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OPTIMIZATION OF REACTOR CONFIGURATION
IN COAL LIQUEFACTION
SEVENTH QUARTERLY REPORT FOR THE PERIOD

1 APRIL - 30 JUNE 1993

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FINAL

WORK PERFORMED UNDER CONTRACT

DE-AC22-91PC-91052

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

AUGUST 1993

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ABSTRACT

This quarterly report covers activities of Optimization of Reactor Configuration in Coal Liquefaction during the period April 1 - June 30, 1993, at Hydrocarbon Research, Inc. in Lawrenceville and Princeton, New Jersey. This DOE contract period is from October 1, 1991 to September 30, 1993 and has been extended to December 31, 1993.

The overall objective of the program is to achieve a new approach to liquefaction that generates an all distillates product slate at reduced cost of about \$25 per barrel of crude oil equivalent.

The quarterly report covers work on Laboratory Support, Laboratory Scale Operations, Technical Assessment, and Project Management.

SUMMARY

There was no experimental work during this reporting period. The experimental fixed bed data obtained with L-772 product slurry containing unreacted coal obtained during PDU operations on Black Thunder coal was compared with simulated ebullated bed performance at conditions equivalent to those of fixed bed tests. The simulated ebullated bed performance are in accord with experimental results in that fairly low degrees of conversion were to be expected.

In a separate simulation the performance of two-stage and several different three-stage reactor configurations were compared in terms of 975°F⁺ residuum conversion. Using kinetic correlation obtained from the bench unit operations, improvements from three stage and interstage separation operations ranging from 4.5 to 15.0 W%, were observed.

INTRODUCTION

The studies conducted in this the sixth quarterly report of Contract No. DE-AC22-91PC-91052 is reported by task and in sequence.

Task 1 is the Project Work Plan and is complete. Task 2 is for Laboratory Support which includes feed and product characterization and general analytical support for Task 3. Task 3 is for Laboratory Scale Operations evaluating three reactor configurations: fixed bed reactor as a 'finishing' reactor, three-stage close-coupled Back-Mixed Reactor System, and interstage product stream concentration. Task 4 is the Technical Assessment, including modelling, design and economics. Task 5 is Project Management.

The contract period is October 1, 1991 to September 30, 1993 and has been extended to December 24, 1993.

TASK 2 - LABORATORY SUPPORT

In order to optimize the reactor configuration for coal liquefaction, the rate of coal dissolution was determined at various stages. In the early part of this program samples of partially converted coal were obtained from the first and second stage of the bench and PDU operations. However, most of these partially reacted coal samples were very mature in the dissolution process. Coal conversion of these samples were mostly higher than 75 W%.

To further study the initial stage of coal dissolution, samples with low degree of conversion are needed. Dr. Anthony Cugini of Pittsburgh Energy Technology Center has agreed to prepare a couple of partially converted Illinois coal using a 1-liter autoclave system. It is anticipated that samples with coal conversion ranging between 60 to 75 W% can be prepared under strictly controlled experimental environment.

The PETC samples will be available in August for microautoclave kinetic evaluation.

TASK 3 - LABORATORY SCALE OPERATIONS

There are no experimental activity during this reporting period.

TASK 4 - TECHNICAL ASSESSMENT

The fixed bed data obtained with product slurry (L-772), slurry containing unreacted coal obtained during PDU Run 260-03 on Black Thunder coal, was compared with simulated ebullated bed performance at conditions equivalent to those of fixed bed tests ACL-01 and 02. The kinetic correlations of the Bench Unit CTSL operations was used to provide the simulation.

In a separate simulation the performance of two-stage and several different three-stage reactor configurations were compared in term of 975°F⁺ residuum conversions.

A. Fixed Bed Tests

The objective of the fixed bed tests was to determine the critical velocity above which solids (unreacted coal and mineral matters) accumulation will be minimized. Relationships between the critical velocity and other operating parameters like flow direction, solid loading, the size of catalyst and unreacted coal particles, etc, are required for successful application of fixed reactor systems as a finishing reactor in multi-stage coal liquefaction. With this objective in mind, the fixed bed tests were conducted at relatively short space time and were not expected to give high degree of additional coal and residuum conversions.

