and related to catalytic severity, minute * catalyst/oil.

In Figure 1, nominally all of the tests with the 227-70 samples gave greater degrees of residual oil conversion than the 227-55 derived materials. At the lower severity condition, 31.5% of the 227-70-5 residuum was converted, 29.7% of the 227-70-12 residuum, compared to 19.4% and 22.7% conversions for tests with the 227-55-23 residuum. For the higher severity condition, 55.9% of the 227-70-05 residuum was converted, compared to 45.7% and 48.8% conversion for the 227-55-23 material. The reactivity of 227-70-05 residuum was 1.93 times (low severity test) and 1.59 times (high severity test) than that of the 227-55-23 residuum. The reactivity of 227-70-12 residuum was 1.76 times (low severity test) that of the 227-55-23 residuum. The reactivity of 227-70-05 residuum was 1.93 times (low severity test) and 1.59 times (high severity test) than that of the 227-55-23 residuum. However, there are two considerations that might qualify these conclusions:

A) The TGA residuum analysis of the feeds for tests RE-07 through RE-09 was very much higher, 37.5 and 37.9%, than the nominal 30% of the blend preparation. If there was a calibration shift at the time of the analyses of these feeds it could be considered to affect the product analyses as well so that the critical product/feed concentration ratio would not be greatly affected. However, the products were analyzed on November 24th, while the feeds were analyzed on December 3rd. It is understood that the TGA instrument did require some readjustments before the feed analyses could be completed. If this proves to have been the case, it is recommended that the feed and products for Runs RE-07, RE-08, and RE-10 be reanalyzed at the same time.

B) Product oil recoveries were very high for these later runs compared to those for Runs RE-01 through 06, over 100% and up to 122% (see the attached table). This indicates possible THF or solids retention in the rotoevaporated microautoclave washings. However, the reported THF contents (by TGA) were not exceptionally high (see the table), on the average being very close to those of products the earlier runs. Also, ash contents of the products all were very low, of the order of 0.01 W%. Nevertheless, there is the possibility of relatively poor rotoevaporator performance which should be reviewed. It is planned to carry out a replicate of Run RE-07 to resolve this anomaly, along with a

replicate of Run RE-09 where the product sample was contaminated during product handling.

LABORATORY SUPPORT FOR BENCH RUN CMSL-04

The next Bench Run, CMSL-4, is to be carried out on Black Thunder Coal using syngas and supported (CoMo or NiMo/Alumina) first stage catalyst (and Shell-317 Ni-Mo in the second stage) and an interstage separator. It is deemed necessary to carry out a few microautoclave tests comparing the dispersed moly catalyst (ammonium heptamolybdate additive), employed in the last run, CMSL-3, with the supported Co-Mo/Alumina (Amocat 1A) catalyst for CO- shift Conversion Activity. It is also necessary that in order for this supported catalyst to be effective for an insitu H₂-generation by shift reaction, it should not act as a methanation catalyst. Earlier tests with equimolar amounts of CO and water (without any coal) have shown that Amocat 1 A catalyst was as active or even more so that the dispersed molybdenum containing, ammonium heptamolybdate catalyst (although the active metal Mo-concentration in supported catalyst was as high as 50 times that in the dispersed catalyst). In the sulfided form it did not yield significant amount of methane in the products. The microautoclave tests listed below will be carried out to substantiate the results obtained earlier with the supported Co-Mo catalyst further and get more confidence in the catalytic behavior of this system under shift conversion conditions.

Test #	Catalyst	Solvent
CL-96	AHM+DMDS	L-769
CL-97	DMDS	L-769
CL-98	AMOCAT 1A+DMDS	L-769
CL-99	AMOCAT 1A	L-769
CL-100	AMOCAT 1A+DMDS	NONE
CL-101	AHM+DMDS	NONE
CL-102	SHELL-317 + DMDS	L-769
CL-103	SHELL-317 + DMDS	NONE

[Conditions: 750°F, 30 min, 800 psig CO (cold), 0.85 gm water]

In the above reactions, shift activity of a catalyst will be determined based on the CO-Conversion, as per the gas-phase analysis results.

TASK 3 - BENCH-SCALE STUDIES

RUN CMSL-04 : IMPACT OF SYNGAS ON LIQUEFACTION

OBJECTIVES

To evaluate the effect of reaction severity on the dissolution of Black Thunder Mine coal using syngas as reducing gas in the first stage of a two-stage ebullated bed configuration with an on-line hydrotreater.

Specifically, technical objectives are:

1. To determine the relative performance of CO/H₂ vs H₂/H₂ in a fully - ebullated two-stage system.
2. To determine the effect of an interstage letdown on CTSL process performance.

