Task 4.0
Advanced Fuel Forms and Co-Products

Semi-Annual Report
April 1 - June 30, 1993

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July 1993

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For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

By
University of North Dakota
Energy and Environmental Research Center
Grand Forks, North Dakota

MASTER

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EXECUTIVE SUMMARY

Summarized below is the work carried out over the six-month period, July 1 to June 30, 1993, on the subtasks Beneficiation for Advanced Systems, Co-Products, and Low-Rank Coal Liquefaction. Beneficiation for Advanced Systems consists of two parts: Dust Generation and Oil Agglomeration.

● BENEFICIATION FOR ADVANCED SYSTEMS

A. Dust Generation

Hydrothermal drying (hot-water drying and saturated-steam drying) was determined to be an effective method of causing a permanent reduction in the equilibrium moisture of low-rank coals and removing sodium. Moisture reduction for three test coals varied from 56 to 86 wt%, while sodium reduction was as high as 75%. Various stability tests were conducted on raw and hydrothermally treated coals to determine the effect of drying on the friability of the lump coal. The results indicated that as moisture was reduced, the amount of fugitive dust and fines generation increased substantially. An additional task of the program was to develop stability tests based on American Society for Testing and Materials (ASTM) procedures which could accommodate a smaller coal size and reduced amount of coal. The development of improved methods is continuing for assessing the propensity of coals to dust generation.

B. Oil Agglomeration

Carbonic acid treatment of lignites and subbituminous coals reduced the sodium contents of these coals by 60 to 70 wt%. Float/sink washability testing of low-sulfur subbituminous coals produced ash reductions of 30 to 40 wt% at +95 wt% moisture and ash-free (maf) coal recovery, indicating their potential for beneficiation by selective agglomeration.

Lignites and subbituminous coals were successfully agglomerated without prior chemical treatment of the coal surface or without adjusting the pH of the water. Selective agglomeration of a low-sulfur Powder River Basin (PRB) subbituminous coal produced ash reductions of 35 wt% with maf coal recoveries over 85 wt%. Agglomerates with higher ash content than average for PRB coals from selective agglomeration were successfully enlarged with additional coal-derived oil.

Ineffective agglomerants were induced to agglomerate low-rank coals by mixing with a polar oil or polar alcohol. Effective agglomeration promoters were crude phenol, *m*-cresol, cresylic acid, methanol, ethanol, propanol, and butanol.

Preliminary results show the potential for enhancing agglomerate integrity using a partially polymerized coal gasification-derived oil as a binder. Air-dried agglomerates containing presumably polymerized oil were appreciably resistant to degradation and generation of nuisance dust. Thermal deoiling of these agglomerates yielded a product with reduced strength.

● CO-PRODUCTS

Three coals, a North Dakota Lignite, a North Dakota Leonardite, and an Alaskan subbituminous coal, were pyrolyzed under nitrogen at a temperature of 850°C and ambient pressure using rapid and slow heatup and staged heating programs. The resultant chars were activated with and without steam. Proximate analysis showed that the subbituminous char collected from the reactor was typically lower in volatiles than the lignite. Lower recoveries of lignite char than subbituminous char from the reactor were due to greater fines production of the lignite coal. Fines recovered downstream from the reactor were insufficiently pyrolyzed. Adsorption of sulfur dioxide by the lignite char and by the subbituminous char were indistinguishable from one another, but both were at least comparable to commercial chars prepared from coal.

● LOW-RANK COAL LIQUEFACTION

Coal can be effectively solubilized by treatment with carbon monoxide reductant in an aqueous solvent (CO steam process). As demonstrated recently with U.S. and Australian low-rank coals, sodium aluminate improves the conversions in the CO/H₂O system and in CO/H₂O/hydrogen donor solvent mixtures. Further development of this technology requires information on how this solubilization can be coupled with subsequent hydrotreatment. In this report, the catalytic hydrotreatment of the solubilized low-severity products from sodium aluminate-catalyzed and uncatalyzed CO/H₂O reactions of a Wyodak subbituminous coal are compared. Catalytic hydrogenations of the THF-soluble fractions obtained from the two low-severity products were performed with a conventional cobalt-molybdenum catalyst as well as two clay-supported iron catalysts at 425°C for 3 hours in the presence of 1000-psi (cold) hydrogen pressure. Liquefaction with the cobalt-molybdenum catalyst gave 68% conversion to heptane solubles for both the sodium aluminate and the uncatalyzed low-severity reaction intermediates. In contrast, the supported iron catalysts gave much higher conversions for the intermediate from the sodium aluminate-catalyzed reaction compared to those from the uncatalyzed reaction. These results have important implications for multistage liquefaction processing schemes.

TASK 4.0 ADVANCED FUEL FORMS AND CO-PRODUCTS

Fundamental studies have been undertaken to develop and test new methods for upgrading low-rank coals (LRCs) to produce advanced fuel forms, high-value-added carbons, and liquid co-products using various techniques including cleaning, drying, carbonizing, aggregating, liquefying, and liquid upgrading. Supporting research has been performed for evaluating product properties, including physical stability toward moisture reabsorption, dust generation, and strength testing; developmental work has also been undertaken on activated carbons and their sulfur dioxide adsorption behavior, all in reference to current industry specifications as well as potential new market specifications. Basic research on liquefying low-rank coals using carbon dioxide as a reductant together with cobalt-molybdenum and upon catalysts has been conducted. The results to be described have important implications for developing the concept of a coal refinery and implementing processes for advanced coal products directed towards fuel and nonfuel applications.

The project on Advanced Fuel Forms and Co-products from Low-Rank Coals has been divided into four subtasks:

1. Dust Generation
2. Oil Agglomeration (beneficiation)
3. Co-Products (char and coal liquids upgrading)
4. Liquefaction

In this report the objectives and accomplishments of each task are discussed separately.

Subtask 4.1 Beneficiation for Advanced Systems

A. Dust Generation

Introduction

Because of the new acid rain regulations, many Midwestern electric utilities are switching to low-sulfur Western coals. The switch from Midwestern or Eastern coals to Western coals creates key problems, notably, degraded boiler performance, derating, and poor particulate collection (1). Many of these problems can be alleviated by proper blending of two or more coals. Because the friability (breakability) of Western coals is higher than Eastern coals they fracture more easily, thus producing a high percentage of fines. The greater friability also increases the potential for dust formation. As a consequence, utilities are forced to deal with a new problem with which they have had little experience, namely, excessive dust generation; the result is increased expenditures for dust control (2).

Dust generation, moisture reabsorption, and spontaneous combustion have generally received minor attention during development of the coal upgrading technology. Over this

past test period, three methods of drying (air, hot-water, and saturated-steam) were used to generate low-moisture, upgraded products for physical stability measurement via drop-shatter, tumble, and equilibrium moisture tests. The program concentrated on the evaluation of standard methods of coal friability testing as well as the development of new techniques for comparing the propensity of raw and upgraded coals to produce dust.

The saturated-steam-drying (SSD) process was developed by Fleissner for German brown coals to reduce moisture, increase the heating value, and alleviate the problem of size degradation resulting from the removal of moisture as a vapor (3). Because of the saturated-steam atmosphere, water is removed as a liquid and continues to be removed until the particles are uniformly heated. Saturated-steam drying can also reduce the ash content if inorganics are water soluble, i.e., ionically bonded to the coal.

As an advancement of the Fleissner process, hot-water-drying (HWD) was developed at the Energy & Environmental Research Center (EERC) to permit production of low-rank coal-water fuels (LRCWFs) from low-cost low-rank coals at dry solids concentrations and energy densities approaching those obtained from bituminous coals (4). HWD simulates coalification on a time scale of minutes, rather than geological eras, and irreversibly removes water, as well as some alkaline material, from low-rank coals.

Objectives

The major goals are to assess the stability of as-received and upgraded low-rank coals based on dust generation, moisture reabsorption, and spontaneous combustion. The objective of this year's program is to develop new methods and modifications to the existing ASTM standards used to evaluate the propensity of coal and coal products to generate dust.

Accomplishments

Experimental

● AIR DRYING

A known amount of 12.7- x 6.68-mm coal was placed into open-faced pans and placed in a laboratory hood for a period of approximately 24 hours. Subsequently, the pans of coal were reweighed and the amount of moisture via evaporation was calculated. If the final moisture content has not reached the desired level, the coal is again placed in the hood for another 24-hour period. Once acceptable levels are reached, the moisture content is verified by an ASTM-approved moisture determination method. The samples were then double-bagged and stored for future testing.

● HOT-WATER DRYING/SATURATED-STEAM DRYING

The systems and procedures used for performance of hydrothermal treatment have been described elsewhere (5) (6) (7). Briefly, drying tests were performed in an externally heated 2-gallon autoclave instrumented for temperature measurement/control and pressure measurement. HWD was performed on slurries containing approximately 2000 grams of 12.7- x 6.68-mm coal and 2000 grams of deionized water. Based on previous HWD studies on LRCs, the lump coal/water slurries were heated to 300°C and then

maintained at temperature for 30 minutes. The autoclave and contents were allowed to cool overnight prior to recovery of the treated coal and process water.

The steam-drying tests were similarly performed, except the 12.7- x 6.68-mm coal was suspended above the water to prevent contact. Approximately 2000 grams of coal and 500 grams of deionized water were charged in each test. To remain constant with hot-water drying, the residence time was again 30 minutes at 300°C. At the completion of the constant temperature period, the autoclave was vented, releasing steam to the condensate collection system. The autoclave and contents were allowed to cool overnight prior to recovery of the treated coal and process water.

The masses of raw and treated coal and feed and process water and the volume of process gas were measured to determine material balances.

● TUMBLER TESTING

The basic procedures of loading the coal, size determinations, and indices calculation remain similar to ASTM procedure. (see Appendix 4.1-1) However, the existing method for tumbling could not be used for the upgraded low-rank coal product since the ASTM requires the coal size to be 38.1 x 26.5 mm and all of the coal products were 12.7 x 4.75 mm. Therefore, all design efforts on the tumbler cell, such as the flights used to provide adequate mixing action during tumbling, are based upon the larger-size coal. The test program examined the difference between using the existing dimensions of the flights versus readjustment of the flights to the size of the coal, namely reducing the gap between the ledge and the edge of the cell from 15.9 mm (5/8") to approximately 3.18 mm (1/8"). This flight setup or insert will be referred to as the "new" insert in the text of this report. Figure 4.1-1 indicates the sizes of the two different inserts used for tumbler testing.

The amount of coal used was 100 grams (versus 1000 grams in the ASTM methods) to utilize appropriately the small amount of product material that is generated from bench-scale autoclaves. Another change to the ASTM procedures was increasing the rpm level from 40 to 80 in order to provide more testing within a shorter time frame. Preliminary tests indicated no significant difference between 40 and 80 rpm for the same amount of total revolutions.

● DUST INDEX TESTING

As of 1986, the labor-intensive ASTM dusting index test, which required large samples of coal, is no longer accepted due to large experimental errors. Efforts were focused on standardizing a new method that incorporated better dust analyzing equipment and continuous data logging in order to average out the large fluctuation in the data, although 20% experimental error has been considered acceptable for ASTM testing (see Appendix 4.1-1).

To simulate the dustiness test, a light-scattering device was attached to a 2.1-ft³ cylindrical vessel. The top portion of the vessel was equipped with a top seal and sample dumping section. Approximately 100 grams of sample was dumped into the top section then quickly sealed. Attached to the main drum were two sample ports to allow continuous monitoring or sampling of dust generated. The fugitive dust generated is

Figure 4.1-1. ASTM design versus modified tumbler cell design.

analyzed by a real-time aerosol monitor (RAM-1) for measuring airborne particulates less than 20 microns in size. Data were collected for a 10-minute increment or until the instrument returned to zero. This test reports the amount of respiratory and explosive dust that would occur from simply dumping the (12.7- x 6.68-mm) product material size, approximately 4 feet.

● DROP-SHATTER TESTING

The coal to be used for this test was originally screened to 12.7 x 6.68 mm to reflect better the anticipated sizes for the product coal. Weight fractions were calculated with dry screening methods at a variety of sizes between 12.7 and 6.68 mm. The amount of coal per test was 50 grams (50 lb in ASTM method) to accommodate the lack of treated coal. The drop-shatter test consisted of dumping a coal sample through a 6-inch PVC pipe which was 6 feet in length. At the bottom of the pipe, a collection vessel made of stainless steel received the falling coal. The coal was then emptied from the vessel, and a dry sieve analysis was completed. Based upon a comparison of weight percentages and specific size factors, a friability index is then generated to indicate the amount of breakage that occurred from the 6-foot drop. Multiple drops were performed to simulate coal breakage from coal transfer and unloading.

Results

● DRYING

A series of hydrothermal drying tests was performed with three test coals. Saturated-steam drying and hot-water drying were performed at the same temperature for each of the test coals. The acceptable particle-size distribution was 12.7 x 4.75 mm. The

coal size for these autoclave experiments was determined from a literature search and personal communications with companies that are currently seeking to produce dried LRC at the bench-, pilot-, or demonstration-scale level (5). (The companies currently developing LRC drying process are ENCO, WECO, K-Fuels, and Nu-Fuels.) Samples for the program were requested from these companies also, but only one company, Wisconsin Power and Light—K-Fuels, sent samples. Others indicated that they are currently performing "in-house" stability analysis of their products.

Table 4.1-1 summarizes the proximate and ultimate analysis for three LRCs recently upgraded using the hydrothermal method at the EERC. Each of the prospective samples was weighed and classified in terms of size with dry sieve methods. Table 4.1-2 summarizes the product recoveries for each of the hydrothermal tests. Sample calculations and methods used for determining values in Table 4.1-2 are located in Appendix 4.1-2. Table 4.1-3 indicates the effect hydrothermal drying had on the various ash components for Knife River coal. The ash results show a significant decrease from 4.5 wt% sodium to below 2 wt% for the hot-water drying and below 3.0 wt% for saturated-steam drying. However, the relative overall ash content did increase from the processing, due to the loss of CO₂ via decarboxylation.