Since there are no previous fixed bed data on Black Thunder coal the performance of the fixed bed tests are compared with the performance of an ebullated bed if the same conditions had been used as in Fixed bed Run ACL-01 and 02. These calculations indicates that experimental conversions in the fixed bed tests scattered above and below the values projected using the kinetic correlation. However, at the most severe conditions resulting in the highest degree of conversion, the experimental conversions were lower than the projected values.

Summary of Experimental Results in Fixed Bed Tests

The correlation of the bench unit CTSL used the space velocity based on the total reactor volume. There was very little impact of catalytic activity, over the normal range of catalyst deactivation, upon coal conversion, so that it is probable that the residence time for coal reaction was the volume external to the extrudates, which was 72% of an individual fixed bed reactor (73 cc). Accordingly, the equivalent volume for evaluating the CTSL correlating parameter for coal conversion was taken to be 47 cc, and the slurry space-time rate on this basis is given in *Table 1*, as the equivalent CTSL space rate.

The L-772 slurry feed to the fixed bed tests contained 84.6 W% liquid, 3.35 W% ash, and 12.05 W% quinoline insoluble organic matter (IOM). The maximum amount of coal converted was 1.66 W% of the slurry feed, at the most severe condition involving the lowest slurry feed rate and the highest test temperature. The lowest severity operation, at low temperature and high slurry feed rate, had minimal amounts of coal conversion. There was one anomalous result, at an intermediate severity, in which the apparent amount of coal in the product was greater than the amount fed.

Composition of Feed Solids to Fixed Bed Tests

The feed to Fixed Bed Tests was L-772 product slurry from PDU operations on Black Thunder Mine Coal. The composition of the oil free solids was:

IOM	78.3 W%
Ash	21.7 W%

This composition corresponding to 74.6 W% conversion of the original coal fed to the PDU Operation. As modelled the unreacted matter consisted of a high reactivity component, a low reactivity component, and an unreactive component, which were originally present in the following proportions:

High Reactivity	55 W%
Low Reactivity	42 W%
Unreacted	3 W%

However, because of the differences in the reactivity of the three components, the distribution of the unreacted material in the feed to the fixed bed tests did not correspond to this distribution.

For the calculation of the further reaction of these solids, the proportion of the three constituents in the feed to the fixed bed tests was estimated using the kinetic model parameters. *Table 2* summarizes the results of this estimate, which uses the CSTR first order kinetic equation:

$$-KC_p = F(C_p - C_f)$$

which reduces to:

$$\frac{C_p}{C_f} = \frac{1}{1+KF}$$

where

C_p = Concentration in product slurry
 C_f = Concentration in feed slurry
 F = Slurry flowrate, lb/h/ft³
 K = Rate constant, lb/h/ft³

The subject solids were generated in a two stage system so that the final two stage equation becomes:

$$\frac{C_p}{C_f} = \frac{1}{(1+K_1/F)(1+K_2/F)}$$

where K_1 and K_2 correspond to the rate constants in the two stages. *Table 1* gives the results of such calculations, assuming equal stage temperatures and also assuming 50°F temperature difference between the two stages, to match 74.6 W% conversion of the original material i.e. 25.4 W% residual material. there is very little impact of the assumed change in the stage-to-stage temperature profile.

The estimated distribution of the unreacted material in the feed to the fixed bed tests was taken to be the following:

High Reactivity	0.5 W%
Low Reactivity	87.7 W%
Unreactive	11.8 W%

Estimation of Equivalent Ebullated Bed Performance

Table 3 summarizes the results of the calculation of the coal conversions that would be expected in a single ebullated bed reactor having the same volume as that of the equivalent volume in the fixed bed reactor(s) used in these tests. The calculations are based on the CSTR kinetic equations given above. The ratio of reaction rate constants for the two reactive coal components at 750°F is 58.48, and the activation energy for both these components is 38.5 Kcal/mole. A comparison of the experimental and calculated degree of coal conversions, as a percentage of slurry feed, is given in below:

Run-Period	Temp. (°F)	Flow	Cat. Shape	Exp. Conv.	Calc. Conv.
ACL-01-2B	783	Up	Trilobe	0.7	2.4
ACL-01-3B	791	Up	Trilobe	1.7	3.0
ACL-01-4AB	760	Up	Trilobe	-1.1	0.9
ACL-01-5B	697	Down	Trilobe	0.4	0.2
ACL-02-2B	699	Down	Cylind.	0.4	0.1
ACL-02-3B	774	Up	Cylind.	1.0	0.6

* Sandbath mid-point temperatures

The kinetic model projections are in accord with experimental results in that fairly low degrees of conversion were to be expected.

