EXPLORATORY RESEARCH ON NOVEL COAL LIQUEFACTION CONCEPT

Quarterly Technical Report

Reporting Period: 10/1/1997 End Date 12/31/1997

DOE CONTRACT No. DE-AC22-95PC95050

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CONTRACT TITLE AND NUMBER:

Exploratory Research on Novel Coal Liquefaction Concept
DOE Contract No. DE-AC22-95PC95050

CONTRACTOR NAME:

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Research & Development
4000 Brownsville Road
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CONTRACT INITIATION DATE: May 24, 1995

ANTICIPATED COMPLETION DATE: May 23, 1998

GOVERNMENT AWARD: \$1,314,477 Total, \$1,292,800 Obligated

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REPORTING PERIOD: October 1 through December 31, 1997

CONTRACT OBJECTIVES: No Change

SUMMARY OF TECHNICAL PROGRESS - OVERALL

Task 4 experimental testing was continued. Six first-stage one-liter autoclave tests were made at reduced severity conditions. A device to reduce the in-line filter diameter proved difficult to use and resulted in little usable filtration data. Its use was discontinued. The second-stage reactor system was overhauled and used to process Wilsonville Run 263J resid. Resid conversion and yields were commensurate with expected results.

The economic and engineering evaluation of the Novel Concept process, based on Task 2 and Task 3 experimental data, was begun. The design of a conceptual commercial plant was completed. The economic and engineering evaluation illuminated components of the process operating and capital cost estimates which, if appropriately altered, could significantly reduce the

cost of product (gasoline) from the process. This provided direction for the Task 4 experimental program.

SUMMARY OF TECHNICAL PROGRESS BY TASK

Task 4 - Integrated Flow Sheet Testing

First-Stage Tests

Microautoclave Tests. The combined distillate (454 °C⁻) of first-stage products from Runs 23-, 23a-, 23c-, 23d-, 23f-, and 23g-LA was analyzed by gas chromatography/mass spectrometry (GC/MS) and for ultimate analyses. The ultimate analyses is essentially the same as that of the feedstock Reilly Industries Oil (Table 1). A precipitate forms in the composite sample at room temperature. GC/MS of the whole, homogenized sample indicates that it does not contain a preponderance of 'wax', although a regular progression of n-paraffins is evident (Figure 1). A major component of the material was identified as phenanthrene. The oil was used in a single microautoclave tests to simulate recycle around the first stage. The use of the recycled oil did not affect coal conversion (Table 2).

One-liter Autoclave Tests. Six first-stage one-liter autoclave tests were successfully completed this quarter (Table 3). All tests were designed to address operating conditions that strongly affect the cost of the Novel Concept process. Run objectives were to test low solvent/coal ratios and low catalyst loadings. Additionally, the post first-stage filter diameter was reduced to produce a thicker filter cake, which would more closely simulate commercial operation of the filter. This was accomplished by insertion of a conical filter-diameter reduction-liner in the body of the filter unit. The liner, constructed of 316 stainless steel, fits inside the filter with less than 1 mm wall clearance. The center is machined as a conical funnel terminating in a 2.54 cm cylinder, thus providing a reduction of filter area from 45.6 cm² to 5.1 cm². The liner weighs 2.44 kg; its weight resting on the glass fiber filter paper was considered to be sufficient to prevent filter cake from building under the liner.

Run 26-LA was designed to test a low solvent to dry coal ratio (1:1 vs. the lowest tested to date, 1.4:1 for Run 25-LA). The reactor system developed a leak at the transfer valve to the filter. System pressure of 4900 psi approached, but did not exceed, the valve pressure limit of 5000 psi (at 450 °F). The run was safely aborted.

Run 27-LA was made with a solvent/coal ratio of 1 and half of the catalyst loading used in the Run 23-LA series tests conducted under Task 3 (111 mmole KOH/kg dry coal). Only a small amount of product filtered through the on-line filter; the majority of the product was found in the autoclave. Examination of the valve, located between the autoclave and the filter unit, showed that it was partially blocked. It appears that any filtration which took place occurred across the partially blocked valve. Gas analyses, including direct hydrogen analysis, were obtained. All liquid and solid products were recovered and re-filtered off line (see below).

Because of the filtration problems encountered in Run 27-LA, Run 28-LA was made at the same conditions as Run 25-LA (solvent/dry coal = 1.4). This test was made with the conical filter-diameter reduction-liner in place. The products were found in the filter unit, not in the receiver. It is not known if the products did not filter because insufficient time was provided or because the over pressure was too low during filtration. All products were collected and reserved for off-line work-up.