TABLE 4.1-1

Proximate, Ultimate, and Heating Value for Raw, HWD, and
SSD Subbituminous and Lignite Coal (Equilibrium Moisture Basis)

Coal Type:	Little Tonzona			Colstrip			Knife River		
Drying Type	—	Raw	SSD	—	HWD	SSD	—	HWD	SSD
Proximate, wt%									
Equil. Moisture	29.7	11.1	9.5	24.8	9.3	8.8	35.1	15.0	12.6
Volatile Matter	36.8	39.4	39.1	30.1	34.4	34.2	29.7	35.1	36.2
Fixed Carbon	26.3	39.5	41.0	37.5	47.6	48.2	27.7	38.8	39.9
Ash	7.2	10.0	10.4	7.6	8.7	8.9	7.5	11.1	11.3
Ultimate, wt%									
Hydrogen	6.7	5.2	5.1	6.0	5.3	4.9	6.7	5.4	5.3
Carbon	42.0	58.3	59.1	50.8	63.8	63.6	40.3	55.7	56.9
Nitrogen	0.5	0.6	0.6	0.6	0.7	1.0	0.5	0.7	0.8
Sulfur	1.1	1.3	1.2	0.8	0.8	0.7	0.9	1.4	1.4
Oxygen	42.5	24.6	23.5	34.4	20.6	20.8	44.0	25.7	24.3
Ash	4.2	10.0	10.4	7.6	8.8	8.9	7.5	11.1	11.3
Heating Value, Btu/lb	7,170	10,030	10,200	8,610	10,850	10,810	6,740	9,400	9,550

TABLE 4.1-2

**Material Balances, Coal Recovery, and Moisture Reduction
for 300°C HWD and SSD Samples**

Coal Type:	Little Tonzona		Knife River		Colstrip	
Drying Type	HWD	SSD	HWD	SSD	HWD	SSD
Material Recovery, wt%	95.8	93.8	96.4	96.1	98.3	98.3
Water Recovery, wt%	101.7	106.4	96.2	101.7	100.6	102.0
Solids Recovery, wt%	84.6	83.6	96.6	90.4	94.3	93.2
Btu Recovery, %	93.8	92.5	102.8	95.2	98.5	96.5
Coal Recovery, lb/100 lb	72.1	61.9	72.0	64.4	78.8	75.8
Moisture Reduction, wt%	56.0	86.1	69.5	77.5	75.7	82.9

TABLE 4.1-3

Ash Analysis for Knife River Coal Samples

Ash Component, Oxide	Raw Coal, wt%	HWD Coal, wt%	SSD Coal, wt%
Silicon	31.20	35.20	34.10
Aluminum	12.30	12.10	11.60
Iron	4.60	5.70	4.20
Titanium	1.20	1.10	1.00
Phosphorous	0.20	0.20	0.20
Calcium	20.00	18.40	19.90
Magnesium	7.10	6.60	7.00
Sodium	4.50	1.20	2.90
Potassium	0.10	0.10	0.10
Sulfur	18.70	19.40	18.80
Ash Content (moisture-free)	11.60	13.10	12.90

● **TUMBLE TESTING**

Initial tumbler tests were completed using raw Colstrip and Little Tonzona coals to determine tumbling parameters for the treated coals and to compare ASTM methods to the modified tumbler test. Test parameters for the rotation of the tumbling cell ranged from 40 to 80 rpm (ASTM = 40 rpm), the amount of coal used per test was adjusted from

100 to 1000 grams, and the total revolutions were also varied from 600 to 14,400 (ASTM = 2,400). The initial coal samples were screened and classified into seven different size criteria ranging from 9.5 mm to less than 0.60 mm. Weights were then recorded for each screen size and the total coal sample was placed into the cell and tumbled at the appropriate rpm level and the total number of revolutions.

Comparison of the results for the different tests was aided by a derived formula that allowed the sizing data to be quantified on a common basis when differences were due mainly to the variability in feed coal sizing data. Equation 4.1-1 yielded the data for the different tumbler tests. The results from the study indicated a substantial increase in fines generated as the revolutions were increased, little difference in fines generated as rpm levels changed, and a proportional relationship between fines generated and the amount of coal used for the tumbler test. After this initial screening study, the parameters were set for tumbler tests for the other raw coals and their respective dried products. Figure 4.1-2 indicates the effects of varying the number of revolutions for a set speed of 80 rpm for 100-gram samples of raw and treated Little Tonzona coal. As anticipated, an increase in the revolutions led to an increase in the tumble index. The negative values reflect the comminution which occurred during the tumbling; the positive tumble index indicates an overall increase in the smaller sized particles due to communication of the large material. The results show high tumble index levels for the 2.36-mm and -0.60-mm sizes, and negative numbers for 6.68-mm sizes and above. The drier the coal, the more dust that was created, as indicated by the larger tumble index. Figures 4.1-3 and 4.1-4 illustrate the effect of drying and total revolutions on the various Colstrip and Knife River samples. The results were again similar, in that the drier the coal, the larger the tumble index. The results indicate that Little Tonzona had the lowest value and Knife River had the highest of the three test coals.

$$T_i = (W_T - W_F) * \left(\frac{100}{W_A} \right) \quad [\text{Eq. 4.1-1}]$$

Where T_i = tumble index
 W_T = weight of tumbled coal for particular screen size, grams
 W_F = weight of feed coal for particular screen size, grams
 W_A = weight of total feed coal for test, grams

Both the raw and treated materials for the three coals were subjected to the ASTM tumbler test and tumbler test with the "insert" or ledges designed for smaller coal sizes to establish the effects of cell modifications. Tables 4.1-4, 4.1-5, and 4.1-6 summarize the results of processing and tumbling each of the coals. Results are expressed in terms of a friability index and dust index calculated similarly to ASTM procedure, with slight modifications due to the coal size used for testing. Tests were also performed with the original dimensions of the tumbler cell with ASTM insert with the three test coal samples of 38.1- x 26.5-mm material and compared to the results from tumbling 12.7- x 6.68-mm material. The results indicate that the modified insert (1/8" ledge) compared more favorably to the indices attained with the ASTM insert and 38.1- x 26.5-mm coal size than did the 5/8" ledge size. The results also indicate that as the equilibrium moisture is decreased, the friability greatly increases for the test coals. No specific conclusion can be

Figure 4.1-2. Tumble indices for Little Tonzona coal and coal products at various revolutions and constant coal weight.

Figure 4.1-3. Tumble indices for Colstrip coal and coal products at various revolutions and constant coal weights.

Figure 4.1-4. Tumble indices for Knife River coal and coal products at various revolutions at a constant coal weight.

made for process specifics; it seems that the results will vary from coal to coal. The tables also show the effect of increasing the revolutions and the variance from switching from the ASTM-designed tumbler insert to a the new insert.

● DROP-SHATTER TESTING

The results from drop-shatter testing, noted in Table 4.1-7, indicate that the dried coals have a much higher friability index. As with the tumbler test, the higher the friability index, the more breakage that occurred to the sample. Specifically for the raw coals, Little Tonzona friability index varied from 0.7 to 3.8 for the raw coal, while the more friable Colstrip and Knife River coals varied from 2.0 to 10.7 and 0.5 to 5.3, respectively. A similar trend emerges from the tumbler test results where Colstrip coal values were higher than those of Knife River coal. For ten drops, however, the Knife River coal results were higher than for the Colstrip coals.

● DUST INDEX TESTING

The results from the tests are reported in Table 4.1-8, including the maximum and average concentrations and the total amount of dust collected during data logging. Averages were generated by dropping the same test coal in three different tests. The results indicate a substantial increase in dust between raw and treated coal products for all three of the test coals. In addition, as with all of the other stability tests, as the moisture decreases, the amount of fugitive or nuisance dust (20 micron and below)

TABLE 4.1-4

Tumbling Results for Raw, AD, HWD, and SSD Little Tonzona Subbituminous Coal

Type	Coal Size, mm	Moisture, wt%	Tumbling Ledge, mm	Revolutions	Friability Index, %	Dust Index, %
Raw	38.1 x 26.5	30.0	15.9	2400	9.3	1.8
Raw	12.7 x 6.68	30.0	15.9	2400	1.4	0.4
Raw	12.7 x 6.68	30.0	15.9	4800	3.1	0.7
Raw	12.7 x 6.68	30.0	3.18	2400	6.7	0.7
	12.7 x 6.68	30.0	3.18	4800	5.7	0.9
AD*	12.7 x 6.68	20.4	3.18	2400	8.8	2.0
AD	12.7 x 6.68	20.4	3.18	4800	13.8	2.9
AD	12.7 x 6.68	9.0	3.18	2400	14.1	2.9
AD	12.7 x 6.68	9.0	3.18	4800	15.4	2.9
HWD**	12.7 x 6.68	10.5	15.9	2400	13.7	2.9
HWD	12.7 x 6.68	10.5	15.9	4800	14.9	4.4
HWD	12.7 x 6.68	8.5	3.18	2400	20.9	6.8
HWD	12.7 x 6.68	8.5	3.18	4800	28.2	13.0
HWD-AD	12.7 x 6.68	5.2	3.18	2400	24.9	7.1
HWD-AD	12.7 x 6.68	5.2	3.18	4800	36.7	13.6
SSD***	12.7 x 6.68	7.2	15.9	2400	22.1	5.6
SSD	12.7 x 6.68	7.2	15.9	4800	26.3	7.7
SSD	12.7 x 6.68	6.0	3.18	2400	37.1	13.6
SSD	12.7 x 6.68	6.0	3.18	4800	38.3	17.9
SSD-AD	12.7 x 6.68	5.0	3.18	2400	30.6	11.2
SSD-AD	12.7 x 6.68	5.0	3.18	4800	38.1	17.2

* Air-dried.

** Hot-water dried.

*** Saturated steam dried.

increases dramatically. Trends similar to those of the other stability tests were found for the raw coals; namely, Little Tonzona indicated the least amount of breakage or dust generation followed by Knife River and Colstrip. Also, Table 4.1-8 illustrates the large increase in dust generation of samples which have been tumbled as compared to coal samples which were not tumbled. This increase can partially be attributed to a decrease in moisture as the coal was tumbled (approximately 1 to 2 wt% moisture was removed).

Multiple tests were also run with the RAM-1 in-line assisted by computer analysis logging the data collected during the tumbling of the cell. Various sample rates were adjusted with the computer every 0.25 to 1 second per sample reading. The goal of the work was to enable direct measurement of the amount of dust continuously during the tumbling test, by drawing off dust samples directly from the cell. The vacuum pump on the RAM-1 will pull at approximately 2 liters/minute. An attempt was made to stop the cell or to delay 5 to 10 seconds (similar to former ASTM standard) in order to allow

TABLE 4.1-5

Tumbling Results for Raw, AD, HWD, and SSD Knife River Lignite Coal

Type	Coal Size, mm	Moisture, wt%	Tumbling Ledge, mm	Revolutions	Friability Index, %	Dust Index, %
Raw	38.1 $\pm$ 26.5	37.5	15.9	2400	15.5	1.9
Raw	12.7 $\pm$ 6.68	37.5	15.9	2400	6.6	1.3
Raw	12.7 $\pm$ 6.68	37.5	15.9	4800	8.6	2.1
Raw	12.7 $\pm$ 6.68	37.5	3.18	2400	7.2	1.7
Raw	12.7 $\pm$ 6.68	37.5	3.18	4800	10.4	3.5
AD*	12.7 $\pm$ 6.68	18.5	3.18	2400	29.7	6.1
AD	12.7 $\pm$ 6.68	18.5	3.18	4800	34.3	9.4
AD	12.7 $\pm$ 6.68	8.1	3.18	2400	37.4	6.0
AD	12.7 $\pm$ 6.68	8.1	3.18	4800	41.8	8.2
HWD**	12.7 $\pm$ 6.68	14.6	15.9	2400	15.2	2.9
HWD	12.7 $\pm$ 6.68	14.6	15.9	4800	18.0	3.6
HWD	12.7 $\pm$ 6.68	9.6	3.18	2400	41.1	10.3
HWD	12.7 $\pm$ 6.68	9.6	3.18	4800	43.9	14.5
HWD-AD	12.7 $\pm$ 6.68	6.1	3.18	2400	48.0	9.3
HWD-AD	12.7 $\pm$ 6.68	6.1	3.18	4800	51.8	10.4
SSD***	12.7 $\pm$ 6.68	13.1	15.9	2400	22.7	3.9
SSD	12.7 $\pm$ 6.68	13.1	15.9	4800	23.8	4.9
SSD	12.7 $\pm$ 6.68	11.6	3.18	2400	38.4	7.5
SSD	12.7 $\pm$ 6.68	11.6	3.18	4800	43.1	8.3
SSD-AD	12.7 $\pm$ 6.68	6.8	3.18	2400	41.4	9.2
SSD-AD	12.7 $\pm$ 6.68	6.8	3.18	4800	51.0	13.2

* Air-dried.

** Hot-water dried.

*** Saturated steam dried.

separating of fine and coarse dust particles, yet in both cases, the results were once again variable. It seems that the instrument is too sensitive for the small air volume of the dust cell, resulting in large experimental errors. The concept of the RAM-1 was designed to monitor large volumes of air such as in a coal preparation building or in an underground mine operation.

● HARDGROVE GRINDABILITY INDEX

The Hardgrove results for the three raw test coals, and dried coal are contained in Table 4.1-9.