BACKGROUND:

Operation using syngas while feeding Black Thunder sub-bituminous coal has been demonstrated in Run CMSL-03 with promising results, i.e. improved yields, kinetic and hydrogen efficiency. This exceptional performance was obtained using ammonium heptamolybdate (AHM) in the feed to a non-supported catalyst first stage followed by a supported catalyst second stage. The AHM used in CMSL-03 was equivalent to 1500 ppm Mo per dry coal feed.

In this 15-day operation, four conditions will be examined using supported CoMo or NiMo catalyst in both stages. This will permit a direct operating and cost comparison of syngas vs hydrogen and the effect of interstage separation. The proposed Run Plan is given in Table 3.

Microautoclave test results indicated Amocat 1A, a CoMo catalyst, was as active as AHM (1500 ppm of Mo) in promoting the water gas shift reaction, nitrogen removal and coal dissolution.

EXPECTED RESULTS

1. Equivalent yields with syngas or hydrogen but with better hydrogen efficiency for syngas operations,
2. A direct comparison of syngas/H₂O vs all hydrogen feed,

TASK 5. PROJECT MANAGEMENT

The planning/review meeting for the CMSL Program with DOE was held during December 1993. Plans for the two upcoming bench Runs, CMSL-04 and CMSL-05 were discussed. The plans for CMSL-04 are addressed in the earlier sections of this Report. It has been proposed that the bench Run CMSL-05 be conducted with Illinois No. 6 coal to investigate the effect of the interstage separation, an on-line hydrotreater, and the use of synthesis gas in the first stage ebullated bed reactor. These two bench Runs will be conducted in late February and March 1994.

TABLE 1. SCHEDULE FOR MICROAUTOCLAVE EVALUATION OF THE RESIDUAL OIL ACTIVITY

CHARGE NO. - 846-211

CONDITIONS FOR PREPARATION OF PRESULFIDED CATALYST

Presulfiding Agent - 3.5 W% TNPS in Tetralin

Catalyst Charge - 2 * 180 cc (about 220 grams)

Oil Feed Rate - 2 x 300 grams/hour (Total requirement about 17000 grams)

Pressure - 2000 psig hydrogen

Temperatures - 1 hour at 450 F

3 hours at 500 F

8 hours heating 500 to 700 F

2 hours at 700 F

CONDITIONS FOR MICROAUTOCLAVE TESTS

Pressure - 2000 psig

Pressurizing Gas - Hydrogen

Solvent - HRI 5868 Wilsonville Distillate (Blended with Test Residuum)

Catalyst (where specified) - HRI 5902P, Presulfided Criterion 1/32" S-317 Catalyst, HRI 5902

Run	----- Test Oil -----	-----Charge, Gms-----			Gas	Pressure	Time	Temp.
		PFL	Blend	Catalyst		Psig	Minutes	F

SCOPING TESTS

RE-01	227-55-23A PFL	2	0	2	H2	2000	30	825
RE-02	227-55-23A PFL	8	0	2	H2	2000	30	825
RE-03	227-55-23A PFL	2	0	2	H2	2000	60	825
RE-04	227-55-23A PFL	8	0	2	H2	2000	60	825
RE-05	30% 227-55-23A 975 F+ Blend *	0	2	2	H2	2000	30	825
RE-06	30% 227-55-23A 975 F+ Blend *	0	8	2	H2	2000	30	825

BLACK THUNDER MINE COAL PRODUCTS

RE-07	30% 227-70-5 975 F+ Blend *	0	2	2	H2	2000	30	825	
RE-08	30% 227-70-5 975 F+ Blend *	0	8	2	H2	2000	30	825	
RE-09	30% 227-70-12 975 F+ Blend *	0	2	2	H2	2000	30	825	
RE-10	30% 227-70-12 975 F+ Blend *	0	8	2	H2	2000	30	825	
RE-07A	30% 227-70-5 975 F+ Blend *	0	2	2	H2	2000	30	825	Replicate RE-07
RE-09A	30% 227-70-12 975 F+ Blend *	0	2	2	H2	2000	30	825	Replicate RE-09
RE-11	30% 227-71-13 975 F+ Blend *	0	2	2	H2	2000	30	825	
RE-12	30% 227-71-13 975 F+ Blend *	0	8	2	H2	2000	30	825	
RE-13	30% 227-75-8 975 F+ Blend *	0	2	2	H2	2000	30	825	
RE-14	30% 227-75-9A 975 F+ Blend *	0	2	2	H2	2000	30	825	Interstage Sample

