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DEVELOPMENT OF AN ADVANCED, CONTINUOUS MILD GASIFICATION PROCESS FOR THE PRODUCTION OF CO-PRODUCTS

Quarterly Technical Progress Report
for the Period of April-June 1992

by

Brian D. Runge, Research Supervisor
Robert O. Ness, Jr., Research Supervisor
Laura L. Sharp, Research Engineer
Richard E. Shockey, Research Engineer

Energy and Environmental Research Center
University of North Dakota
Box 8213, University Station
Grand Forks, North Dakota 58202

Contracting Officer's Representative: James D. Westhoff

for

Laramie Project Office
U.S. Department of Energy
P.O. Box 1189
Laramie, WY 82070

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1.0 INTRODUCTION

As the end of the period of performance on the project approaches, efforts are being focused on completing the goals set forth in the contract. The char produced in the 100-lb/hr process development unit (PDU) has been magnetically cleaned by AMAX and returned to the Energy and Environmental Research Center (EERC). The final calcining step of the process is currently being performed in the 4-lb/hr continous fluidized-bed reactor (CFBR). The liquid products generated by the PDU have been collected and split into usable fractions and fractions to be discarded. Samples of the coal-derived liquids have been sent to Merichem Corporation of Houston and Koppers Industries of Pittsburgh for determination of their usefulness as chemical feedstock for the production of cresylic acids and anode-grade-binder pitch.

The technical and economic assessment performed by Xbi and J.E Sinor Consultants has been completed. The report will not be released as a stand-alone document, but will be incorporated in the final report.

The briquette testing being conducted at the EERC has produced high-quality briquettes using a number of binder agents. The next step in the test matrix will include the use of coal-derived liquids from the PDU as the binder.

An additional coal has been added to the mild gasification test matrix. AMAX recently acquired two eastern low-sulfur bituminous coals and suggested that a limited test schedule be conducted to determine the suitability of these coals for the mild gasification process. The sulfur levels in the raw coals are below the target levels suggested by the steel industry for metallurgical coke use. To date, it has not been possible to reach these goals using the high-sulfur Illinois Basin coals tested.

2.0 CONTRACT MODIFICATION

During the month of April, the subcontract to J.E. Sinor was modified to extend the period of performance to the end of May so that new information provided by the conceptual plant design study, completed by Xbi, could be used in the updated market study and economic assessment. The final study by J.E. Sinor has been completed and will be incorporated in a future report.

In June, a modification of the Mild Gasification contract was signed, changing the scope of work to be completed by the project to include the testing of an additional coal. The work to date using the high-sulfur Illinois Basin coals has not been able to reach the target sulfur levels set forth by the steel industry. AMAX has recently acquired new eastern coal reserves with the purchase of the Cannelton Coal Company. This holding produces two coals (Sandlick and Stockton) that show good promise for use in the mild gasification process. Proximate analysis of the Sandlick and Stockton coals can be found in Table 1. As indicated in the analytical data, both of these coals have very low sulfur and ash levels. The free-swelling index of each coal is slightly higher than that of the Indiana #6 previously

TABLE 1*

Analytical Results for P-027 Liquids

	Oil Fraction	Light Fraction	Heavy Fraction
Carbon	87.23	88.08	86.44
Hydrogen	11.35	9.37	7.79
Nitrogen	1.32	0.62	0.80
Sulfur	1.03	1.95	2.37
Oxygen	2.20	0.95	2.79
Distillation			
204°C	85	21	21
204° - 371°C	11	73	61
371°C+	4	6	18
Water Content (ASTM D-95-83)	<0.1	<0.1	<0.1

* Values are given in wt%.

utilized extensively in the test matrix; this should not, however, preclude operational testing.

3.0 COAL LIQUID ANALYSIS

A sample of the coal liquids generated during mild gasification test P-027 was sent to AMAX R&D for analysis. The sample was separated into three fractions: oil, light, and heavy in order of increasing boiling point. The results of the analysis for each of the fractions can be found in Table 1. The heavy fraction contains 18 wt% in the pitch boiling range. Given this pitch content, it was decided to perform vacuum distillation to produce a pitch sample.