In three cases the experimental conversions were higher than the estimated conversions, and in three cases they were lower. The highest experimental conversion was obtained using the conditions expected to results in the highest conversion, and the lowest experimental conversion (disregarding the anomalous ACL-01-4AB result) was under conditions expected to give the lowest conversion, although the increase in experimental conversions with increase severity was not as great as projected by the kinetic model. In a strict statistical sense the experimental conversions were not consistently higher or lower than the projected values, largely because of the unlikely results of the ACL-01-4AB operation. Also, there was no consistent impact of flow direction or nature of the extrudate catalyst on coal conversion.

B. Three Stage and Stream Concentration Configurations

The performance of two stage liquefaction was compared with that of three stage operations. Two specific cases of three stage operations were simulated using a simple first order kinetic model. In the first case there are three equal volume reactors, connected in series, with a total volume equals that of the two stage system. The second case has a similar reactor arrangement as that of the former case. In addition to the three reactors, an interstage separator is placed between the second and the third reactor for removing hetero-gases and light hydrocarbons generated in the first two stages.

The comparisons were based on 975°F⁺ residuum conversions projected by a kinetic model in which the residual oil is formed as portion of the primary liquefaction of the coal, and subsequently undergoes secondary reaction to lighter products. A single species of uniform composition and reactive properties was assumed. An activation energy of 32 Kcal/mole was used. Temperatures, space velocity, degree of interstage concentration, calculated reaction severity and the simulated overall residuum conversion are given in *Table 4*.

The two stage operation (Case A) was simulated at typical CTSL conditions of 20.6 lb coal/h/ft³ reactor per stage, first and second stage temperature of 750° and 825°F, corresponding to reaction severity index of 1.0. Using kinetic model parameter derived from the Bench Unit operations, the projected 975°F⁺ residuum conversion was 77.4 W%.

Under similar reaction severity conditions both three stage configurations, with and without interstage separation, resulted in higher residuum conversions. Case C, a three stage operation with no interstage separation, has a higher projected residuum conversion (81.9 W%) reflecting the advantage of being closer to a plug flow performance.

Interstage separation of lighter product and concentration of the feed stream to the third reactor further improves the conversion of 975°F⁺ residuum as shown in Case D with 30, 40 and 50 W% removal of light distillates. The improvements range from 8.6 to 15.1 W% proportional to the degree of removal of lighter liquid product. As a result of the removal of part of the lighter product from the process stream, the liquid space velocity through the third reactor was increased correspondingly and in turn raised the reaction severity index.

Task 5 PROJECT MANAGEMENT

A progress review meeting with COR was held at HRI on May 11 and 12, 1993. Due to scheduling problem with the Robinson Mahoney CSTR unit, there will be further delay in conducting the simulated three stage test. The projected run date is 10/20 to 11/7. An updated schedule is shown in *Figures 1 and 2*.

Table 1

**Fixed Bed Tests with L-722 Slurry from PDU
Operations with Black Thunder Mine Coal**

		Feed -----Run ACL-01-----Run ACL-02					
		2B	3B	4AB	5B	2B	3B
Temp, °F		783	791	760	697	699	774
Feed Gram/Hr		189	171	359	294	339	406
Lbs/Hr/ft ³ (stage)*		162	146	307	251	290	347
Lbs/Hr/ft ³ (CTSL equivalent) **		251	227	477	390	450	539
Reactors		2	2	2	1	1	1
Flow Direction		Up	Up	Up	Down	Down	Down
Total in Liq.							
IBP-650°F	17.27	21.65	28.93	22.41	16.18	19.65	22.24
650-850°F	52.69	43.49	38.69	42.84	51.01	51.23	46.80
850-975°F	7.48	16.97	8.87	12.49	8.19	7.00	8.82
975°F+	7.14	0.94	6.60	4.28	7.28	7.62	6.21
Change							
Unreacted Coal		-0.69	-1.66	1.09	-0.41	-0.44	-0.96
IBP-650°F		4.38	11.66	5.14	-1.10	2.38	4.97
650-850°F		-9.20	-14.00	-9.85	-1.68	-1.46	-5.89
850-975°F		9.49	1.39	5.01	0.70	-0.48	1.34
975°F+		-6.20	-0.54	-2.86	0.13	0.48	-0.93