Sample preparation involved riffing of 12.5- by 9.5-mm (1/2- by 3/8-inch) coal samples to obtain a representative sample for size reduction. The sample was reduced in size using a bucking board. The bucking board consists of a heavy cast-iron mallet-like hammer and a cast-iron plate for crushing a coal sample between the two pieces. The bucking board was used for sample preparation to keep losses to a minimum due to the

limited amount of treated coal available. The samples were reduced in size until all of the material was reduced to minus 1.18 mm (16 mesh). Material was saved at the minus 1.18- by 0.6-mm (30 mesh) size for Hardgrove grindability testing (see Appendix 4.1-1).

The Hardgrove grindability index (HGI) is calculated using the following formula:

$$\text{Hardgrove Index} = (13 + 6.93W) \quad [\text{Eq. 4.1-2}]$$

Where W = weight of material passing 75 microns (200 mesh).

Previous studies on Knife River lignite show Hardgrove values to range from 56 to 81 (8); for Little Tonzona, a value of 28 has been determined (9). Hardgrove data presented in this report should be fairly representative for the raw coals. Moisture contents of the treated coals ranged from 4 to 5 wt%, which is in the area of high-rank coals. The Hardgrove indices for the treated coals increased to a range of 64 to 74, which implies reduced energy input for grinding these coals. However, the higher the index, the more dust or loss of product that would occur during transport and utilization. The greatest increase in grindability is noted with the Little Tonzona coal, which had a raw

TABLE 4.1-6

Tumbling Results for Raw, AD, HWD, and SSD Colstrip Subbituminous Coal

Type	Coal Size, mm	Moisture, wt%	Tumbling Method Ledge, mm	Revolutions	Friability Index, %	Dust Index, %
Raw	38.1 x 26.5	22.5	15.9	2400	15.5	1.9
Raw	12.7 x 6.68	22.5	15.9	2400	6.6	1.3
Raw	12.7 x 6.68	22.5	15.9	4800	8.6	2.1
Raw	12.7 x 6.68	22.5	3.18	2400	7.2	1.7
Raw	12.7 x 6.68	22.5	3.18	4800	10.4	3.5
AD*	12.7 x 6.68	10.7	3.18	2400	26.0	7.0
AD	12.7 x 6.68	10.7	3.18	4800	32.0	10.5
HWD**	12.7 x 6.68	7.7	15.9	2400	24.2	4.0
HWD	12.7 x 6.68	7.7	15.9	4800	25.9	4.9
HWD	12.7 x 6.68	9.4	3.18	2400	33.0	6.2
HWD	12.7 x 6.68	9.4	3.18	4800	36.6	7.1
HWD-AD	12.7 x 6.68	5.3	3.18	2400	35.7	9.2
HWD-AD	12.7 x 6.68	5.3	3.18	4800	42.9	12.2
SSD***	12.7 x 6.68	4.8	15.9	2400	25.4	3.0
SSD	12.7 x 6.68	4.8	15.9	4800	28.8	5.1
SSD	12.7 x 6.68	4.4	3.18	2400	39.2	10.3
SSD	12.7 x 6.68	4.4	3.18	4800	46.4	16.4
SSD-AD	12.7 x 6.68	3.7	3.18	2400	38.3	10.7
SSD-AD	12.7 x 6.68	3.7	3.18	4800	40.2	13.7

* Air-dried.

** Hot-water dried.

*** Saturated steam dried.

coal Hardgrove index of 22, and its treated coals had values greater than 60. Knife River and Colstrip coals showed less of a percentage increase in HGI as a result of steam- or hot-water drying.

The Hardgrove index was used, initially, as a means to evaluate the stability of coals and products for this project. Subsequently, it was found that this method is not viable for determining the stability of the coal products because a size reduction has to be performed prior to Hardgrove determinations. This size reduction takes away from the original product integrity, since it is no longer in an as-received form for typical applications. As stability issues of coals are becoming of greater concern, methods to evaluate these coal products in their original state need to be investigated, such as the above-reported dust generation work.

● EQUILIBRIUM MOISTURE

Tests using ASTM procedure (described in Appendix 4.1-2) were performed on the following six combinations of fuels: Colstrip raw, HWD (stirred and unstirred) and SSD; and on Knife River raw and SSD. All hydrothermal treatment tests had been performed

TABLE 4.1-7

Drop-Shatter Results for Raw, AD, HWD, and SSD Coal Samples

Type	# of Drops	Friability Index, (%)		
		Little Tonzona	Colstrip	Knife River
Raw	2	0.7	2.0	0.5
Raw	6	2.4	6.6	3.3
Raw	10	3.8	10.7	5.3
AD*	2	5.6	14.0	18.1
AD	6	9.9	28.3	27.4
AD	10	13.2	33.1	35.6
HWD**	2	6.4	10.4	15.4
HWD	6	14.6	20.6	28.9
HWD	10	20.7	26.3	34.8
SSD**	2	9.6	17.3	16.5
SSD	6	20.8	31.5	27.5
SSD	10	26.6	40.5	34.2

* Air-dried.

** Hot-water dried.

*** Saturated steam dried.

TABLE 4.1-8

Dust Index Results for Raw, HWD, and SSD Coal Samples

Fuel Type	Moisture, wt%	Tumbled, yes/no	Maximum, mg/m ³	Average, mg/m ³	Total, (μg)
Little Tonzona					
Raw	30.0	no	2.2	1.1	22.9
Raw	27.5	yes	18.7	8.5	171.1
HWD*	8.5	no	5.6	2.3	46.6
HWD	7.5	yes	32.4	10.2	205.4
SSD	6.0	no	11.5	5.0	101.1
SSD	5.0	yes	36.6	12.2	245.7
Colstrip					
Raw	22.5	no	2.7	1.2	24.2
Raw	21.2	yes	16.2	6.6	132.2
HWD	9.4	no	2.6	1.7	34.2
HWD	7.2	yes	22.6	10.2	206.2
SSD**	4.8	no	6.1	2.6	51.6
SSD	3.0	yes	20.7	12.5	252.6
Knife River					
Raw	37.5	no	2.8	1.2	23.4
Raw	35.5	yes	39.8	17.1	345.3
HWD	9.6	no	13.1	4.0	81.7
HWD	7.0	yes	100.1	21.0	424.5
SSD	11.6	no	8.6	2.6	53.3
SSD	9.7	yes	53.5	18.1	365.0

* Hot-water dried.

** Saturated steam dried.

at 300°C. The results indicated that an additional 24-hour incubation period caused further decreases in moisture content ranging from 0.4 to 4.1 wt%. The change in moisture content was calculated assuming that the weight loss over the entire incubation period of 96 hours was due to moisture evaporation only.

The weight losses and changes in moisture contents for these preliminary tests were considered excessive. Additional equilibrium moisture tests were performed in which the incubation period was extended until the weight loss over a 24-hour period was approximately 0.01 gram (0.2 wt%) or less. The test procedure was further modified to include measurement of the initial moisture content of the sample. The moisture contents on successive weighing days were calculated by assuming that weight loss was due to moisture evaporation only. Consequently, at the completion of testing, the calculated equilibrium moisture content was compared to the moisture content measured by weight loss at 105°C. The modified procedure was performed on the six fuels tested above; new fuels tested included HWD Knife River lignite, and HWD and SSD Little Tonzona Creek subbituminous coal. The results of these latter tests and the preliminary

96-hour equilibrium moisture tests are presented in Table 4.1-10. Equation 4.1-3 represents the method used to obtain calculated equilibrium moisture contents on the samples.

$$M_c = 1 - \left(\frac{W_o (1 - M_o)}{W_i} \right) * 100 \quad [\text{Eq. 4.1-3}]$$

Where M_c = calculated moisture content, wt%
 W_i = sample weight on day i , grams
 W_o = initial sample weight, grams
 M_o = initial moisture content, wt%

The extended tests resulted in lower equilibrium moisture contents for the raw and SSD Knife River and HWD (stirred) Colstrip coals. The extended period did not effect the equilibrium moisture content of the remaining fuel types. The calculated equilibrium moisture values were in reasonable agreement with the measured values. The most significant effect of the equilibrium moisture tests was that several samples lost additional mass over the extended period, but the equilibrium moisture contents were minimally affected. The effect was prominent with raw Knife River lignite and HWD and SSD Colstrip coal. No conclusions were drawn regarding the cause of this phenomenon.

TABLE 4.1-9
Hardgrove Grindability Index

Fuel Type	+75 μ m wt., grams	-75 μ m wt., grams	Hardgrove Index
Little Tonzona			
Raw	48.40	1.20	21
HWD	41.30	8.00	69
SSD	42.60	7.30	64
Colstrip			
Raw	44.70	4.40	44
HWD	42.40	7.40	65
SSD	42.70	7.30	64
Knife River			
Raw	42.40	7.20	64
HWD	41.10	8.60	74
SSD	40.70	8.70	74

* Hot-water dried.

** Saturated steam dried coals

TABLE 4.1-10

Comparison of 4-day and Extended Equilibrium Moisture Tests

Fuel Type	4-day Test			Extended Test		
	Wt. Loss, wt%	Moisture ¹ , wt%	Test Length, days	Wt. Loss, wt%	Moisture ¹ , wt%	Moisture ² , wt%
Knife River						
Raw	18.0	37.1	18	35.5	35.1	33.7
HWD	ND	ND	11	15.5	15.0	15.1
SSD	10.0	14.3	11	20.9	12.6	14.0
Colstrip						
Raw	19.3	25.7	13	20.5	25.3	26.1
HWD (stirred)	12.4	11.0	11	21.8	9.3	10.3
HWD	6.1	9.6	11	16.4	9.3	10.5
SSD	4.1	8.4	7	15.3	8.6	8.3
Little Tonzona						
Raw	ND	ND	ND	ND	ND	ND
HWD	ND	ND	9	18.9	11.1	7.8
SSD	ND	ND	6	16.9	9.5	13.1

¹ Measured equilibrium moisture content.

² Calculated equilibrium moisture content.

ND Not Determined.

An alternative equilibrium moisture procedure was investigated for assessing the proper incubation period for the ASTM D1412 procedure when using raw and beneficiated (thermally and hydrothermally dried, pyrolyzed) LRCs. The modified equilibrium moisture procedure was investigated using the raw and HWD Colstrip subbituminous coal, the same coal used in concurrent dust tests and hydrothermal treatment tests. The detailed procedure is presented in Appendix 4.1-2. Briefly, ten nearly equal mass samples of raw or treated coal were prepared according to standard equilibrium moisture procedure. Eight samples were incubated and the remaining two samples were analyzed to determine initial moisture content. Following incubation periods of 3, 5, 7, and 10 days, two samples were removed and their respective moisture contents determined. The measured moisture contents were compared against calculated moisture contents as determined from Equation 4.1-3.

A relative humidity gauge placed in the incubation cell verified that the required humidity level was attained within 30 minutes of evacuating the incubator and placing the incubator in the 30°C thermostated environment.

The calculated and measured moisture contents are presented in Table 4.1-11 as a function of incubation duration. The preliminary tests indicated that an incubation period of 72 hours may not be sufficient to achieve equilibrium; a more reasonable time period may be 5 days for raw coal and as much as 7 to 10 days for hydrothermally treated

TABLE 4.1-11

**Extended Equilibrium Moisture Data for Raw and
HWD Colstrip Subbituminous Coal**

Incubation Period, days	Raw Coal		Hot-Water-Dried Coal	
	Measured	Calculated	Measured	Calculated
0	36.7	36.8	26.9	27.4
3	26.3	25.8	10.7	12.1
5	24.8	24.7	10.4	9.5
7	24.7	24.4	9.6	9.1
10	24.3	24.9	9.3	8.9

coal. The measured and calculated values were in good agreement; the largest variation was approximately 0.6 wt%, which is within the range of permissible repeatability (testing by same laboratory). The good agreement between measured and calculated values indicates that this modified procedure can be used to track current incidental moisture contents of samples.

These results suggest that the present ASTM procedure should be evaluated further, considering the extreme importance placed on this value, especially when trying to market the virtues of a particular coal type or beneficiation process. The LRCs beneficiated by hydrothermal techniques, for example, may need longer incubation periods to achieve equilibrium, owing to changes in coal physical and chemical properties.

● FUTURE WORK

- Design a modified Jameson cell (10) to determine the dustiness of coals and coal products.
- Integrate the modified Jameson cell into the stability test program by testing the three test coals and products.
- Correlate equilibrium moisture data with critical moisture content as determined by Jameson test procedures (10).
- Continue to correlate ASTM and modified procedure results.

● CONCLUSIONS

This report presents data for three raw coals and dried coal products analyzed by various strength and stability test methods. The results show that as the moisture content is decreased, the amount of dust generated substantially increased to levels viewed as unacceptable by industry (fines not to exceed 10 wt% less than 0.5 mm) (11). If commercial drying of low-rank coals is to be successful, efforts must continue on stability analysis and the development of cost-effective stable products.

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B. Oil Agglomeration

Introduction

New feedstock preparation processes for low-rank coals (LRCs) must achieve the irreversible removal of moisture, increase the coal Btu content, and yield a stable product not prone to spontaneous combustion, dustiness, or moisture reabsorption. These processes must also produce fuels that have reduced propensity for fouling, thus requiring removal of troublesome inorganic species. Ion exchange of finely ground coal followed by

processes must also produce fuels that have reduced propensity for fouling, thus requiring removal of troublesome inorganic species. Ion exchange of finely ground coal followed by oil agglomeration has the potential to accomplish these improvements as well as produce a fuel transportable by conventional methods.