Pitch vacuum distillation was conducted in a bench-scale glass apparatus. A vacuum of 46-mm Hg absolute pressure was obtained. At this pressure, the final temperature was 276°C, which should yield a pitch boiling above 397°C at atmospheric pressure. The pitch yield was 30 wt%, indicating that the single-stage distillation used was fairly inefficient and the pitch will contain a significant fraction of sub-397°C material. Nonetheless, evaluation of the distillation residue should give a good indication of the potential of this material for use in anode-binder manufacturing.

Several properties of the pitch are shown in Table 2, along with typical aluminum industry specifications for anode-binder-quality material. Based on the elemental analysis, it is apparent that the sulfur content of the P-027 pitch is high. This is not surprising given the high sulfur content of the parent coal.

Ash content is also high, but can probably be lowered by improved cyclone design. The carbon and hydrogen analyses were used to compute the C/H atomic ratio. For P-027 pitch, this ratio is too low, indicating that the pitch contains some low boiling material and also suggesting that the carbon aromaticity is low. Given that this material was produced at temperatures

TABLE 2

Properties of P-027 Pitch

	P-027 Pitch	Binder Pitch Specifications
Ultimate Analysis, wt%		
Carbon	86.17	--
Hydrogen	5.76	--
Nitrogen	1.02	--
Sulfur	2.57	<0.60
Oxygen	3.65	--
Ash	1.56	<0.35
C/H Atomic	1.25	>1.70
Ca, ppm	--	<100
Na, ppm	--	<100
Softening Point, °C	114	108-114
Toluene Insolubles, wt%	24	>26
Quinoline Insolubles, wt%	8	12-17
Coking Value, wt%	43	>54

much lower than used in coke ovens, it is not surprising that aromaticity is low.

In addition to elemental analysis, the pitch was evaluated for several properties important in anode manufacture. The softening point was measured by the cube-in-air method and is in the acceptable range. Toluene insolubles (TI) are slightly low. Quinoline insolubles (QI), which are suspended solids thought to be similar to carbon black, are also low. Both QI and TI could be increased by adding a few weight percent of carbon black to this material. This might also increase the coking value into the acceptable range.

Overall, this mild gasification pitch could not be utilized as an anode binder because of its high sulfur content. However, other properties of the pitch look very promising. If a similar pitch had been produced from low-sulfur coal and modified by the addition of carbon black, aluminum industry pitch specifications could be approached.

We have also initiated discussions with Merichem and Koppers regarding an outside evaluation of the mild gasification liquids. Merichem is interested in obtaining new sources of cresylic acids and has agreed to evaluate the lighter (<260°C) fractions produced in mild gasification. Koppers has agreed to evaluate the heavy liquid for its potential in manufacturing anode-binder pitch.

4.0 CHAR UPGRADING

Approximately 400 pounds (4 drums) of mild gasification char was physically cleaned by AMAX using a permanent roll magnet system. The cleaned material was shipped to the EERC on June 30 to be run through the final calcining step. Seventy-four percent of the feed material was recovered as nonmagnetic, cleaned char, which was in close agreement with the results obtained in scoping tests conducted previously. Each drum of char and the cleaning products from it were sampled. Complete analytical results, including ash content, will be reported in the next monthly report. The current results indicate that char sulfur content was reduced from about 3.3 to 2.9 wt%. These results are similar to those obtained in scoping tests performed earlier.

A sample of the cyclone fines from Run P-028 has also been analyzed. Results are reported in Table 3. Analytical data for a typical char are included for comparison. No significant difference appears between the cyclone fines and the char, indicating that the fines can be used in the final briquetted char product.

4.1 Char Briquetting

The briquetting tests performed in June and the results of strength testing on the briquettes are presented in Table 4. The data for tests conducted previously are presented in Table 5. The tests are listed in reverse chronological order from most recent to oldest.