* 73 cc per stage

** 47 cc per stage (Equivalent to Ebullated Bed, 72% free space)

Table 2

CALCULATION OF DISTRIBUTION OF FEED COMPONENTS IN UNREACTED COAL USED IN FIXED BED TESTS

	Feed	Calculated Product	
T2-T1		0	50
k2/k1		1	3.139
Khi/Klo		58.5	58.5
(k1/s)lo		0.3727	0.1875
(k2/s)lo		0.3727	0.589
(k1/s)hi		21.8	11.0
(k2/s)hi		21.8	34.4
(Cp/Cf)lo		0.5307	0.5301
(Cp/Cf)hi		0.0019	0.0024
Unreact lo	42.00	22.29	22.26
Unreact Hi	55.00	0.11	0.13
Unreactive	3.00	3.00	3.00
Total	100.00	25.40	25.39
Distribution Of Unreacted			
Low Reactivity		87.8	87.7
High Reactivity		0.4	0.5
Unreactive		11.8	11.8

Table 3

CALCULATION OF COAL CONVERSIONS EXPECTED USING CTSL EBULLATED BED CORRELATIONS FOR CONDITIONS USED IN UNIT 254 FIXED BED TESTS

	Feed	-----Run ACL-01-----				- Run ACL-02 -	
		2B	3B	4AB	5B	2B	3B
Temp., F		783	791	760	697	699	774
Catalyst, grams		66	66	66	45	37	38
cc		87	87	87	43	43	43
Total Reactor(s) Volume, cc *		146	146	146	73	73	73
Feed Gram/Hr		189	171	359	294	339	406
Lbs/Hr/ft3(CTSL equivalent stage) **		251	227	477	390	450	539
Reactors		2	2	2	1	1	1
Lbs/Hr/ft3(total volume)		125	114	238	390	450	539
Rate Constant, Lbs/Hr/Ft3 Reactor							
Lo Reactive Component		36.8	44.0	21.7	4.6	4.8	30.0
Hi Reactive Component		2149	2572	1267	267	281	1752
Conversion of components							
W% of Component in Feed							
Lo Reactivity Component		22.7	27.9	8.3	1.2	1.1	5.3
High Reactivity Component		94.5	95.8	84.2	40.6	38.5	76.5
Calculated Product Rates	Feed						
W% of Total Feed							
Low Reactivity Component	10.58	8.18	7.62	9.70	10.45	10.46	10.02
High Reactivity Component	0.06	0.00	0.00	0.01	0.04	0.04	0.01
Unreactive	1.42	1.42	1.42	1.42	1.42	1.42	1.42
Total Organic Coal	12.06	9.61	9.05	11.13	11.91	11.92	11.46
Total Reacted		2.45	3.01	0.93	0.15	0.14	0.60
Experimental Reacted							
W% of Total Feed		0.69	1.66	-1.09	0.41	0.44	0.96

* 73 cc per reactor ** Volume Equivalent to Ebullated Bed Reactor, 47 cc

Table 4**Comparison of Various Reactor Configurations
975°F⁺ Residuum Conversion**

Case	Reactor Temp. (°F)			Space Velc. lb coal/h/ft ³	Severity Index	Interstage Separation	Predicted 975°F ⁺ Conv.
	1	2	3				
A	Two Stage 750 825			20.6	1.000	0	77.4
B	Three Stage 750 750 825			30.9	0.735	0	74.8
C	750	805	825	30.9	1.010	0	81.9
D	750	805	810	30.9	0.977	0.3	86.0
	750	805	810	30.9	1.071	0.4	89.0
	750	805	810	30.9	1.203	0.5	92.5
E	750	805	825	30.9	1.267	0.3	88.0
	750	805	825	30.9	1.410	0.4	90.7
	750	805	825	30.9	1.609	0.5	93.7

Activation Energy = 32 Kcal/mole

FIGURE 1

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OPTIMIZATION OF REACTOR CONFIGURATIONS

FIGURE 2

OPTIMIZATION OF REACTOR CONFIGURATIONS

DATE

FILMED

2/28/94

END