The EERC has demonstrated that low-ash, low-sodium fuel can be produced by a combination of physical cleaning followed by chemical cleaning of fine coal (1, 2, 3). These clean coal products, however, are difficult to transport, handle, and store because of their high moisture content, fine size, and propensity toward oxidation. The EERC two-step process of dilute acid leaching followed by oil agglomeration accomplishes similar ash reductions and produces a low-moisture, high heating value fuel. Nitric, hydrochloric, and sulfuric acids are effective for significant sodium, calcium, magnesium, and potassium reduction in brown, lignite, and subbituminous coals. Coal-derived oils possessing high oxygen and polar contents are the most suitable for agglomerating chemically cleaned LRCs.

Testing was initiated to demonstrate the reduction of sodium in LRCs via carbonic acid treatment and to demonstrate the reduction of minerals (and ash) in LRCs via selective agglomeration. The oil agglomeration process was modified by eliminating the ion-exchange and process water pH treatments. Additional oils derived from coal gasification, one a polymerized fraction, were investigated as potential bridging and binding oils. Preliminary strength evaluations (drop and tumble) were performed on air-dried and thermally deoiled agglomerates.

Objectives

The overall goal of this program is to develop advanced low-rank coal beneficiation techniques to the stage where their application is justified solely on their combined technical and economic merit.

Accomplishments

Carbonic Acid Coal Cleaning

● OBJECTIVE

The main objective was to test the feasibility of carbonic acid treatment of low-rank coals at an elevated pressure for the removal of alkali/alkaline earth metals organically bound in the coal matrix. Carbonic acid derived by dissolving CO₂ in water under pressure is probably the lowest-cost acid available for acid cleaning. It also provides a sink of CO₂ disposal.

● INTRODUCTION

Past LRC preagglomeration chemical treatment tests using dilute solutions of nitric, hydrochloric, and sulfuric acid were effective for significant reduction of all organically associated alkali and alkaline earth metals (4, 5). The cost of the acids alone, processing costs aside, may make LRC treatment with these ion-exchange species cost-prohibitive, save possibly for future production of ultralow ash fuel for advanced power systems. Consequently, carbonic acid treatment at an elevated pressure was explored as a potential

lower-cost option for preagglomeration treatment of LRCs, especially to reduce sodium content. A low-sodium agglomerated coal fuel would, hypothetically, be superior to untreated raw coal with respect to high-temperature convective pass fouling when used as a suspension-fired boiler fuel.

● EXPERIMENTAL

Chemical treatment (ion exchange) of LRCs via carbonic acid treatment was performed in a batch mode using a stainless steel 2-gallon autoclave system that has been described elsewhere (4). Briefly, a slurry consisting of pulverized coal (-60 mesh) and deionized water was top-loaded to the autoclave, after which the system was sealed, evacuated, and then pressurized to the desired level with carbon dioxide (CO_2). Agitation was provided by a head-mounted stirrer. The slurry was allowed to mix for a predetermined length of time, and periodically the pressure level was noted. After treatment, the system was depressurized and the slurry recovered for subsequent coal recovery and analysis. Analysis of the feed and treated coals included moisture and ash determination; select coal samples were analyzed for composition of ASTM high-temperature ash. Weights of the feed and treated coals were determined to allow calculation of ash and sodium reductions.

Two North Dakota lignites (Knife River and Gascoyne) and a Montana subbituminous coal (Spring Creek) were evaluated for amenability to reduction of sodium and other ion-exchangeable metals via carbonic acid treatment. The coals were selected primarily based on the high Na_2O content of their ash. Test conditions and characteristics of the raw and treated coals are presented in Tables 4.1-12 and 4.1-13. Approximately 100 grams of coal were treated per test, except where noted, and coal:water solution ratios ranged from 1:5 to 1:10. The CO_2 pressure was maintained at 85 psig in each test, although the effect of residence time was evaluated by varying mixing time from 30 to 120 minutes.

Baseline tests were also performed with the Knife River and Gascoyne coals to determine the removal of water-soluble inorganics. These tests were performed without the addition of CO_2 .

● RESULTS

The moisture-free (mf) ash contents of the raw Knife River, Gascoyne, and Spring Creek coals were 10.2, 9.7, and 4.95 wt%, respectively. The sodium oxide contents of the ASTM ash of these same coals were 10.5, 11.2, and 9.5 wt% (SO_3 -free), respectively. The high sodium content of the subbituminous coal is somewhat atypical of the otherwise low-ash, low-sodium, and low-sulfur Powder River Basin coals; the high sodium contents of the two tested lignites are characteristic of North Dakota coals.

Baseline testing without carbonic acid indicated that the water-soluble inorganic content of the two lignites was relatively insignificant. Carbonic acid treatment, however, resulted in modest reductions in ash content for all coals tested with the highest ash reductions, up to 17 wt%, achieved with the Knife River lignite. The only parameter appearing to have a significant effect on ash reduction was the coal:water ratio. One probable explanation for this result could be that decreasing the water volume resulted in

less solubilization of CO₂ to produce H⁺ for ion exchange. With Knife River lignite, doubling the coal:water ratio reduced the effectiveness of ash removal by almost 50%.

Treated coal samples from Tests 3, 11, and 13 (see Table 4.1-12), along with raw coal samples, were submitted for x-ray fluorescence analysis (XRFA) of their individual ASTM high-temperature ashes. On comparing the analyses presented in Table 4.1-13 it is noted that the removal of sodium was the predominant cause of the reduced ash contents. The sodium reductions for the Knife River, Gascoyne, and Spring Creek were 63, 80, and 72 wt%, respectively.

Coal Washability Testing

● OBJECTIVES

The purpose of the float/sink washability testing was to evaluate the amenability of select subbituminous coals toward excluded (extraneous) mineral liberation and, hypothetically, amenability to high coal recovery (+85 wt%) and significant ash reduction (+30 wt%) via selective agglomeration.

TABLE 4.1-12
Carbonic Acid Coal Treatment Results

Test	Coal	Coal:Water Ratio	Residence Time, min	Ash, mf wt%	Ash Reduction, wt%
1*	Knife River	1:10	30	9.96	2.1
2		1:10	30	8.73	14.2
3		1:10	30	8.41	17.3
4		1:10	30	9.15	10.0
5		1:10	60	8.57	15.7
6		1:10	120	8.73	14.2
7		1:5	120	9.33	8.3
8		1:5	120	9.30	8.6
9*	Gascoyne	1:10	30	9.58	1.6
10		1:10	30	8.61	11.6
11		1:10	30	8.43	13.5
12		1:10	60	8.51	12.6
13	Spring Creek	1:10	30	4.34	12.3
14		1:10	30	4.37	11.7
15**		1:10	30	4.76	3.8

* Coal treated without carbonic acid.

** Coal charge increased to 300 grams.

TABLE 4.1-13

ASTM Ash Analysis of Raw and Carbonic Acid
Treated Coals (wt% SO₃-free)

Ash Component	Knife River		Gascoyne		Spring Creek	
	Raw	Treated	Raw	Treated	Raw	Treated
Silicon	27.4	33.4	29.8	34.3	30.5	36.0
Aluminum	16.4	18.4	16.8	19.3	21.2	24.0
Iron	9.94	7.92	3.69	3.93	7.07	8.53
Titanium	0.25	0.28	1.12	1.21	1.54	1.87
Phosphorous	0.98	0.53	0.30	0.26	0.27	0.23
Calcium	26.1	27.2	27.9	29.6	23.7	20.6
Magnesium	8.25	7.84	9.00	9.15	5.65	5.51
Sodium	10.5	3.87	11.2	2.21	9.51	2.68
Potassium	0.15	0.13	0.14	0.12	0.48	0.19

● EXPERIMENTAL

A description of standard centrifugal float/sink washability methods for low-rank coals is documented elsewhere (6). Briefly, the coals were crushed and then dry-pulverized using lab-scale mills; selected top sizes were achieved by screening and refeeding the oversize coal until all the coal passed the desired mesh size. Typically the sized coals were floated using Certigrav solutions of 1.3, 1.4, 1.5, and 1.6 gravities. Centrifugation was performed with a Model K IEC lab centrifuge operated at 2500 rpm for 20 minutes per sample. The samples were air-dried to remove residual Certigrav solution, and then the raw and treated coals were analyzed to determine moisture and ash contents. The moisture- and ash-free (maf) coal recoveries and ash reductions were then calculated from these analyses.

The LRCs evaluated for washability were two Powder River Basin coals: the Spring Creek previously tested for carbonic acid treatment and a second Montana subbituminous, Colstrip (Rosebud). The former coal was chosen because of its potential to produce a low-fouling fuel by combining a carbonic acid treatment step with a physical cleaning step, e.g., selective agglomeration. The Colstrip coal was chosen because it is the feedstock for the Rosebud SynCoal® Advanced Coal Conversion Process (ACCP). The ACCP, presently being demonstrated as a DOE Clean Coal Technology-funded project, contains a novel pneumatic/vibrating coal-cleaning circuit for separating clean coal and minerals.

● RESULTS

The Spring Creek subbituminous coal was evaluated at top sizes of 60-, 100-, and 200-mesh at specific gravities of 1.3 to 1.6; the Colstrip was only evaluated at a top size of 100-mesh at specific gravities of 1.4 and 1.5. The conditions used for the Colstrip were essentially those determined to be adequate for the Spring Creek. The conditions and results of washability testing are presented for the two coals in Table 4.1-14.

TABLE 4.1-14

Washability Analysis of Spring Creek and Colstrip Coals

Feed	Product	Coal Recovery, maf wt%	Ash, mf wt%	Cum. Ash, mf wt%
Spring Creek				
-60 mesh	Raw	---	5.23	---
	Float - 1.30	66.3	3.49	3.49
	1.30 - 1.40	87.0	4.34	3.69
	1.40 - 1.50	97.9	6.37	4.00
	1.50 - 1.60	98.9	17.3	4.15
	Total	99.5	---	5.07
-100 mesh	Raw	---	5.21	---
	Float - 1.30	52.8	3.47	3.47
	1.30 - 1.40	82.7	3.33	3.40
	1.40 - 1.50	98.5	5.38	3.74
	1.50 - 1.60	100.0	16.8	3.96
	Total	100.5	---	4.81
-100 mesh	Raw	---	5.21	---
	Float - 1.40	95.3	4.24	4.24
	Total	100.1	---	5.29
-100 mesh	Raw	---	5.21	---
	Float - 1.40	97.3	3.86	3.86
	Total	100.2	---	4.95
-200 mesh*	Raw	---	4.12	---
	Float - 1.30	28.5	2.55	2.55
	1.30 - 1.40	82.5	2.90	2.78
	1.40 - 1.50	101.1	3.59	2.93
	Total	101.4	---	3.27
Colstrip				
-100 mesh	Raw	---	13.9	---
	Float - 1.40	77.0	6.39	6.39
	Total	100.2	---	13.6
-100 mesh	Raw	---	13.9	---
	Float - 1.50	95.5	7.98	7.98
	Total	99.9	---	13.4

* Sample taken from different storage container.

Washability testing indicated that grinding the coals to a top size larger than or equal to conventional combustion grinds (80% < 200 mesh) resulted in significant

liberation of minerals for both coals. The Spring Creek coal ash content was reduced to as low as 3.7 wt% (from 5.2 wt%) at a maf coal recovery approaching 99 wt%. Reducing the coal top size from 60 down to 100 mesh improved mineral liberation slightly. However, the minor absolute change in ash content for the Spring Creek as a result of grinding and physical cleaning would probably preclude this type of treatment, save for the production of a very low-ash fuel for advanced power systems. Colstrip with a 100-mesh top size, on the other hand, exhibited an ash reduction of up to 50 wt% at a maf coal recovery of 95 wt%. The superior ash reduction with Colstrip was presumably due to its high initial ash content relative to the Spring Creek. As a consequence, Colstrip lends itself as a candidate for an advanced physical cleaning process, e.g., selective agglomeration or micronized magnetite cleaning. These processes ideally would approach float/sink washability in cleaning efficiency.

Agglomeration Testing

● OBJECTIVES

The purpose of agglomeration testing was threefold: 1) to demonstrate that coal acid treatment and/or water pH adjustment are not required to effect agglomeration, 2) to demonstrate selective agglomeration for separation of excluded minerals and clean coal, and 3) to investigate new agglomerating oils for bridging and binding.

Agglomeration Without Coal Pretreatment or pH Adjustment

● BACKGROUND

The EERC agglomeration process was originally designed to combine a dilute acid coal cleaning preagglomeration first stage with a fine coal aggregation (or agglomeration) second stage (7). The acid-treated coal was agglomerated while suspended in the dilute acid process water; the pH of the coal-water slurry was typically below 2, due to residual acid. Dilute acid treatment to remove ion-exchangeable elements was hypothesized to effect a surface modification deemed necessary to facilitate wetting of the coal surface by the agglomerating oil. Agglomeration within the low-pH acid solution was also hypothesized to be equally necessary to aid displacement of surface and pore moisture by the agglomerating oil via a mechanism similar to osmosis.

There are three reasons, however, why the present processing methodology may be undesirable. First, measurements of acid consumption indicated that the use of even dilute solutions of the strong acids (nitric, hydrochloric, sulfuric) may be too costly for preparation of a fuel for conventional utility applications (4, 5). Second, ion exchange may not be necessary for low-sodium coals or for fine coal recovery. Third, process water that contains both residual acid and residual agglomerating oil may be difficult and costly to treat. Consequently, obvious modifications to this process include the use of a potentially less costly acid such as carbonic acid or the elimination of acid treatment and water pH adjustment altogether.

Carbonic acid treatment at elevated pressure, described previously, has been demonstrated to be effective at inorganic, primarily sodium, reduction. Demonstration that water pH adjustment was not necessary to facilitate oil agglomeration was performed using a high-sodium subbituminous coal previously treated at elevated pressure with

carbonic acid. Demonstration that neither coal pretreatment nor water pH adjustment was necessary to facilitate agglomeration was performed using several raw subbituminous and lignite coals.