4.2 Briquetting and Strength Tests

Briquettes made with cooked pearl starch, regardless of char density, were similar in strength to briquettes made with the modified starch, Sta-Lok 600. Low-density char briquettes made with the cooked pearl starch were slightly better than modified starch briquettes in abrasion resistance (+2%), but had a slightly lower compressive-load strength (-14 psi). The drop resistances were equivalent for low-density char briquettes made with the two binders. Similarly, high-density char briquettes made with the cooked pearl starch were equivalent to modified starch briquettes in abrasion and drop resistance, but had a slightly lower compressive-load strength (160 vs. 175 psi).

The addition of low-sulfur Amoco resid had a small positive effect on abrasion resistance (3%) and a small negative (11 psi) effect on compressive strength when used in conjunction with the cooked pearl starch.

TABLE 3

Analytical Results for P-028 Cyclone Fines and Typical Char

	Cyclone Fines	Char
Ultimate Analysis, wt%		
Carbon	66.85	68.24
Hydrogen	2.56	2.63
Nitrogen	1.73	1.61
Sulfur	3.36	2.94
Oxygen	7.92	6.98
Proximate Analysis, wt%		
Moisture	1.74	0.93
Volatile Matter	16.78	16.15
Fixed Carbon	62.87	64.26
Ash	20.35	19.59

TABLE 4

Strength Testing of Char Briquettes Made During June

Briquette Type	Days Dried	Drop wt%	Tumble wt%	Crush psi	Moist. wt%	Density g/mL
14) High-Density Char	OD	61	49	45	2.5	
1% PVA 523-S	4	76	49	78	1.6	
2.5% Hydrated Lime	10	73	46	73	ND	
13) High-Density Char	OD	52	46	39	3.2	
1% PVA 523-S	4	69	38	47	1.4	
1% Lime	10	66	35	50	ND	
12) High-Density Char	OD	75	43	42	6.9	
0.5% PVA 523-S	4	55	37	33	2.0	
2% Sta-Lok 600 Starch	11	64	42	38	ND	
11) Low-Density Char	OD	ND	ND	50	7.8	
2% Molasses	4	88	78	96	2.7	
2% Sta-Lok 600 Starch	7	89	70	106	1.7	
10) Low-Density Char	OD	ND	ND	50	0.1	
3% Sta-Lok 600 Starch	4	88	64	80	4.6	
	7	83	70	84	2.0	
9) High-Density Char	OD	45	51	20	3.7	
6% Molasses	4	73	42	46	2.6	
3% Hydrated Lime	7	67	57	45	3.1	
8) High-Density Char	OD	ND	44	6.5	5.5	
4.6% Amoco Low-Sulfur Resid.	4	36	18	18	1.9	
	7	25	26	16	2.4	
7) Low-Density Char	OD	91	86	89	6.5	
4.1% Sta-Lok 600 Starch	4	98	88	123	3.7	
4.6% P-028 Scrubber Tar	7	98	87	118	3.6	
6) High-Density Char	OD	86	76	39	3.5	
4.1% Cooked Pearl Starch	4	96	91	106	4.8	
4.6% P-028 Scrubber Tar	7	97	87	119	3.1	
5) Reject Low/High-Den. Char	OD	93	92	79	0.9	
2.3% Sta-Lok 600 Starch	8	98	96	156	3.9	
4) Reject Low/High-Den. Char						
No Binder	12	83	70	70	3.7	
3) Low-Density Char	4	98	95	123	3.7	
4.1% Cooked Pearl Starch	7	98	93	141	2.4	0.89
2) High-Density Char						
4.1% Cooked Pearl Starch	4	99	96	112	4.4	
4.6% Amoco Low-Sulfur Resid.	7	98	95	149	2.4	1.03
1) High-Density Char	4	98	92	144	3.0	
4.1% Cooked Pearl Starch	7	98	92	160	3.0	0.86

OD - Oven-dried.
ND - Not determined.