A duplicate of Run 28-LA (Run 28a-LA) was made in the one-liter autoclave. Because it was speculated that the filtration time had not been long enough in Run 28-LA, filtration time for Run 28a-LA was extended to two hours with an over pressure of N₂ at all times ≥ 30 psi. All the product was found in the receiver, no material was found on the filter. Apparently, the glass fiber filter was breached and sufficient bridging of the Conidur plate apertures did not occur.

Run 28b-LA (a duplicate of Runs 28-LA and 28a-LA) was made to test the filter liner and to provide additional sample for a second-stage hydrotreating test. All products transferred to the filter unit and approximately 80 g of product filtered through the glass fiber paper and the Conidur plate. After one hour of continuous N₂ flow through the filter, a small dry filter cake and about 50 g of tarry product remained in the filter unit. It appears that the filter liner was not providing an appropriate simulation of commercial filter application; it will no longer be used in Task 4 first-stage tests. Run 28-LA series products were shipped to UK/CAER for filtration and distillation to produce feedstock for second-stage tests (see below).

Run 29-LA was successfully executed. The test was made at the same solvent/dry coal ratio and catalyst loading as Run 28-LA series tests, however, at a reduced water loading. No added water was fed to the reactor. Only the inherent (ca. 26 wt %) moisture content of the coal was present in the reactor. This resulted in reducing the total system pressure from ca. 4500 psi to ca. 4000 psi. Coal conversion was found to be only ca. 80 wt %.

Run 30-LA was completed. The test was made at the same solvent/dry coal ratio and catalyst loading as Run 29-LA. As in Run 29-LA, no additional water was fed with the 26 wt % moisture coal. In this test, however, the HI "E" charge was reduced, which reduced the total system pressure at temperature from ca. 4000 psi in Run 29-LA to ca. 3100 psi. Filtration occurred through the Conidur plate but not the glass fiber filter paper. This was unintentional and occurred because the filter paper was shifted during assembly of the filter unit. Products found in the receiver are very viscous and, unlike other one-liter autoclave products, do not flow at room temperature. Coal conversion was determined to be 75.2 wt %.

Filtration

It has been reported that the filtrate product from Run 23h-LA had been divided into three parts and distilled to leave residues of 33% (23hLADR2, containing 33.9% <566 °C), 59% (23hLADR3, containing 63.7% <566 °C), and 76% (23hLADR1, containing 75.8%<566°C) (Table 4). THFI was determined on samples 23hLADR1 and 23hLADR3 and compared with the distillation feedstock (23hLA) to see if insolubles were generated during the distillations. The feedstock 23hLA contained 2.8% THFI, whereas the samples 23hLADR1 and 23hLADR3 contained 3.3% and 5.1% THFI, respectively. When an allowance is made for the THFI's concentrating during distillation, this equates to THFIs in the original feedstock of 2.5% and 3.0%, respectively. This indicates that there is no generation of insolubles during the distillation process.

Material from Run 27-LA which had not passed through the transfer valve between the autoclave and the filter unit (see above) was filtered off-line. The sample yielded virtually no filtrate. Subsequent analysis of the material gave 47.3% QI and 50.5% THFI, which is typically the composition of filter cake. These findings support the conclusion that the filtration occurred through a plug in the transfer valve.

Second-Stage Catalytic Upgrading

Reactor Modifications. The main sealing closure of the 300 mL CSTR was re-machined. The unit was successfully pressure tested. It was suspected that the previously reported increase in the THFI of 225% (product/feedstock) and a 20% gas make during the hydrotreatment of Wilsonville Run 263J interstage residue in the 300 mL CSTR was due to coking. To address this concern, the reactor was modified to ensure that the temperature of the reactants is measured accurately. This was achieved by positioning a 3.2 mm diameter thermocouple well in line with the base of the agitator. This replaces the 6.4 mm thermocouple well that was positioned above the agitator.

Another modification made to the reaction procedure was to increase the stirrer speed from ~350 rpm to ~700 rpm to ensure adequate mixing.

Baseline tests. A second-stage CSTR run was completed with the modified system. The run was made with Wilsonville 263J interstage residue as the feedstock at the standard conditions of 440 °C for 60 min with 1% Mo. The heat-up time for the run was ~120 min. The reactor product was visually inspected; no solids were observed. Preliminary gas analysis indicates a small gas yield, estimated at ~3%. Residue conversion was 46%. This compares to 43% before the modifications were made. However, there was a substantial reduction in the hydrocarbon gas yield, with a corresponding increase of ca. 17% in the yield of liquid products. The hydrogen to carbon ratio for the liquid product was determined to be 0.99, compared with 0.79 previously achieved. (The H/C ratio for the feedstock is 0.86.) This improvement reflects the improved performance of the CSTR in its current configuration. The previously reported increase in mass of IOM from feedstock to product of 225% (prior to modifications) was not observed in the current test. In the most recent test, the mass of IOM was reduced by 33%. These results indicate that the hydrotreatment was successful.