● EXPERIMENTAL

The test coals were reduced to the desired top size, slurried in deionized water at a 1:2 coal:water ratio, and then mixed for 5 minutes at approximately 400 rpm with a T-bar mixer to facilitate wetting of the coal surface. Appropriate polar oils were incrementally added to the slurry until evidence of agglomeration was observed. Agglomerate growth was controlled by adding oil and by controlling mixing speed and mixing time. Agglomerates were separated from the process water and tailings via screening and were air-dried prior to analysis or further testing.

Spring Creek and Colstrip subbituminous coals and Knife River and Beulah lignites were tested at top sizes, ranging from 60- to 100-mesh. The agglomerating oils tested included crude phenol, tar oil, and tar oil lights.

● RESULTS

Experiments with Spring Creek subbituminous coal successfully demonstrated that the carbonic acid-treated coal can be separated from the acid solution, reslurried in a neutral pH water solution, and successfully agglomerated using traditional polar agglomerating oils.

Agglomeration testing also indicated that each of the subbituminous and lignite coals tested could be aggregated without coal pretreatment or pH adjustment at oil volumes and mixing conditions previously determined to be suitable for acid-treated coals. Hence, the majority of agglomeration experiments described in the following sections, including all selective agglomeration experiments, were performed without concurrent acid treatment or water pH adjustment.

Selective Agglomeration

● BACKGROUND

As the EERC oil agglomeration process was originally developed, inorganic reduction was achieved principally through the removal of alkali and alkaline earth metals via ion exchange (acid treatment). However, in the instances where the ash content of an LRC is predominantly associated as minerals and has relatively low fouling characteristics, i.e., low sodium content, separation of minerals may be effective for ash reduction. Consequently, selective agglomeration of LRCs was investigated as a method of reducing inorganic content via the separation of excluded (extraneous) minerals and mineral-laden coal from the clean coal fraction. This process variation was also considered to be applicable to treated (acid-cleaned) coals for the production of a low-fouling fuel for conventional utility applications or, possibly, a very low-ash fuel for advanced power systems.

● EXPERIMENTAL

The test coals were reduced to the desired top size, slurried in deionized water at a 1:2 coal:water ratio, and then mixed for 5 minutes at approximately 400 rpm with a T-bar mixer to facilitate wetting of the coal surface. Selective agglomeration was accomplished by adding appropriate agglomerating oil(s) to the coal-water solution in varying oil:coal ratios, after which the agglomerates were separated from tailings and process water. Agglomerates produced with -100-mesh coal were separated from tailings and process water using a 100-mesh screen; likewise a 60-mesh screen was used when agglomerating -60-mesh coal. Tailings were recovered from the process water via vacuum filtration. The agglomerates and tailings were air-dried overnight, and each was analyzed for ash content; select agglomerate and tailing samples were analyzed for Karl Fischer moisture and Soxhlet oil content.

The coals investigated for amenability to selective agglomeration included Spring Creek (carbonic acid-treated) and Colstrip subbituminous coals and Knife River and Beulah lignites. The two subbituminous coals and the Knife River lignite were pulverized (dry) to 100-mesh top size, and Beulah lignite was pulverized to 60-mesh top size. All four coals were agglomerated using crude phenol, the principal oil of the EERC process; a supplemental test with Colstrip used tar oil as the agglomerant. Characteristics of the tar oil, also a Great Plains coal gasification-derived by-product, are described in the following section.

● RESULTS

The conditions and results of selective agglomeration testing are presented in Table 4.1-15. The mf ash contents of the Spring Creek, Colstrip, Knife River, and Beulah were 4.76, 13.97, 10.09, and 7.76 wt%, respectively. Based on preliminary selective agglomeration testing, only Colstrip appeared to be substantially improved by this physical cleaning method. The indicators of Colstrip's amenability for selective agglomeration were the substantial tailings ash content relative to the raw coal ash content plus the progressive increase in tailings ash content as tailings yield decreased. This selectivity was obtained with both the crude phenol and tar oil. The difference in ash content of Colstrip agglomerates made with crude phenol and tar oil may be due to the lower volatility of tar oil relative to crude phenol. As a consequence, the tar oil agglomerates may contain more oil after air drying.

The relatively few tests with the three remaining coals preclude judgment on their amenability to selective agglomeration for ash reduction, although the low ash content of the tailings indicate inadequate concentration of ash in this fraction. Maximizing the ash content of the tailings is essential to maximizing coal recovery in the product, as well as maximizing ash reduction and producing agglomerates with the lowest ash possible. Further tests should be performed with the Beulah and/or Knife River, particularly to assess pyritic sulfur reduction, as these coals may have the potential to be cleaned to emission-compliant levels for sulfur dioxide (SO₂).

Soxhlet extraction (oil/moisture) and Karl Fischer (moisture) analysis of the Colstrip agglomerates produced with a 5:10 oil:coal ratio were used to calculate agglomerate coal recovery, ash reduction, and theoretical ash content of moisture- and oil-free (mof) agglomerates. The agglomerate coal recovery and mof ash content were also estimated

TABLE 4.1-15

Selective Agglomeration Test Conditions and Results

Test Coal	Oil:Coal Ratio	Agglomerates		Tailings	
		Recovery, wt%	Ash, wt%	Recovery, wt%	Ash, wt%
Colstrip	1:10	34.7	7.11	65.3	13.4
	2:10	58.1	7.19	41.9	15.9
	3:10	68.9	6.62	31.2	19.5
	4:10	72.8	6.94	27.2	19.4
	5:10	87.7	6.60	12.3	28.3
	3:10*	63.0	6.37	37.0	14.0
	5:10*	68.8	4.72	31.2	15.0
Spring Creek	5:10	85.1	3.11	14.9	5.02
Knife River	4:10	32.0	5.67	68.0	7.79
	5:10	34.0	5.20	66.0	7.56
	6:10	44.0	5.49	56.0	8.03
	7:10	46.2	5.09	53.8	7.86
Beulah	5:10	85.5	3.91	14.5	6.69

* Tar oil used as the agglomerant.

from the ash contents of the agglomerates and tailings. The tailings were assumed to contain no oil; thus the estimated results were conservative relative to the calculated values. An ash balance, using agglomerate and tailing ash contents, accounted for 91 wt% of the initial coal ash. The calculated ash reduction was 42 wt%, although the actual value may be as low as 35 wt%, depending upon the distribution of the unaccounted ash among the agglomerates and tailings. The agglomerate coal recovery ranged from 87 to 95 wt%, and the agglomerate mof ash content ranged from 8.9 to 9.6 wt%; the estimated (conservative) values corresponded to the lowest coal recovery and the highest agglomerate mof ash content. In any instance, the results indicate substantial removal of ash and impressive coal recovery, thus indicating the viability of selective agglomeration with this particular coal. Additional tailings analysis may be needed to determine the tails oil content, as deoiling would be required if the potential oil loss was substantial.

Agglomerating Oil Evaluation

● BACKGROUND

Dakota Gasification Company has demonstrated that crude phenol, the principal oil of the agglomeration program to date, can be economically fractionated and sold as

phenols and cresylic acid (mixed cresols and xylenols). Consequently, crude phenol probably would be too costly for use as an agglomerant (8). Therefore, two additional coal gasification-derived materials, tar oil and tar oil lights, were investigated for their suitability as agglomerants for LRCs.

The Great Plains synfuels plant produces 624 tpd tar oil (compared to 164 tpd crude phenol) which is captively used as boiler fuel. The tar oil contains approximately 6 wt% benzene, toluene, xylene (BTX) and 56 wt% creosote with the balance considered to have fuel value (8). Tar oil is comprised of a small but unquantified fraction of phenolics and a substantial polar content (48 wt%) (9). Separation of the tar oil into the salable components is presently being evaluated by Dakota Gasification Company.

Tar oil lights is a low boiling point distillate produced by tar oil fractionation at 235°C. The specific tar oil lights fraction used in recent agglomeration testing was produced 6 years ago. Analysis performed at that time indicated that phenolics and polars, ideal components for LRC agglomeration, were the major constituents of the tar oil lights.

● EXPERIMENTAL

The test coals were reduced to the desired top size, slurried in deionized water at a 1:2 coal:water ratio and then mixed for 5 minutes at approximately 400 rpm with a T-bar mixer to facilitate wetting of the coal surface. The agglomerating oils were incrementally added to the slurry until evidence of agglomeration was observed. Agglomerate growth was controlled by adding oil and by controlling mixing speed and mixing time. Agglomerates were separated from the process water and tailings via screening and were air-dried prior to analysis or further testing.

Spring Creek (carbonic acid-treated) and Colstrip subbituminous coals were tested at a top size of 100-mesh using tar oil and tar oil lights.

● RESULTS

Tar oil was determined to be a suitable agglomerant for treated (chemically cleaned) and untreated subbituminous coals. The tar oil/LRC compatibility was presumed to be due to the components comprising the fuel (non-BTX and noncreosote) fraction. The tar oil-based agglomerates, however, were weaker than agglomerates produced with crude phenol, and the agglomerates also exhibited an excessively oily appearance. The presence of the creosote components was considered to be the cause of the reduced integrity and oiliness of green and air-dried agglomerates. Further potential drawbacks to using tar oil as an agglomerant include thermal instability (high boiling point components), as previously experienced during D86 distillation (9). If thermal recovery of agglomerating oil is necessary, economically prohibitive losses of agglomerants may result from thermal instability. Principally for these reasons, a lower boiling point fraction of the tar oil may be more suitable for LRC agglomeration.

The tar oil lights, in contrast to tar oil, failed to agglomerate treated or untreated subbituminous coals. The inability to cause agglomeration was hypothesized to have been caused by catalyzed polymerization of the phenolic and polar components. The contributing factors were presumably the presence of pyridines, and the exposure to light,

heat, and metal (containers) during storage. Tar oil lights, however, were determined to be suitable for aiding in agglomerate growth when blended with other polar oils. Similarly, the tar oil lights could be induced to agglomerate LRCs by blending with polar solvents.

Several coal-derived oils and other polar solvents were investigated as agglomeration promoters to facilitate the use of tar oil lights (polymerized). The oils included crude phenol plus the commercial oils, cresylic acid (a coal tar and petroleum oil derivative) and *m*-cresol. The solvents were composed entirely of aliphatic-based alcohols: methanol, ethanol, 2-propanol, and 1-butanol. Agglomerates produced with crude phenol, *m*-cresol, or cresylic acid as the promoter were typically larger than agglomerates produced with the alcohols, even at comparable tar oil lights concentrations. Further, air-dried agglomerates derived from crude phenol/tar oil lights were considerably stronger than air-dried agglomerates produced with *m*-cresol (or cresylic acid)/tar oil lights or crude phenol alone. The integrity of crude phenol agglomerates relative to *m*-cresol and cresylic acid agglomerates has been discussed previously (4, 5). The maximum tar oil lights:coal ratio was determined to be 1:2, after which further oil addition resulted in a complete loss of agglomerates and eventual production of an oily, clumped mass.

Two batches of agglomerates were produced using a combination of crude phenol and tar oil lights (polymerized) as the agglomerants and Spring Creek subbituminous as the coal source. The ratio of crude phenol:coal (as-received) ranged from 3:10 to 4:10, whereas the tar oil lights:coal ratio was maintained at approximately 5:10 in both tests. After 4 to 6 days air drying, the agglomerates, appeared stronger and resistant to crushing under finger pressure. The Karl Fischer moisture content for agglomerates from Test 1 was 2.7 wt%, and the Soxhlet extraction-determined oil content was 34.6 wt%.

Strength testing, including drop (shatter) resistance and tumble (abrasion) resistance, was performed on the air-dried agglomerates. Shatter-resistance testing was performed by dropping a charge of agglomerates through a PVC pipe into a stainless steel vessel from a height of 6 feet. The vessel, with a ½-inch-thick bottom, was used to retain the agglomerates and prevent material loss. The agglomerates were dropped ten times and screening was performed after the second, sixth, and tenth drops. Abrasion-resistance testing was performed using a stainless steel vessel with dimensions equivalent to an ASTM D441 coal-tumbling apparatus. The spacing between the lifting shelves and vessel wall was obstructed to assure that the agglomerates were continually lifted and dropped. Agglomerates were tumbled for 30 minutes at 40 rpm.

The size distributions of pre- and post-strength tested agglomerates, from Test 1 described above, are presented in Table 4.1-16. Agglomerates were sized using ¼-inch, and 4-, 6-, 10-, and 30-mesh screens; screening was performed manually to minimize separation of clumped agglomerates into discrete agglomerates. The most significant results of drop and tumble testing were twofold: only minimal degradation of agglomerates occurred, and fine coal (< 30 mesh) generation was minor. The primary cause of the change in size distribution as indicated in Table 4.1-16 was the cleavage of the clumped agglomerates at the weaker contact or bridging points. The distinct agglomerates were typically larger than 6-mesh (0.132"). The most significant breakup of the clumped agglomerates occurred during tumble testing. The fine coal which was produced during strength testing also had diminished adhesive properties relative to raw

TABLE 4.1-16

Drop and Tumble Strength Results for Test 1
Air-Dried Agglomerates (cumulative wt% larger)

Screen Opening, inches	Tumble Testing		Drop Testing			
	Initial	Final	Initial	2 Drops	6 Drops	10 Drops
0.25	45.7	20.8	36.7	21.0	12.2	12.1
0.187	61.3	41.3	54.1	39.5	34.0	33.0
0.132	87.0	72.8	80.3	72.8	71.8	71.1
0.0787	98.5	91.1	97.2	95.1	95.1	95.1
0.0232	99.7	96.0	99.5	98.2	99.0	99.0

coal fines as the oiled coal fines did tend to stick to the tumble and drop vessels, screens, or other test equipment.