TABLE 5

Strength Testing of Char Briquettes Made Prior to June

Briquette Type	Day	Drop wt%	Tumble wt%	Crush psi	Moist. wt%	Density g/mL
FMC Formcoke		97	88	~295	1.7	0.89
Low-Density Char	4	97	90	144	2.9	0.82
4.1% Sta-Lok 600 Starch	7	97	91	155	3.1	
High-Density Char	5	96	91	150	2.7	
4.1% Sta-Lok 600 Starch	7	98	93	175	2.6	0.88
High-Density Char 4.1% Cooked Pearl Starch 4.6% P-028 Scrubber Tar	7	94	83	91	3.2	0.92
High-Density Char 4.1% Sta-Lok 600 4.6% P-028 Scrubber Tar	7	98	93	165	5.0	0.95
Low-Density Char 4.1% Sta-Lok 600 4.6% P-028 Scrubber Tar	7	94	77	63	2.5	0.80
Reject Low-Density Char ~3% Sta-Lok 600 Starch 4.7% P-028 Scrubber Tar	7	90	80	64	4.9	1.10
Low-Density Char 2% Sta-Lok 600 Starch Batch 1	7	80	65	77	2.6	
Batch 2	6	86	67	75	2.9	0.82
Reject Low-Density Char From 2% Sta-Lok 600 Tests	6	93	78	70	3.0	
74% Low/26% High-Density Char 7.0% Sta-Lok 600 Starch	6	99	98	290	3.2	0.94
Low-Density Char 9.1% HFMS Asphalt Emulsion	9	66	47	19	2.1	0.67
Low/High-Density Char 9.1% CSS Asphalt Emulsion	9	89	74	36	1.8	0.71
High-Density Char 8.7% CMS Asphalt Emulsion	10	22	42	22	2.1	0.87
High-Density Char ~12% Molasses/Lime (2/1)	16	84	64	77	4.0	0.95

The low strength of briquettes made only with the low-sulfur Amoco resid indicated that this material is ineffective alone as a binder. This material may develop additional strength if a coking step is used after briquette formation.

The test with a 2/1 molasses and hydrated lime mixture indicated that, at a 9% binder concentration, this mixture is ineffective at developing sufficient strength to produce an acceptable briquette.

The repeat test with high-density char and 4.1% cooked pearl starch plus 4.6% P-028 scrubber tar as binders was successful at producing a stronger briquette. The drop and abrasion resistances increased modestly by 3% and 4%, respectively, and the compressive load increased 28 psi. The lower strength of the first briquettes made with this binder combination may have been due to improper feed moisture content or improper compaction during briquetting.

The repeat test with low-density char and 4.1% Sta-Lok 600 modified starch plus 4.6% P-028 scrubber tar resulted in even more dramatic increases in briquette strength. The increases in drop and abrasion resistances were 4% and 10%, respectively, and the compressive load increased by 55 psi.

Low-density char briquettes made with 3% Sta-Lok 600 modified starch were roughly equivalent to 2% starch briquettes based on strength testing. Preliminary comparison of low-density char briquettes made with 2%, 3%, 4.1%, and 7% Sta-Lok 600 modified starch indicate that the concentration required for producing an acceptable briquette is between 3% and 4.1%.

The addition of 2% molasses in combination with 2% Sta-Lok 600 modified starch resulted in modest increases in drop and abrasion resistance, 3% each, respectively, when compared to low-density briquettes made with 2% Sta-Lok 600 modified starch alone. The most significant effect was an increase in compressive load of 31 psi.

The high-density char briquettes made with the polyvinyl alcohol (PVA) 523-S in combination with modified starch, lime, or hydrated lime were inferior to briquettes made with natural starches. The PVA may actually have a negative effect when used in conjunction with the 2% Sta-Lok 600 modified starch. This is indicated by the lower drop and abrasion resistances and the lower compressive load of the PVA/starch briquettes compared to briquettes made only with the starch.

4.3 Effect of Curing Time on Strength Development

Preliminary examination of strength testing indicates that the drop and abrasion (tumble) resistances are essentially maximized after 4 days based on comparison with 7-day test results. This parallels briquette moisture-loss measurements, indicating that moisture content typically equilibrates after 4 days. However, it appears the compressive-load strength may not be completely developed after 4 days, and the effect appears to be more pronounced as the briquette compressive strength increases.