ILLINOIS NO. 6 COAL PRODUCTS

RE-15	30%	227-66-5	975 F+	Blend *	0	2	2	H2	2000	30	825
RE-16	30%	227-66-5	975 F+	Blend *	0	8	2	H2	2000	30	825
RE-17	30%	227-66-14	975 F+	Blend *	0	2	2	H2	2000	30	825
RE-18	30%	227-66-14	975 F+	Blend *	0	8	2	H2	2000	30	825
RE-19	30%	227-66-23	975 F+	Blend *	0	2	2	H2	2000	30	825
RE-20	30%	227-66-23	975 F+	Blend *	0	8	2	H2	2000	30	825
RE-21	30%	227-72-17	975 F+	Blend *	0	2	2	H2	2000	30	825
RE-22	30%	227-72-17	975 F+	Blend *	0	8	2	H2	2000	30	825

NEW MEXICO COAL PRODUCTS

RE-23	30%	227-68-16	975 F+	Blend *	0	2	2	H2	2000	30	825
RE-24	30%	227-68-17A	975 F+	Blend *	0	2	2	H2	2000	30	825 Interstage Sample

* Blends are 30% Test Residuum and 70% HRI 5868 Distillate

Resactschd.tab (Revision 8/9/93, Substitute 227-70-5 Residuum for 227-70-6 Residuum)
 (Revision 10/8/93, Substitute 227-71-13 Residuum for 227-71-14 Residuum)
 (Revision 1/3/94, Replicates of Runs RE-07 and RE-09)

TABLE 2. MICROAUTOCLAVE TESTS EVALUATING RESIDUAL OIL ACTIVITIES

Evaluation of 975 F+ Residual Oils From CTSL Run 227-70, with Black Thunder Coal

Catalyst - HRI 5902P, Criterion S-317, Presulfided with TNPS/Tetralin in Fixed Bed

Pressure - 2000 Psig H₂

Run	RE-	Feed	Time, Min	Cat/Oil	Residuum, W%		Min*Cat/Oil	Cprod/ Cfeed	Recovered W%**	Liquid THF, %
					Charge	Product				
1		227-55-23 PFL	30	1.00	29.64	15.17	30.0	0.512	96.5	4.4
2		227-55-23 PFL	30	0.25	29.64	22.90	7.5	0.773	89.4	2.1
3		227-55-23 PFL	60	1.00	29.64	11.74	60.0	0.396	91.5	7.2
4		227-55-23 PFL	60	0.25	29.64	20.96	15.0	0.707	90.8	3.4
5		30% 55-23 Res(1)	30	1.00	34.82	18.90	30.0	0.543	85.0	3.3
6		30% 55-23 Res(1)	30	0.25	34.82	28.06	7.5	0.806	94.3	1.1
7		30% 70-05 Res(2)	30	1.00	37.88	16.69	30.0	0.441	116.5	3.4
8		30% 70-05 Res(2)	30	0.25	37.88	25.95	7.5	0.685	102.1	2.2
9		30% 70-12 Res(3)	30	1.00	37.53	25.28*	30.0	0.673*	122.0	5.0
10		30% 70-12 Res(3)	30	0.25	37.53	26.39	7.5	0.703	98.2	1.9

* Possible contamination when rubber beaker lid fell into recovered THF Autoclave Washings.

(1) 30% 975 F+ from 227-55-23 PFL Blended with 70% HRI 5868 Coal Liquefaction Diatillate

(2) 30% 975 F+ from 227-70-05 PFL Blended with 70% HRI 5868 Coal Liquefaction Diatillate

(3) 30% 975 F+ from 227-70-12 PFL Blended with 70% HRI 5868 Coal Liquefaction Diatillate

** Recovered liquid W% represents the material recovery weight percent; Liquid THF % is the THF contamination in the recovered liquid and Cprod/Cfeed is the Ratio of Resid Concentrations in Products and Feed.

Table 3**CMSL-04 Run Plan**

Black Thunder Coal (HRI-5828)

Back Pressure: 2500 psig

Catalyst: (to be determined)

Condition Period		1 1-5	2 6-9	3 10-12	4 13-15
Feed Gas:	1st Stage	H2	CO/H2 (90/10)	CO/H2 (90/10)	CO/H2 (75/25)
	2nd Stage	H2	H2	H2	H2
Temperature [F]	1st Stage	750	750	730	730
	2nd Stage	800	800	800	800
	Hydrotreater	675	675	675	675
Space Velocity [lb coal/h/ft ³ cat.]		67	67	67	67
Solvent/Coal Ratio		1.2	1.2	1.2	1.2
Sulfur Additives:					
1st Stage (TNPS)		— Sulfur Equ. to 1 W% of dry coal —			
2nd Stage (H2S)		— Sulfur Equ. to 2 W% of dry coal —			

RESIDUAL OIL REACTION IN MICROAUTOCLAVE TESTS

RESIDUAL OILS FROM RUNS 227-55 AND 227-70

FIGURE 2

FIGURE 2

HRI SYNGAS - H₂ TWO-STAGE COAL LIQUEFACTION SCHEME

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