Feedstock Resid Concentration. To determine if the number of first-stage one-liter tests required to provide enough feedstock for a single second-stage catalytic upgrading test could be reduced, tests were made with distillation residues containing different proportions of the <566 °C distillate fraction of the first-stage product (see above). The results from microautoclave tests using the three feedstocks from three distillations of Run 23h-LA are provided in Table 5. The second-stage hydrotreating results of the different distillation products show that the feedstock with the highest concentration of <566 °C (75.8%) resulted in the lowest conversion. Although the intermediate concentration of 566 °C⁻ gave the same result as the feedstock with the lowest concentration of 566 °C⁻, it was decided that for the remainder of the program, the concentration of <566 °C fraction in the feedstock for second stage catalytic upgrading should be kept low, at ca. 30 %.

Task 5 - Engineering and Economic Study

Conceptual commercial plant designs for two Novel Concept cases were evaluated. The first case is based on using the as-measured light hydrocarbon gas yields from second-stage Runs 23oac-1, 300 CSTR and 23dfg-1, 300 CSTR. The second case is based on using one-half the gas yields obtained in those two tests. The lower values are more representative of

anticipated commercial reactor performance. Completed for the two cases were the electric power requirements, makeup HI "E" balance for the first-stage reaction, makeup H₂ balance for the second-stage reaction, overall fuel balance, and LPG product rate. In addition, the reactors for stages one and two were sized. (Data are presented in Confidential Appendix II.)

The partially completed evaluation provides direction for Task 4 experimental work and continued Task 5 economic evaluation. Experimental studies of reduced catalyst loading (first stage), system pressure, first-stage HI "E" loading, solvent to coal ratio, and first-stage residence time are indicated to improve the cost of producing final product (gasoline). Task 5 studies will address the placement of the solids removal system to post second-stage, the evaluation of pressurized slurry feed equipment, and the potential reduction in cost associated with reduced HI "E" loading.

Task 6 - Reporting

Bi-monthly conference calls were held as scheduled with UK/CAER and LDP. Reports documenting the calls were issued. The Task 3 Topical Report will be issued in the next quarter.

FORECAST AND PLANS

The Task 3 Topical Report will be completed. First-stage tests designed to reduce process costs, including reduced first-stage residence time, reduced catalyst loading, reduced solvent/dry coal ratio, and reduced system pressure will be continued under Task 4. Tests will be made with first-stage products in the renovated second-stage 300 mL CSTR. Second-stage microautoclave tests with feedstocks derived from Run 23h-LA and products of Run 28-LA series first-stage tests will be made. Tests with recycled second-stage resid will be initiated.

Capital and operating costs for the conceptual commercial plant based on the Novel Concept process will be completed. A revised conceptual commercial plant design, which will incorporate economic improvements indicated in the primary design, also will be evaluated. These improvements will include close coupling of the first- and second-stage reactors, reduced first-stage catalyst loading, reduced system pressure, reduced first-stage residence time, and reduced HI "E" loading. The completed economic evaluation will be compared to the first Novel Concept configuration and to the base case (Wilsonville Run 263J).

TABLE 1

**ANALYSES OF REILLY INDUSTRIES ANTHRACENE OIL
AND RECYCLED DISTILLATE FROM RUN 23-LA SERIES**

Ultimate Analysis, wt%	Reilly Industries Anthracene Oil	Composited Distillate from Runs 23-, 23a-, 23c-, 23d-, 23f-, 23g-LA
C	91.21	90.00
H	5.77	6.41
N	1.00	0.83
S	0.55	0.52
O (by diff)	1.47	2.24

TABLE 2

**TASK 4 FIRST-STAGE MICROAUTOCLAVE TESTS, EFFECT OF RECYCLE SOLVENT
ON COAL CONVERSION, REILLY INDUSTRIES ANTHRACENE OIL vs. RECYCLED
DISTILLATE FROM RUN 23-LA SERIES**

Black Thunder Mine Subbituminous Coal

HI "E", 375°C, 60 min

Run No.	Oil	Solvent/ dry coal, g/g	KOH catalyst, mmole/kg coal	Coal Conversion, wt %
247	Fresh	1.00	50	89.4
248	Recycled	1.00	50	89.2

