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TECHNICAL PROGRESS REPORT NO. 6

CONTRACT TITLE AND NUMBER:

Development of an Extraction Process
for Removal of Heteroatoms From
Coal Liquids
DE-AC22-91PC91057

DATE: October 25, 1993**REPORTING PERIOD:** 7/1/93-9/30/93**AUTHOR:** Hemant B. Gala**CONTRACTOR NAME:**

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OBJECTIVE

The objective of this contract is to develop a CO₂-water extraction process for the removal of heteroatoms from coal-derived naphtha, diesel, and jet fuel. Coal liquids are characterized by their high content of heteroatoms. Conventional techniques could remove the heteroatoms from coal liquids, but at a high hydrogen consumption and at a high cost. A successful development of the CO₂-water extraction process will increase the environmental acceptability of coal liquids and reduce the H₂ requirements for the upgrading of coal liquids.

Task 2.0 Feed Procurement

As described in the Technical Progress report No. 5, Wilsonville Coal liquids from Run 257H tested under this contract resulted in very little nitrogen and sulfur removal that can be attributed to CO₂-water extraction. Part of the problem may be the feed, which was stored for a long period of time under adverse conditions. As a result, and with DOE Project Manager's concurrence, new coal liquid feed samples were procured from a DOE contractor, namely HRI, Inc. of Princeton, New Jersey. This new feed for the CO₂-water extraction process comprises of distillates from HRI's CTSLTM Process. Typical feed analysis of the samples shipped to UOP is shown in Tables 1 and 2. Both nitrogen and sulfur content of these samples (nitrogen in the

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range of 800 to 1,100 ppm and sulfur in the range of 300 to 500 ppm) is lower than that desired for the current program. For comparison, the analysis of the Wilsonville coal liquid feedstock is provided in Table 3.

One should note that all of these feeds are much lower in sulfur and nitrogen than that described in the PRDA solicitation for this contract. The naphtha fraction resulting from liquefaction of a Wyodak coal from the Wilsonville pilot plant was described to contain 2,500 ppm sulfur and 2,200 ppm nitrogen. Since the feedstock from HRI is the best available source of the coal liquids at this time, UOP will plan CO₂-water extraction tests with this feedstock.

Task 3.0 Process Variable Screening Studies

Run 24 was completed with a sample of Kern Diesel. This feedstock was tested because of its high sulfur content (4,000 ppm). The hydrocarbon to water ratio was set at 1:1 and a CO₂ pressure of 600 psig was applied to the test cell. At the completion of a 30-minute agitation period, no sulfur was extracted in the aqueous phase. As a result, it was decided not to conduct any further testing of the alternative feedstocks.

Data from all the previous tests were critically reviewed and two areas of concerns were identified as: material balance and sulfur analysis. Both of these areas will be addressed and modifications to the operating procedure and/or test cells will be planned.

To get a better handle on the material balance and to get a larger quantity of the product streams for detailed analysis, an autoclave assembly will be used to run the next series of the extraction experiments. This set up will enable us to test 250 ml of the liquid instead of the 25 ml samples tested previously. Once a decision is made on which sample of the coal liquid to test, a run will be carried out in the autoclave assembly.

Table 1
Operating Summary
Product Properties

Unit	227	227
Run	78	78
Period Number	16	18
Atmospheric Overheads		
Gravity, DEG-API	24.00	21.80
Elemental Analysis, wt-%		
Carbon, wt-%	87.25	86.47
Hydrogen, wt-%	11.53	11.41
Sulfur, wt-%	0.02	0.05
Nitrogen, wt-%	0.08	0.08
Distillation, ASTM D-86		
IBP, °F	284	300
5 vol-%	363	383
10 vol-%	406	418
20 vol-%	458	465
30 vol-%	494	490
40 vol-%	520	525
50 vol-%	549	546
60 vol-%	570	566
70 vol-%	589	586
80 vol-%	607	603
90 vol-%	631	624
95 vol-%	645	637
End Point, °F	675	664
Vol-% at 350°F	8	6
Vol-% at 500°F	32	33
Vol-% at 650°F	96	98
IBP-350°F, wt-%	6.2	4.3
350-500°F, wt-%	22.3	25.5
500-650°F, wt-%	64.7	65.3
650°F+, wt-%	6.8	4.6
Loss, wt-%	0.0	0.3
* Data provided by HRI, Inc. Analysis of Atmospheric still overhead obtained from HRI's Bench Run 227-78 (CMSL-2) from periods 16 and 18.		

Table 2
Operating Summary
Product Properties*

Unit	227	227
Run	78	78
Period Number	16	18
Separator Overhead Plus Knockouts		
Gravity, DEG-API	33.70	30.10
Elemental Analysis, wt-%		
Carbon, wt-%	86.50	86.38
Hydrogen, wt-%	12.43	12.12
Sulfur, wt-%	0.03	0.05
Nitrogen, wt-%	0.08	0.11
Distillation, ASTM D-86		
IBP, °F	178	181
5 vol-%	216	228
10 vol-%	236	254
20 vol-%	272	297
30 vol-%	317	349
40 vol-%	370	408
50 vol-%	423	459
60 vol-%	480	516
70 vol-%	538	567
80 vol-%	593	620
90 vol-%	650	680
95 vol-%	696	720
End Point, °F	757	757
Vol-% at 350°F	44	37
Vol-% at 500°F	63	57
Vol-% at 650°F	90	86
IBP-350°F, wt-%	39.3	32.6
350-500°F, wt-%	19.5	20.1
500-650°F, wt-%	28.4	30.0
650°F+, wt-%	12.4	16.6
Loss, wt-%	0.4	0.7
<p>* Data provided by HRI, Inc. Analysis of separator overhead obtained from HRI's Bench Run 227-78 (CMSL-2) from periods 16 and 18.</p>		

Table 3
CO₂/Water Extraction Project
Feedstock Characterization

	Naphtha	Jet Fuel	Diesel
Specific Gravity	0.7730	0.9601	0.9883
API Gravity	51.5	15.9	11.7
Distillation (C)			
IBP	42	190	288
5	64	201	295
10	74	205	297
20	87	210	299
30	95	216	298
40	105	223	301
50	114	228	304
60	114	235	209
70	133	241	314
80	142	248	322
90	152	254	334
95	180	260	348
EP	180	268	352
% over at EP	95.0	98.5	98.3
Sulfur (wt-ppm)	725	463	552
Basic N (wt-ppm)	630	4290	5550
N by Chemil (wt-ppm)	3000	5600	8500
Arsenic (AAS wt-ppm)	<0.1	<0.1	0.11
Carbon (wt-%)	76.8	83.0	86.6
Hydrogen (wt-%)	11.8	9.4	9.6
Oxygen (wt-%)	2.5	6.3	3.1
Bromine Number	24.9	5.4	5.3
Paraffins (vol-%)	33.8		
Naphthenes (vol-%)	41.7		
Aromatics (vol-%)	15.5	74.4	77.7
Olefins (vol-%)		5.8	3.5
Naphthenic	4.7		
Paraffinic	2.4		
Polynaphthenes (vol-%)	1.7		

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