The air-dried agglomerates from the two tests described above were thermally deoiled and evaluated for resistance to drop and tumble conditions. Thermal deoiling and strength testing results are presented in the next section.

Thermal Deoiling

● OBJECTIVES

The primary objective of thermal deoiling was to reduce agglomerate oil content to between 5 and 10 wt% and to evaluate the effect of thermal deoiling on agglomerate strength.

● EXPERIMENTAL

The system used for deoiling agglomerates has been depicted and described elsewhere (4). Briefly, air-dried agglomerates were weighed and charged to a 30-mesh cylindrical basket. The basket, with a 4-inch ID, was outfitted with a 2.3/4-inch OD pipe, which created an annulus in which the agglomerates were charged. The annular configuration was hypothesized to aid circulation of the flushing gas as well as to improve heat transfer to the agglomerates. The basket and agglomerates were treated in a 2-gallon externally heated autoclave equipped with temperature monitoring and control. A thermocouple was inserted into the agglomerate charge to allow temperature monitoring. A continuous nitrogen purge was used to prevent agglomerate combustion and to sweep vaporized oils and water from the autoclave. The condensation train consisted of a 20-foot coil (1/4-inch ID) immersed in a room temperature water bath followed by a knockout pot immersed in a 0°C (32°F) ice water bath; noncondensables

were vented to atmosphere. The weight of recovered agglomerates and condensate was determined after an overnight cooldown period.

● RESULTS

The Spring Creek coal agglomerates produced with crude phenol/tar oil lights (polymerized), including those previously tested for air-dried strength, were thermally deoiled. The conditions for both deoiling tests were a temperature of 310°C (590°F) and a residence time at temperature of 60 minutes. The lengthy residence time was intended to produce complete oil removal at the deoiling temperature.

The mass loss of the agglomerates was 36.7 wt%, compared to a combined oil and water content of 37.3 wt%, indicating that the agglomerating oil was, presumably, almost completely removed. Direct oil content determinations of the deoiled agglomerates were not planned because previous Soxhlet extraction testing has shown a lack of total elution of coal-derived oils from thermally treated agglomerates (5).

Deoiled agglomerates from both tests were evaluated for strength via the previously described drop (shatter) and tumble (abrasion) tests. The size distribution of deoiled agglomerates prior to and following drop and tumble testing are presented in Tables 4.1-17 and 4.1-18. Preliminary results indicated that the deoiling conditions were possibly too severe as the strength of the deoiled agglomerates was inferior, relative to the air-dried agglomerates. Subjecting the deoiled agglomerates to drop and tumble testing resulted not only in the breakup of clumped agglomerates, but also the degradation of agglomerates into fragments and fine coal (< 30 mesh). As with air-dried agglomerates, tumble testing produced the most significant agglomerate degradation. Approximately 20 wt% of the agglomerates from both deoiling tests were reduced to under 30 mesh (0.0232"). These preliminary results indicate that the agglomerates would experience considerable size reduction and production of dust during transport and handling.

The weight of oils and water collected by the condensation system was about 60 wt% percent of the mass loss of the agglomerates. Several explanations for the discrepancy may be valid, including insufficiently low temperatures for the oil knockout pot. Further, the relatively high temperature of deoiling may have decarboxylated the coal (produced CO₂) and thermally degraded the agglomerating oil into noncondensable species. The chemical complexity and potential thermal instability of the agglomerating oils combined with the low-temperature devolatilization of LRCs may preclude quantitative evaluation of agglomerating oil recovery.

● FUTURE WORK

Testing to be initiated and concluded during the remaining 6-month period includes 1) preparation of agglomerates for thermal deoiling and strength evaluation, 2) preparation of process water for determination of residual oil content and amenability to oil recovery, and 3) evaluation of the economics for a commercial plant producing an agglomerated fuel.

TABLE 4.1-17

Drop and Tumble Strength Results for Test 1
Deoiled Agglomerates (cumulative wt% larger)

Screen Opening, inches	Tumble Testing		Drop Testing			
	Initial	Final	Initial	2 Drops	6 Drops	10 Drops
0.25	15.0	2.5	23.8	11.8	2.8	2.4
0.187	31.2	12.4	44.7	30.6	20.0	14.3
0.132	66.7	42.7	79.5	69.1	57.8	49.1
0.0787	96.8	74.9	98.1	94.9	88.7	81.7
0.0232	99.7	82.3	99.5	98.2	95.9	92.1

TABLE 4.1-18

Drop and Tumble Strength Results for Test 2
Deoiled Agglomerates (cumulative wt% larger)

Screen Opening, inches	Tumble Testing		Drop Testing			
	Initial	Final	Initial	2 Drops	6 Drops	10 Drops
0.25	23.5	6.0	33.5	17.6	8.4	7.7
0.187	57.5	26.3	70.3	54.5	43.5	39.7
0.132	90.0	62.1	90.7	84.3	75.0	69.5
0.0787	99.9	79.8	97.2	96.2	90.9	87.2
0.0232	99.9	81.1	98.3	97.9	95.1	93.0

The most plausible source of agglomerant for LRCs is the Great Plains tar oil lights fraction produced by stripping virgin tar oil of BTX and creosote. Additionally, designed polymerization of a portion of the tar oil lights could produce a binder potentially capable of enhancing agglomerate integrity. The bulk of the tar oil lights would be used as a bridging or carrier oil which would, ideally, be entirely recovered during agglomerate thermal deoiling. This approach will be simulated by preparing agglomerates with crude phenol (as the bridging liquid) and polymerized tar oil lights (as the binder). The polymerized tar oil lights will be added in a ratio suitable to leave between 5 and 10 wt%

binder on the agglomerates after thermal deoiling. The air-dried agglomerates will be deoiled at temperatures deemed to be appropriate for producing these desired levels of residual binding oil. The agglomerates will be evaluated for strength via the previously described methods and for stability toward moisture reabsorption under simulated conditions of high humidity and water immersion.

The process water produced during preparation of these agglomerates will be analyzed for Total Carbon (TC) in order to estimate the soluble agglomerating oil concentration. An adsorption technique with coal will be used to reduce the residual oil level of the process water, ideally to a level suitable for activated sludge cleanup while simultaneously achieving an economic recovery of oil for recycle.

Preliminary economic evaluation will be performed on a commercial plant producing agglomerates from a Powder River Basin subbituminous coal and tar oil lights. The nominal capacity of the proposed plant is 1 MM tpy and the intended product is fuel for switching or blending in utility boilers designed for bituminous coals and located in the Midwest. Sensitivity will be assessed with regard to agglomerating oil usage, and the level of coal cleaning (chemical, physical, or both).

● CONCLUSIONS

1. Carbonic acid can significantly reduce the sodium content of high-sodium lignites and subbituminous coals, turning a high-fouling coal to a low-fouling one.
2. Significant mineral removal (+30 wt%) can be achieved via physical cleaning and selective agglomeration while achieving coal recoveries above 85 wt%.
3. Tar oil, although containing a significant fraction of creosote and BTX, can effectively agglomerate LRCs.
4. Polymerized tar oil, ineffective alone for LRC agglomeration, can aid agglomerate formation and growth when blended with phenolic and other polar species, including alcohols.
5. Polymerized tar oil, when used as a binder, has the potential to enhance the integrity of LRC agglomerates to produce a transportable fuel.
6. Thermal deoiling of LRC agglomerates produced with coal-derived oils resulted. Based on the limited number of tests, in oil instability and breakdown and a concurrent degradation of agglomerate strength.

● RECOMMENDATIONS

1. Other advanced cleaning techniques (e.g., micronized magnetite cycloning) should be tested with LRCs, which are amenable to mineral rejection using coal prepared to a standard combustion grind or larger grinds.
2. Chemical treatment of high-sodium LRCs should be investigated further, including demonstration of a continuous flow treatment system.

3. In conjunction with the previous two processes, nonslurry techniques, which accomplish dewatering and aggregation, should be investigated.
4. Polymerized tar oils should be investigated further as potential LRC binders and moisture barriers.

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Subtask 4.2 Co-Products

Introduction

Besides being a direct combustion fuel and a conversion (gasification and liquefaction) feedstock, coal has valuable conversion products. Conversion processes include coal gasification, which is a proven technology as a commercial process both here (Dakota Gasification Plant at Beulah, ND) and abroad (Sassol, South Africa), and direct

liquefaction, which has yet to be successful to the point of commercialization. Other conversion processes, such as pyrolysis, produce gas, liquid and solid products, have potential niche markets that would make coal more valuable than as a mere heating fuel (1). Char markets include gas and liquid sorption applications, briquetted heating and cooking fuels, and formed coke (replacing or supplementing conventional coke) in the metallurgical industries. Uses of pyrolysis liquids include heating fuel, feed for catalytic cracking to light gas for fuel use, chemical feedstock, beneficiation, and as a binder for coal briquetting. Gas produced during pyrolysis generally has little value since it contains only small amounts of hydrocarbon fuels along with carbon monoxide and carbon dioxide. The co-products project is concerned with generating high-value pyrolysis products from coal and testing them for specific applications.

Objectives

The overall objective of research on co-products is to develop new process concepts for upgrading coal chars and liquids to meet product specifications applicable in the marketplace. The naturally high reactivity of low-rank coals, based on their surface area and oxygen content, has long been felt to provide a basis for producing activated carbons tailored to gas and water treatment applications, but the technical basis for realizing this potential is still lacking. The first objective is to conduct parametric tests on selected low-rank coals to assess activated carbon quality with respect to industry specifications for gaseous pollutant sorption and water treatment. Key issues to be examined include beneficiation, carbonization and activation conditions, aggregation, and densification techniques for imparting physical strength. The second objective is to conduct exploratory tests on techniques for improving the quality of primary coal liquids by in-process modifications starting in the freeboard of a bench-scale fluidized-bed carbonizer. These modifications are to prevent polymerization reactions of volatile species and to promote controlled cracking in lighter products. Test conditions will establish a variable residence time in a fluid bed of dolomite or other material known to promote the cracking of coal tar.

Accomplishments

● EXPERIMENTAL

Feed Coal

An Alaskan (Beluga) subbituminous coal, a North Dakota (Beulah-Zap) lignite and a North Dakota Leonardite were selected for testing as sources of char for use as adsorbent in gas stream and wastewater cleanup. One test was done with North Dakota lignite containing 10 wt% polyvinyl alcohol (LigPVA). This test was meant to determine whether quality briquettes could be produced from the char. The coal was crushed, ground, and sieved in the usual manner to recover the -12- x +30-mesh fraction for use in the tests. The test coal was stored in plastic bags without headspace in covered 5-gallon pails. Thermogravimetric analysis (TGA) and proximate analyses are shown in Table 4.2-1.

TABLE 4.2-1
Proximate Analyses of Feed Coals

Coal	wt%				Moisture-Free, wt%			Moisture-and-Ash Free, wt%	
	Moisture	Volatiles	Fixed C	Ash	Volatiles	Fixed C	Ash	Volatiles	Fixed C
Beulah Lignite TGABM46	31.83	29.95	33.99	4.23	43.93	49.86	6.21	46.84	53.16
North Dakota Leonardite TGABB14	25.03	38.73	28.54	7.70	51.66	38.07	10.27	57.58	42.43
Alaskan Beluga Subbituminous	21.63	36.44	36.29	5.60	46.50	46.31	7.15	50.08	49.87

● CHAR PREPARATION AND TESTING

Char was prepared in milligram, gram and multigram batches from 20-40 mg, 5-10 grams, and 50-100 grams of raw coal in three reaction systems: the DuPont 2100/951 TGA, the so-called "large-scale" TGA built at the EERC, and in an Integrated Bench-Scale Gasifier (IBG), respectively. The IBG is a fluidized-bed reactor in which the coal serves as its own bed material. The TGAs are fixed-bed units.

Shakedown of the IBG under pyrolysis conditions preceded char preparation experiments. During the shakedown, adjustments in operating procedure were made, and an operator's manual was written. Heatup rate was determined to be $\sim 4^{\circ}\text{C}/\text{minute}$; the unit could be pressurized to 150 psig and operated best with 50 - 80 grams of feed coal. The IBG was then used to prepare chars under a variety of test conditions for characterization and testing as a sorbent. The operating conditions, feed, and recovery are shown in Table 4.2-2.

During selected char preparations with the IBG, gas was sampled periodically and the gas stream was monitored continuously with a Fourier transform infrared spectrometer (FTIR).

The small TGA was used for proximate analysis and to determine SO_2 adsorption-desorption of all chars prepared. The SO_2 adsorption-desorption values were used to compare char quality. A mixture of 100 cm^3/min of 5000-ppm SO_2 in argon provided the adsorbate. Sulfur dioxide-quality adsorption-desorption characterization of IBG030 to IBG040 chars was carried out at both ambient temperature and 100°C . The remainder of the IBG chars were characterized at 100°C only. Desorption measurements were made at 100°C and at 400°C under flowing argon.

