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TECHNICAL PROGRESS REPORT NO. 7**CONTRACT TITLE AND NUMBER:**

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

DATE: February 28, 1994**REPORTING PERIOD:** 10/1/93-12/31/93**AUTHOR:** Hemant B. Gala**CONTRACTOR NAME:**

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CONTRACT PERIOD: September 30, 1991 to September 29, 1994**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

Last quarter, new coal liquid feed samples were procured from a DOE contractor, namely HRI, Inc. of Princeton, New Jersey. This feed for the CO₂-water extraction process comprises of distillates from HRI's CTSLTM Process. The distillates samples from the separator overhead (SOH) and atmospheric still overhead (ASOH) of HRI's Bench Run 227-78 (CMSL-2) Periods 14, 15, and 17 were consolidated in four samples and analyzed. Sample 8033-12 represents ASOH from Period 17, 8033-13 represents SOH from period 17, and 8033-14 and 8033-15 represent composites from period 14 and 15. Analytical results for these four samples are presented in Table 1. Nitrogen content of these samples ranged from 633 (wt.) ppm (basic

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nitrogen of 470 (wt.) ppm) for composite sample 8033-15 to 1606 (wt.) ppm (basic nitrogen 1180 (wt.) ppm) for ASOH sample 8033-12. Sulfur content of these two samples was 232 and 479 (wt.) ppm, respectively. For comparison, the analysis of the Wilsonville coal liquid feedstock, which has been tested under this contract, is provided in Table 2.

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, ASOH sample 8033-12 was used to carry out a proof-of-the-principle CO₂-water extraction test.

Separately, concerns about this feedstock were discussed with DOE's Program Manager and possible sources of an un-hydrotreated feedstock were discussed. DOE will pursue this feedstock need with other contractors working on coal liquefaction.

Task 3.0 Process Variable Screening Studies

Run 25 with feed sample 8033-12 was completed in the autoclave assembly. The operating procedure was slightly modified and the run was conducted at ambient temperature and with a 1:1 hydrocarbon to de-ionized (DI)-water volume ratio. The experimental procedure consisted of several steps. First, 250 ml each of the coal liquid and the DI-water were placed in the autoclave and then the autoclave was pressurized to 600 psig with CO₂. After plant pressure was stabilized, the autoclave contents were vigorously mixed with an internal mixer for 30 minutes. After mixing, the autoclave was allowed to settle for 30 minutes. Samples of the hydrocarbon, aqueous phase and the interphase were taken. The interphase was then mixed with n-hexane to separate aqueous and organic phases. All four samples were then characterized.

Table 3 shows the analysis of each of the four phases. The numbers highlighted in this table are estimated. Various material balance and heteroatom rejection calculations are shown in Exhibit 1. The feed, hydrocarbon phase, and interphase hydrocarbon were analyzed by the ASTM D2887 chromatographic distillation technique. Results from these analyses are shown in Figure 1.

Overall material balance for this run was quite good as all of the material fed to the reactor was recovered. Also, the nitrogen balance was good, but the sulfur balance was poor. The hydrocarbon product yield was quite low at 77.1%; however, this was the result of the way in which the experiment was conducted. The interphase level in the autoclave was not visible and operator judgement was used to separate the aqueous phase, interphase, and hydrocarbon phase. When reasonable assumptions were made about the recovery of hydrocarbon phase in the interphase, all of the hydrocarbon was accounted for. Based on the combined hydrocarbon product, 23.2% of nitrogen (24.2% basic nitrogen) and 25.5% of sulfur was rejected. The combined hydrocarbon phase still contains 828 ppm nitrogen and 342 ppm sulfur. This level of heteroatoms in the hydrocarbon phase is still quite high and further heteroatom removal will be necessary before this hydrocarbon stream can be upgraded.