TABLE 3

TASK 4 - FIRST-STAGE ONE-LITER AUTOCLAVE TESTS SUMMARY

Run	26-LA	27-LA	28-LA	28a-LA	28b-LA	29-LA	30-LA
Solvent/dry Coal, g/g	1.0	1.0	1.4	1.4	1.4	1.4	1.4
Water/dry Coal, g/g	0.4	0.4	0.5	0.5	0.5	0.3	0.4
KOH, mmols/kg dry coal	111	111	111	111	111	111	111
Mass Balance, %	N/C*	101.3	101.2	100.7	99.4	98.9	94.6

*N/C = not completed

TABLE 4
SIMULATED DISTILLATION OF DISTILLATION CUTS
OF FIRST-STAGE RUN 23H-LA PRODUCT

Sample No.		23hLA DD1	23hLA DR1	23hLA DD2	23hLA DR2	23hLA DD3	23hLA DR3
Found recovery (%)		103.9	83.5	106.9	45.9	106.3	71
bp (°C)	bp (°F)	amount bp < T° (%)					
150	302	0.0	0.0	0.0	0.3	0.0	0.5
200	392	2.5	0.5	1.5	0.5	1.6	0.8
250	482	19.7	0.7	7.0	0.6	10.6	1.0
300	572	33.0	1.0	12.7	0.7	18.0	1.2
350	662	66.0	11.7	32.0	0.8	42.0	2.5
400	752	96.6	40.8	78.5	2.3	90.5	22.8
450	842	100.0	61.7	96.4	12.7	98.4	45.9
500	932	100.0	71.6	100.0	26.9	100.0	58.3
550	1022	100.0	75.1	100.0	32.6	100.0	62.7
600	1112	100.0	77.3	100.0	36.7	100.0	65.5
650	1202	100.0	79.1	100.0	39.7	100.0	67.6
700	1292	100.0	80.3	100.0	41.8	100.0	69.1
750	1382	100.0	81.5	100.0	43.3	100.0	70.0
800	1472	100.0	83.5	100.0	45.9	100.0	71.0
510	950	100.0	72.3	100.0	28.0	100.0	59.2
566	1050	100.0	75.8	100.0	33.9	100.0	63.7

TABLE 5

HYDROTREATING TESTS ON THE DISTILLATION RESIDUES FROM RUN 23HLA FILTRATE

Run no.	Feedstock 23hLADR1	23h-1, [D7-307-1]	23h-2, [D7-307-2]	Feedstock 23hLADR2	23h-3 [D7-309-1]	23h-4 [D7-314-1]	Feedstock 23hLADR3	23h-5 [D7-316-1]	23h-6 [D7-316-2]
Catalyst precursor	-	Molyvan L	Molyvan L	-	Molyvan L	Molyvan L	-	Molyvan L	Molyvan L
Reaction time, min @ °C	-	60 @ 440	60 @ 440	-	60@440	60@440	-	60@440	60@440
Mo, ppmw feed	-	10041	10032	-	10008	10125	-	9887	9919
Products, wt% MAF feed									
C ₁ -C ₃ gas	-	4.0	3.7	-	5.4	5.5	-	5.1	4.3
C ₄ ⁺ vapor	-	2.0	2.1	-	3.5	3.6	-	4.7	2.8
CO + CO ₂	-	0.2	0.2	-	0.5	0.5	-	0.2	0.2
566 °C ⁻ %	75.8	79.3	77.2	33.9	61.2	59.3	63.7	74.5	74.6
566 °C ⁺ %	24.2	14.5	16.8	66.1	29.4	31.1	36.3	15.5	18.1
Total	100	100	100	100	100	100	100	100	100
Derived values									
Resid conversion, wt % 566 °C ⁺	-	40.1	30.6	-	55.6	53.0	-	57.2	50.1
		avg. 35.4			avg. 54.3			avg. 53.7	
H ₂ consumed, mg/ g MAF feed	-	27.0	24.6	-	35.4	32.2	-	39.7	35.3

Task 4 First-Stage Microautoclave Tests
Reilly Industries Anthracene Oil vs. Recycled Distillate
from Run 23-LA Series

Ultimate Analysis, wt%	Reilly Industries Anthracene Oil	Composited Distillate from Runs 23-, 23a-, 23c-, 23d-, 23f-, 23g-LA
C	91.21	90.00
H	5.77	6.41
N	1.00	0.83
S	0.55	0.52
O (by diff)	1.47	2.24

Figure 1. Gas Chromatography/Mass Spectrometry of Analysis of Composited Distillate from Runs 23-, 23a-, 23c-, 23d-, 23f-, 23g-LA and Reilly Industries Anthracene Oil.