● RESULTS AND DISCUSSION

Proximate analyses in Table 4.2-3 show substantial differences in char product from the feedstock lignite used in Tests IBG030 to IBG047. Tests IBG039, -040, and -045

Table 4.2-2
Pyrolysis Conditions and Char Yield

Sample	Atmosphere	Heatup	Feed, g	Recovery, g	Yield, wt%
Beulah Lignite					
Raw			N/A	N/A	
IBG030	N ₂	Slow to 850°C	52	11	40
IBG031	N ₂	Rapid at 850°C	50	16	61
IBG032	N ₂	To 500°C, then 850°C	52	16	59
IBG030-032	Primary Pot - Clean-out		154	20	25
IBG037	N ₂ , 20% Steam (5)*	To 500°C, then 850°C	53	10	36
IBG038	N ₂ , 20% Steam (5)	Rapid at 850°C	54	10	36
IBG037-038	Primary Pot - Clean-out		107	12	21
IBG039	N ₂ , 20% Steam (5)	Slow to 850°C	50	2	8
IBG040	N ₂ , 20% Steam (5)	Rapid at 850°C	50	0	0
IBG0039-040	Primary Pot - Clean-out		100	41	78
IBG041	N ₂	To 500°C, then 850°C	53	10	36
IBG042	N ₂	Rapid at 850°C	54	13	47
IBG041-042	Primary Pot - Clean-out		107	21	37
IBG043	N ₂ /H ₂ O (5 Min)	To 500°C, then 850°C	59	9	30
IBG044	N ₂	Rapid at 850°C	53	13	48
IBG045	N ₂ /H ₂ O (5 Min)	Rapid at 850°C	53	2	7
IBG046	Ar/CO ₂ cyl 75/25	To 500°C, then 850°C	57	17	55
IBG047	Ar/CO ₂ cyl 75/25	Rapid at 850°C	55	12	41
IBG048					
Beluga Subbituminous					
IBG049	N ₂	Rapid at 850°C	61	21	84
IBG050	N ₂ , 20% Steam (5)	To 500°C, then 850°C	58	24	98
IBG051	N ₂ , 20% Steam (5)	Rapid at 850°C	59	21	85
IBG052	Ar/CO ₂ cyl 75/25	To 500°C, then 850°C	70	21	71
IBG053	Ar/CO ₂ cyl 75/25	Rapid at 850°C	57	18	77
IBG054	Ar/CO ₂ cyl 75/25	Slow to 850°C	60	20	81
IBG055	Ar/CO ₂ cyl 75/25	Rapid at 850°C (H ₂ O)	61	18	68
IBG056	Ar/CO ₂ cyl 75/25	To 500°C, St 5, then 850°C	58	18	73
IBG057	Ar/CO ₂ cyl 75/25	Rapid at 850°C (H ₂ O)	59	19	78
IBG058	N ₂ , H ₂ O 5%	Rapid at 910°C	51	7	33
IBG059	N ₂	Rapid at 850°C (H ₂ O)	50	21	101
TGABM46			88	46	137
BB14			86	39	
Beluga			90	37	

5* Steam activation for 5 minutes.

produced char from the lignite feed that was very high in ash as seen in Table 4.2-3. The recoveries of the lignite chars as compared with the char yield from the proximate analyses were all very low. Material from the primary pot made up some of the deficiency in recovery as seen from the proximate analyses of combined material from Tests 030, 031 and 032 (IBG303132). It is apparent that as the coal is pyrolyzed, it decrepitates and blows over from the reactor to the traps, leaving an ash-enriched char to be collected.

At ambient temperature, SO₂ adsorption-desorption by the lignite char is excellent, but it falls off when the test is carried out at 100°C, as shown in Table 4.2-4. The experimental results in Table 4.2-4 show char wt% SO₂ adsorbed at 100°C followed by char wt% SO₂ desorbed, first under argon at 100°C, then at 400°C (carbon regeneration).

TABLE 4.2-3
Proximate Analysis of Chars

	wt%				Moisture-Free wt%			Moisture and Ash Free wt%	
	Moisture	Volatiles	Fixed C	Ash	Volatiles	Fixed C	Ash	Volatiles	Fixed C
Beulah Lignite									
Raw (BM46)	31.83	29.95	33.99	4.23	43.93	49.86	6.21	46.84	53.16
IBG030	1.93	7.27	77.69	13.11	7.41	79.22	13.37	8.55	91.45
IBG031	9.80	7.70	72.55	9.95	8.54	80.43	11.03	9.60	90.40
IBG032	4.76	6.95	74.33	13.93	7.30	78.04	14.63	8.55	91.41
IBG303132	38.26	15.42	35.77	10.54	24.98	57.94	17.07	30.12	69.86
IBG037	2.21	6.25	80.89	10.65	6.39	82.72	10.89	7.17	92.83
IBG038	1.56	6.52	78.47	13.45	6.63	79.71	13.66	7.67	92.32
IBG039	24.1	36.41	43.45	26.01	8.44	57.27	34.28	12.85	87.14
IBG040	16.99	11.83	51.61	19.57	14.25	62.17	23.58	18.65	81.35
IBG041	0.51	4.65	85.09	9.77	4.67	85.52	9.82	5.18	94.83
IBG042	6.43	6.03	78.30	9.24	6.45	83.68	9.87	7.15	92.85
IBG043	8.66	7.16	73.63	10.55	7.84	80.61	11.55	8.87	91.13
IBG044	6.99	8.72	74.93	9.36	9.38	80.56	10.06	10.42	89.58
IBG045	6.26	10.56	59.68	23.47	11.27	63.67	25.04	15.03	84.93
IBG046	0.74	4.77	83.31	11.19	4.81	83.93	11.27	5.42	94.59
IBG047	0.92	7.58	78.06	13.43	7.65	78.79	13.56	8.85	91.14
IBG048	1.02	3.50	81.95	13.53	3.54	82.80	13.67	4.10	95.91
Beulah Subbituminous									
IBG049	0.98	3.82	79.52	15.68	3.86	80.31	15.84	4.58	95.42
IBG050	2.32	2.85	80.83	14.00	2.92	82.75	14.33	3.41	96.59
IBG051	1.00	5.00	80.49	13.53	5.05	81.30	13.67	5.84	94.17
IBG052	1.09	3.77	78.51	16.64	3.81	79.38	16.92	4.58	95.43
IBG053	1.23	4.76	74.63	19.41	4.82	75.56	19.65	5.99	94.04
IBG054	1.13	3.87	77.92	17.08	3.91	78.81	17.28	4.73	95.27
IBG055	1.15	4.48	73.42	20.96	4.53	74.28	21.20	5.75	94.26
IBG056	2.03	5.04	76.38	16.58	5.14	77.96	16.92	6.19	93.84
IBG057	1.06	4.51	80.29	14.14	4.56	81.15	14.29	5.32	94.68
IBG058	2.21	3.92	78.88	15.01	4.01	80.66	15.35	4.74	95.29
IBG059	1.75	3.60	80.78	13.87	3.66	82.22	14.12	4.26	95.74
TGALIG*	31.83	29.95	33.99	4.23	43.93	49.86	6.21	46.84	53.19
TGALEON**	25.03	38.73	28.54	7.70	51.66	38.07	10.27	57.58	42.43
TGASUBB***	21.63	36.44	32.29	5.60	46.50	46.31	7.15	50.08	49.87

* Beulah-Zap Lignites.

** Leonardite.

*** Subbituminous.

The temperature regime followed in preparing the lignite char has an effect on the activity. Staged heating, in which the coal is introduced into the reactor at 500°C and then heated to 850°C, resulted in lignite char having higher SO₂ adsorption values than char prepared under slow or fast heatup.

On pyrolysis, the subbituminous coal results in much higher char recoveries than does the lignite coal, owing to the loss of more unpyrolyzed fines from the lignite. The subbituminous coal char produced under the same conditions (i.e., mass of coal and process) has SO₂ adsorption-desorption properties that are as good as those of the lignite char (Table 4.2-4). However, on a char mass basis, the lignite char showed better

TABLE 4.2-4

Percentage Weight Increase Due to SO₂ Adsorption Followed by Desorption over Sequential Temperature Ranges

Temp., °C Atm Sample	A Adsorp. Ambient 5000 ppm SO ₂ wt%	B Desorp. at 100°C, N ₂ wt%	C Desorp. at 400°C, N ₂ wt%	A Adsorp. Ambient 5000 ppm SO ₂ wt%	B Desorp. 100°C, N ₂ wt%	C Desorp. 400°C, N ₂ wt%
Lignite						
IBG030	6.1	0.9	-0.8*	2.7	2.3	0.1
IBG031	-0.8	-6.1	-9.8	2.3	1.8	-1.3
IBG032	0.7	-2.3	-5.3	1.4	1.1	-1.6
IBG303132		0	0		0	0
IBG037	7	1.6	-0.4	2.5	2.0	0.3
IBG038	7.7	1.9	-0.1	3.0	2.5	0.8
IBG039	5.4	1.0	-2.8	2.0	1.7	-1.8
IBG040	5.3	1.2	-3.5	2.1	1.7	-2.5
IBG041				1.8	1.6	0.2
IBG042				0.6	0.5	-1.1
IBG043				1.0	0.8	-0.9
IBG044				0.8	0.6	-1.9
IBG045				3.2	2.7	0.2
IBG046				2.5	2.3	1.0
IBG047				2.8	2.3	0.6
IBG048				1.3	1.0	-0.3
Subbituminous						
IBG049				2.1	1.7	0.2
IBG050				1.4	1.0	-0.2
IBG051				2.2	2.1	1.1
IBG052				2.1	1.5	0.5
IBG053				1.9	1.4	0.3
IBG054				2.0	1.5	0.4
IBG055				1.7	1.2	0.2
IBG056				2.5	1.9	0.6
IBG057				1.8	1.3	0.4
IBG058				1.6	1.1	-0.6
IBG059				1.5	1.0	-0.1
Various						
TGALIG				2.4	2.2	1.2
TGALEON				4.2	3.8	2.5
TGASUBB				1.9	1.5	-0.1
LigPVA				2.1	1.5	-0.6
Commercial Char**	4.4			0.7		

* Negative desorption values are due to losses from one or more of the following processes: moisture release, gasification, and decarboxylation.

** Coal Char -80 + 325 mesh

adsorptive behavior. The fixed carbon and ash numbers are consistent with those expected from this coal.

The progress of pyrolysis in selected lignite char preparations was followed with FTIR spectrometry. Examples of the resulting spectra of CO and CH₄ adsorption as a function of time are shown in Figures 4.2-1 and 4.2-2. The spectra show that staged heating (IBG037) results in higher production of methane and carbon monoxide from this lignite than either a rapid heatup (IBG038 and IBG040) at calcining temperature or a slow heatup (IBG039) from ambient to calcining temperature. Methane produced from cracking during rapid heatup and slow heat-up was relatively constant, whereas a much larger quantity of methane results from staged heating. CO follows a similar trend. The beneficial effect of staged heating on char sorption has already been noted.

The last three values on Table 4.2-4 have the SO₂ adsorption-desorption results obtained on the small TGA from the three raw coals. The lignite and subbituminous char values compare very favorably with the results obtained with the char produced in the IBG. Sulfur dioxide adsorption-desorption values for lignite-polyvinyl alcohol char showed this char to be approximately the same as the coal char. However, 1.5-gram pellets prepared from the LigPVA char apparently had improved water resistance and hardness over those prepared from the char without additional binder, but no quantitative measures of hardness or water resistance were taken. Adsorption of SO₂ by a commercial char was lower at both ambient temperature and 100°C than the chars from coals selected for this project.

Figure 4.2-1. Absorbance at 2173 cm⁻¹ by the CO component of product gas from pyrolysis of lignite coal under staged (IBG037), rapid (IBG038) and slow (IBG039) heatup.

Figure 4.2-2. Absorbance at 3018 cm⁻¹ by the CH₄ component of product gas from pyrolysis of lignite coal under staged (IBG037), rapid (IBG038), and slow (IBG039) heatup.

No characterization values for leonardite char prepared in the IBG are presently available for comparison with the lignite and subbituminous chars since the 12- x 30-mesh leonardite sample decrepitated badly when first attempts were made to dry it sufficiently to feed it to the IBG.

● FUTURE WORK

- Develop a means of feeding leonardite so that it can be fed to the IBG for char preparation.
- Prepare leonardite char for testing.
- Collect pyrolysis liquids for characterization.
- Design and fabricate an IBG add-on module for testing tar-cracking catalysts.
- Test tar-cracking catalysts on the IBG.

● CONCLUSIONS

- The amount of char product recovered from the reactor was greater when preparing it from an Alaskan (Beluga) subbituminous coal than from a North Dakota (Beulah) lignite, due to loss of more fines from the lignite. Analysis showed that these fines were insufficiently pyrolyzed.

- Volatile matter in the subbituminous char product was typically lower than in the lignite char.
- Staged heating during pyrolysis of the lignite coal resulted in more methane production than did slow or rapid heating.
- Sulfur dioxide adsorption as measured by TGA at 100°C by both chars prepared in this project was as good as, or better than, the commercial chars prepared from coal purchased for comparative testing.
- Pellets prepared from lignite char and polyvinyl alcohol showed improved water resistance and apparent hardness.

Reference

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Subtask 4.3 Low-Rank Coal Liquefaction

Introduction

New catalysts currently being investigated are basically homogeneous catalysts for first-stage coal solubilization and preliminary reduction. Catalysts obtained from Universal Fuel Development Associates, Inc (UFDA) were tested for the second-stage hydrotreatment of the first-stage liquefaction products from aqueous CO liquefaction of Wyodak coal.

Carbon monoxide and water have been utilized in the liquefaction of coal since 1921, when Fischer and Schrader demonstrated the effectiveness of this process (1). Improvements in the CO steam process have increased conversions to soluble products, but extensive depolymerization and hydrogenation of the coal macromolecules require further catalytic hydrotreatment of the Costeam product. The goal of the coal science team at the University of North Dakota Energy & Environmental Research Center (EERC) is the development of new homogeneous catalysts for the CO reaction. These catalysts are expected to aid in solubilization and preliminary reduction of low-rank coals to a high-quality intermediate product that can be easily catalytically converted to distillate fuels with low heteroatom content.