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TABLE 1
HRI Coal Liquids

	ASOH 8033-12	SOH 8033-13	Composite 8033-14	Composite 8033-15
SPECIFIC GRAVITY	0.9171	0.8669	0.8931	0.8810
API GRAVITY	22.8	31.7	26.9	29.1
Distillation - D86A (Volume % ↓)	Temperature, °C			
IBP	137	75	93	83
5	192	130	139	118
10	213	130	162	136
20	234	139	203	169
30	255	161	235	209
40	270	192	258	233
50	281	224	275	261
60	292	252	289	281
70	302	282	303	298
80	313	311	316	315
90	326	347	334	338
95	338	387	354	366
EP	340	390	363	364
% OVER AT EP	97.6	97.2	97.9	97.6
SULFUR (WT-PPM)	479	484	259	232
BASIC N (WT-PPM)	1180	810	570	470
N BY CHEMIL (WT-PPM)	1606	1121	754	633
ARSENIC (AAS WT-PPM)	<0.1	<0.1	<0.1	<0.1
CARBON (WT-%)	87.3	85.9	86.9	87.0
HYDROGEN (WT-%)	8.9	10.4	10.5	10.7
BROMINE NUMBER	6.6	5.6	4.6	5.1

TABLE 2
Wilsonville Coal Liquids

	NAPHTHA	JET FUEL	DIESEL
SPECIFIC GRAVITY	0.7733	0.9601	0.9883
API GRAVITY	51.5	15.9	11.7
DISTILLATION (Volume % ↓)	Temperature, °C		
IBP	42	190	288
5	64	201	295
10	74	205	297
20	87	210	299
30	95	216	300
40	105	223	301
50	114	228	304
60	123	235	309
70	133	241	314
80	142	248	322
90	152	254	334
95	167	260	348
EP	180	268	352
% OVER AT EP	96.4	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		

TABLE 3
Properties of Feed and Product Streams for Run 25

	Weight, g	Sulfur, wppm	Nitrogen, wppm	
			Basic	Chemilum.
Feed	214	461	930	1083
DI Water	243	0	0	0
Hydrocarbon Phase	165	422	830	974
Aqueous Phase	198	< 10	110	95
Interphase	95	40	256	230
Int. - Aqueous	45	< 10	230	105
Int. - Hydrocarbon	50	77	280	345

Note: Highlighted numbers are estimated.

EXHIBIT 1
Calculations for Run 25

Material Balance

$$\begin{aligned}\text{Total In} &= \text{Feed} + \text{DI water} = 214 + 243 = 457 \text{ g} \\ \text{Total Out} &= \text{Hydrocarbon} + \text{Aqueous} + \text{Interphase} = 165 + 198 + 95 = 458 \text{ g} \\ \text{Material Recovery, \%} &= (\text{out}/\text{In}) * 100 = 100.2\end{aligned}$$

Nitrogen Balance

$$\begin{aligned}\text{Nitrogen In} &= 214 * 1083 * 1\text{E-}06 = 0.2318 \text{ g} && (\text{Basic N}) \\ &&& (0.1990 \text{ g}) \\ \text{Nitrogen Out} &= (165*974 + 198*95 + 95*230) * 1\text{E-}06 = 0.2014 \text{ g} && (0.1831 \text{ g}) \\ \text{Nitrogen Recovery, \%} &= (0.2014/0.2318) * 100 = 86.9 && (92.0)\end{aligned}$$

Sulfur Balance

$$\begin{aligned}\text{Sulfur In} &= 214 * 461 * 1\text{E-}06 = 0.0987 \text{ g} \\ \text{Sulfur Out} &= (165*422 + 198*10 + 95*40) * 1\text{E-}06 = 0.0734 \text{ g} \\ \text{Sulfur Recovery, \%} &= (0.0734/0.0987) * 100 = 74.4\end{aligned}$$

Rejection Efficiencies

$$\begin{aligned}\text{Total Hydrocarbons recovered} &= 165 + 50 = 215 \text{ g} \\ \text{Hydrocarbon Phase Yield, \%} &= (215/214) * 100 = 100.5 \\ \text{N content of Total hydrocarbon phase} &= (165*974 + 50*345)/215 = 828 \text{ ppm} \\ \text{Basic N content of Total hydrocarbon phase} &= (165*830 + 50*280)/215 = 702 \text{ ppm} \\ \text{Sulfur content of Total hydrocarbon phase} &= (165*422 + 50*77)/215 = 342 \text{ ppm} \\ \text{N Rejection, \%} &= [1 - [(165*974 + 50*345)/(214*1083)]] * 100 = 23.2 \\ \text{Basic N Rejection, \%} &= [1 - [(165*830 + 50*280)/(214*930)]] * 100 = 24.2 \\ \text{Sulfur Rejection, \%} &= [1 - [(165*422 + 50*77)/(214*461)]] * 100 = 25.5\end{aligned}$$

FIGURE 1
DISTILLATION BY ASTM D2887

++ Feed

Prod. HC

IP HC

▲ Corr.-IP HC

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