Oven-curing temperatures between 149° and 204°C were effective at reducing the drying time to an hour or less; however, this curing time was often insufficient to allow proper strength development. The briquettes were cured in a 10% oxygen atmosphere produced by mixing bottled air with bottled nitrogen. The abrasion and drop resistances of oven- and air-cured briquettes were roughly equivalent for low-strength briquettes. However, for stronger briquettes, 1 hr of oven-curing resulted in lower drop and abrasion resistances compared to air-curing. The most significant difference between oven- and air-cured briquettes was the underdeveloped compressive-load strength resulting from oven-curing. Apparently, the removal of moisture is not the only factor in the proper curing of binders and the development of strength.

5.0 CFBR TESTING

As outlined above in the area of contract modifications, an additional coal source has been added to the test matrix of the mild gasification project. The new coal is provided by AMAX. AMAX acquired new low sulfur eastern bituminous coal reserves with the purchase of the Cannelton Coal Company. The two coals being tested are Sandlick and Stockton. The initial shipment of eastern coal from AMAX consisted of Sandlick and Stockton coals sized to -1/4" x 0. Initially a feed problem was encountered. The coal contained a large percentage of fines. These were removed by sizing the coal to -1/4" x 12 mesh. This process rejected a large volume of coal, and it became necessary to mix the two coals to obtain a sample of sufficient size for the CFBR testing. The two coals are nearly identical chemically.

Approximately 325 pounds of the Cannelton coal mixture was processed in the CFBR, first at a temperature of 350° and then at 400°C. Proximate and ultimate analyses of the mixture after screening are shown in Table 6 below.

The next scheduled runs will process the char from the 400° run at 450°C, then at temperatures of 500°, 550°, and 700°C. These runs are scheduled to be completed by the end of August.

6.0 LIQUID PRODUCT DISPOSITION

Approximately twenty-eight 55-gal drums of a mixture of #2 diesel fuel, catalytic cracker decant oil, and coal-derived organic liquids were accumulated from the condensation train on the Mild Gasification PDU at EERC. A sampling plan was developed and submitted to the North Dakota State Department of Health (NDSDH) for approval. After approval, a composite sample was taken from ten randomly selected 55-gal drums and analyzed in accordance with the requirements of CFR 40, Part 266, Subpart E. Analysis determined that the oil mixture meets the Specification Used Oil requirements of CFR 40 and would be suitable for energy recovery purposes. The NDSDH approved the

TABLE 6

Analysis for Cannelton Coal

	As Det. (wt%)	As Rec'd (wt%)	Moist. Free (wt%)	Moist./Ash Free (wt%)
Proximate				
Moisture	1.80	3.40	N/A	N/A
Volatile Matter	33.14	32.59	33.75	38.36
Fixed Carbon	53.24	52.39	54.22	61.63
Ash	11.81	11.61	12.03	N/A
Ultimate				
Hydrogen	4.88	4.98	4.76	5.41
Carbon	73.46	72.24	74.80	85.03
Nitrogen	1.27	1.24	1.29	1.47
Sulfur	0.92	0.90	0.93	1.06
Oxygen	7.65	9.00	6.16	7.00
Ash	11.81	11.61	12.03	N/A

burning of the oil mixture under the guidelines of CFR 40 and the UND Boiler Plant Permit to Operate No. 730018 which states that no more than 200 gal per hour shall be burned.

A plan for introducing the oil mixture into the University boiler was developed by the boiler plant supervisor and EERC personnel. Subsequently, during the week beginning July 7, 1992, seven drums per day were delivered to the boiler plant. The oil mixture was then pumped evenly over a pile of approximately 80 tons of coal. After the oil pumping was completed, the coal was transferred into a 100-ton feed bunker for consumption. This bunker was purposely drawn down by the previous shifts to allow room for the oil amended coal. This procedure was repeated for the next three days. Ultimately, 1325 gallons of the oil mixture was consumed at the boiler plant. The boiler plant supervisor noted that no problems were encountered due to burning this oil mixture. He said it burned extremely well. Due to the higher Btu value of the oil-soaked coal, the automatic coal stokers reduced the feed rate.

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