Catalysis of the first stage of coal liquefaction involves improving the rates of bond cleavage reactions leading to improved solubility and the rates of preliminary reduction reactions so that oils and asphaltenes are produced without extensive retrogressive reactions. The catalysts should be able to interact effectively with the colloidal coal matter to generate soluble products at moderate temperature. Thus various inexpensive and disposable inorganic agents that are solvent or soluble in the reaction vehicle are being investigated. Sodium aluminate catalyzed the solubilization of Australian coals in the CO/H₂O system and in water/hydrogen donor solvent mixtures (2,3). Previous work at the EERC demonstrated that aqueous sodium aluminate was also effective for Wyodak

subbituminous coal (4). High conversions comparable to those obtained with hydrogen donor solvents and hydrogen sulfide were obtained. In this report the suitability of the intermediates from catalyzed and uncatalyzed CO/H₂O reactions are compared as a feed for catalytic hydrogenation.

Objectives

The efficient production of environmentally acceptable distillate fuels requires catalysts for hydrogenation and cleavage of the coal macromolecules and removal of oxygen, nitrogen, and sulfur heteroatoms. Currently, two-stage processes for coal conversion are under development. The first stage converts coal to a soluble form with minimal cracking and hydrogenation. This processing presently involves no catalyst other than the coal mineral matter present and addition of a promoter, hydrogen sulfide, which may have a catalytic effect. The second stage involves hydrogenation upgrading of the first-stage product to distillates with fixed- or ebullated-bed catalysts.

The catalysts currently used in the second stage of coal liquefaction for hydrotreating the first stage product are the same as those used in conventional petroleum refining; however, this application has not been very successful. Improvements in upgrading efficiency could be obtained if catalysts with longer life and better activity and selectivity were available. Rapid deactivation of the conventional Co-Mo and Ni-Mo catalysts on an alumina support have been attributed to coke formation (5), metals deposition (6), and inhibition of the active center by chemisorbed compounds (7). The objectives of this research project are to develop and test novel heterogeneous catalysts for hydrotreatment upgrading of first-stage coal liquefaction products. The new hydrogenation catalysts are based on pillared clays and hydrotalcites, which have very large micropore dimensions to accommodate the coal macromolecules, but yet do not possess strong acidities that lead to coking at high temperatures. A second objective is to develop a solid acid catalyst for depolymerization of coal macromolecules. The acid catalysis process for coal liquefaction is believed to operate by ionic mechanisms. Some molten acids have successfully depolymerized coal, but the poor efficiencies of catalyst recovery and the corrosive nature of the catalyst make the process uneconomical. Stable solid acid catalysts will be developed to avoid these difficulties. These catalysts are also based on pillared clays as well as on silica bases.

Accomplishments

Experimental

● PREPARATION OF CATALYSTS

An Amocat-IA cobalt-molybdenum catalyst was presulfided by heating with a small amount of sulfur and 1000 psi of hydrogen in a 15-mL rocking microreactor heated at 350°C for 3 hours. The clay-supported iron catalysts were obtained from Universal Fuel Development Associates, Inc. and were sulfided in situ by adding a small amount of elemental sulfur with the catalyst prior to hydrotreating.

● PREPARATION OF TETRAMETHYLAMMONIUM ALUMINATE

A solution of 1.92 g of aluminum nitrate nonahydrate in 50 mL of deionized water was placed in a 250-mL centrifugation flask. To this solution, 2 g of 30% ammonium hydroxide was added slowly with vigorous stirring. The white gel-like precipitate was separated by centrifugation, and washed with deionized water. The white precipitate was resuspended in 10 mL water. To this suspension, 2.6 g of tetramethylammonium hydroxide was added with stirring. Upon addition of tetramethylammonium hydroxide and stirring, the white precipitate dissolved to give a clear solution. Sufficient water was added to make 25 mL of solution. This solution of tetramethylammonium aluminate was stored for further use.

● PREPARATION OF SOLUBLE ALUMINOSILICATE

A solution of sodium silicate was prepared by dissolving 2.72 g of sodium silicate (27% SiO_2) in 50 mL of deionized water. The sodium silicate solution was ion-exchanged with Amberlite IR (120-H) resin until the pH was between 2 and 3. To this solution was added 4.6 g of tetramethylammonium hydroxide (20%). This solution was mixed with a solution of tetramethylammonium aluminate prepared as above. The clear solution of soluble aluminosilicate was stored for further use.

● PREPARATION OF MAGNETITE AND MAGHEMITE

Magnetite was prepared by a procedure similar to that reported earlier (8). Dry nitrogen was bubbled through 560 mL of deionized water placed in a three-necked flask. Iron(II) sulfate heptahydrate (80 g) was added to the flask and stirred until iron sulfate dissolved. The greenish brown solution was stirred at 90°C under nitrogen for 30 minutes. A solution of 6.46 g of KNO_3 and 44.9 g KOH in 240 mL deionized water was added dropwise to the flask. The black precipitate formed was stirred at 90°C for 60 minutes. The product was then cooled overnight. The black solid was separated by centrifugation and washed with deionized water. The black solid (Fe_3O_4) was vacuum-dried.

A 10-g portion of the magnetite (Fe_3O_4) was calcined in air at 250°C for 3 hours to give a rust-colored powder (maghemite, Fe_2O_3).

● PREPARATION OF IRON OXOALUMINATE

Iron oxoaluminate tetraisopropoxide was prepared by a procedure similar to that reported earlier by Ouhadi and others (9). A 100-mL three-necked flask was attached to a distillation assembly and baked with dry nitrogen to expel moisture. Aluminum isopropylate (2.04 g), iron(II) acetate (0.87 g), and tetralin (10 g) were introduced into the flask. The flask was heated in a stream of nitrogen. Upon heating, the iron acetate and aluminum isopropylate dissolved in tetralin to give a dark green solution, and isopropyl acetate began to distill. The heating was continued until isopropyl acetate ceased to distill. The green solution was stored under nitrogen.

● CO/H₂O REACTIONS OF MODEL COMPOUNDS

In a typical run, 0.5 g of model compound, 2 g of solvent(s), and the desired amount of catalyst (if needed) were placed in a tubing bomb (12-mL microreactor). The microreactor was evacuated, pressurized with 1000 psig of carbon monoxide, placed in a rocking autoclave, and heated to 400°C. At the end of the specified reaction period, the microreactor was cooled in a dry ice-acetone slurry, degassed, and opened. The resulting slurry was acidified with dilute HCl. The desired amount of the internal standard was added to the product slurry, and the product slurry was extracted with methylene chloride. The methylene chloride extract was dried over molecular sieves (4 Å) and analyzed by gas chromatography with flame ionization detection (GC/FID) and gas chromatography/Fourier transform infrared spectrometry/mass spectrometry (GC/FTIR/MS).

● CO/H₂O LIQUEFACTION OF COALS

A slurry consisting of 10.0 g of coal (as-received Wyodak-Clovis Point), 2.5 mmol of NaAlO₂ (if desired) dissolved in 6.0 g of water and 10.0 g of tetralin (solvent) was placed in a 70-mL Parr reactor. The reactor was evacuated and charged with 1000 psi (initial) of carbon monoxide gas. The reactor was heated to 400°C in a rocking autoclave (initial heatup time = 11 minutes) and left at this temperature for 30 minutes. The reactor was cooled to room temperature, and the gases were removed. The products were distilled to remove water. The remaining slurry was extracted with tetrahydrofuran (THF). The THF-insoluble product was dried under vacuum and weighed. The percent conversion was calculated on the basis of the coal (maf) that did not appear in the THF-insoluble fraction. The extract was evaporated to remove THF. The resulting low-severity products from sodium aluminate-catalyzed (SA-LSW) and uncatalyzed reactions (U-LSW) contained the original tetralin as well as the solubilized coal material. These were stored under nitrogen for further catalytic hydrotreating.

The composition of THF-soluble products was determined by adding an aliquot of this product to a large excess of heptane with vigorous stirring. The heptane-insoluble product was separated by centrifugation, washed with heptane, dried in vacuo at 50°C, and weighed. The heptane-soluble product was evaporated to remove heptane and kept for further analyses. The heptane-soluble yield was calculated with the following equation:

$$\% \text{ heptane solubles}^* = \% \text{ conversion} - \% \text{ heptane insolubles} \quad [\text{Eq. 4.3-1}]$$

(* includes gas and water)

● CATALYTIC HYDROTREATMENT OF LOW-SEVERITY INTERMEDIATES

A slurry consisting of 3 g of SA-LSW or U-LSW, 10 wt% of desired catalyst, and 2 wt% of sulfur (if needed) was placed in a 70-mL Parr reactor. The reactor was evacuated and charged with 1000 psi (initial) of hydrogen gas. The reactor was heated to 425°C in a rocking autoclave (initial heatup time = 15 minutes) and left at this temperature for 3 hours. At the end of the reaction, the reactor was cooled to room temperature, and the gases were removed. The product slurry was extracted with THF. The THF-insoluble product was dried under vacuum and weighed. The THF-insoluble fraction was used to

determine the amount of coke formed due to retrogressive reactions during hydrotreatment. The extract was diluted to 250 mL with THF. A 4-mL aliquot of the THF-soluble was mixed with 1 mL of solution of internal standard (a mixture of 2,2,4-trimethylpentane and *n*-octadecane in dichloromethane) and analyzed by gas chromatography (GC). The remaining THF-soluble fraction was evaporated to remove THF, and the dark oil was added to a large excess of heptane and stirred. The heptane-insoluble product was separated by centrifugation, washed with heptane, and dried in vacuo at 50°C. The percent conversion was calculated on the basis of the heptane-insoluble product that was converted to heptane-soluble product (oils). The conversion and yield data are given in Table 4.3-1.

● INSTRUMENTATION

Quantitative GC/FID analyses were performed with a Hewlett Packard 5880A gas chromatograph equipped with a Petrocol capillary column. A mixture of isooctane and *n*-octadecane was the internal standard. GC/FTIR/MS was performed on a Finnigan 800 ITD ion trap detector with a HP 5890A gas chromatograph and a J&W 30-m x 0.32-mm ID, 1.0-micron film of DB-5. A 15-m x 0.25-mm ID, 0.25-micron DB-5 film capillary column was used for the analysis of high boiling point components.

Infrared spectra were obtained in KBr on either a Perkin-Elmer Model 283 spectrometer or a Nicolet 20SXB FTIR spectrometer, equipped with a mercury cadmium telluride (MCTA) detector, and a Nicolet 1280 computer with a fast Fourier transform coprocessor.

Results and Discussion

● CATALYTIC HYDROTREATMENT OF LOW-SEVERITY LIQUEFACTION (LSW) PRODUCTS

The advantage of using a solubilization stage in coal processing is that almost all of the inorganic material present in the coal can be eliminated prior to catalytic hydrogenation over a supported catalyst. Thus the calcium deactivation that has seriously affected catalytic liquefaction in the low-rank coals can be avoided. Aqueous solubilization reactions that utilize carbon monoxide as the reductant gas have been extensively investigated in this and other laboratories over many years (10-12). Basic catalysts have been employed to achieve higher conversions. The CO/H₂O reduction has been shown to be superior to hydrogen for the first stage of liquefaction. A number of candidates for improving the conversion in CO/H₂O were reported by Jackson and others (2, 3). Aqueous sodium aluminate gave good conversions of brown coal to oils at temperatures of 350° to 400°C. The mechanism for sodium aluminate activation of carbon monoxide to produce an effective reducing intermediate is still under investigation.

TABLE 4.3-1

Catalytic Hydrotreating of Low-Severity Products
from CO/H₂O Liquefaction of Wyodak Coal

Reaction Time = 3 hr, H₂ = 1000 psi (cold),
Low-Severity Product wt = 3 g, Catalyst wt = 0.3 g

Low-Severity Product	Catalyst	Sulfur, %	Temp., °C	Heptane Insol.	%-Conv. to Heptane Sol.
U-LSW	---	---	---	0.49	---
U-LSW	None	None	425	0.36	26
U-LSW	APC-Fe ₃ ^a	2	425	0.26	47
U-LSW	K-10/Fe ₃ ^b	2	425	0.22	56
U-LSW	Co-Moly	2	425	0.16	67
SA-LSW	---	---	---	0.61	---
SA-LSW	None	None	425	0.48	24
SA-LSW	APC-Fe ₃ ^a	2	425	0.23	62
SA-LSW	K-10/Fe ₃ ^b	2	425	0.20	68
SA-LSW	Co-Moly	2	425	0.20	68

^a Catalyst washed with ethanol prior to drying and calcination.

^b Triiron was supported on K-10 in ethanol.

SA-LSW = Sodium aluminate-catalyzed low-severity product.

U-LSW = Uncatalyzed low-severity product.

Investigations of homogeneous catalysts for coal liquefaction at the EERC (4) verified that sodium aluminate is also effective in improving the CO/H₂O liquefaction of low-rank western U.S. coals. High conversions to THF solubles were obtained for the Wyodak subbituminous coal (89%). These were substantially higher than those obtained in a similar CO/H₂O reaction with no added sodium aluminate (78%). Conversion of the Wyodak to THF solubles in a CO/H₂O liquefaction experiment with sodium hydroxide catalyst was substantially lower (72%).

A mixed solvent containing an organic solvent with lower vapor pressure (tetralin) was also used for the CO/H₂O reaction. Solubilization reactions of the Wyodak coal were performed in a water/tetralin wt/wt ratio of 0.6, both with and without sodium aluminate, at 400°C for 30 minutes with 1000 psi of cold initial CO pressure. Compared with water only, the operating pressure as well as conversions to THF-soluble products was significantly lower for the mixed solvent system. The sodium aluminate-catalyzed

reaction gave 79% conversion to THF solubles, whereas the uncatalyzed reaction gave only 63% conversion. The lower yields for the mixed solvent in both catalyzed and uncatalyzed reactions may have resulted from the lower water concentration. The dependence of the conversions on the CO and water partial pressure was previously described (13). It should also be pointed out that the lower fluid density in the mixed solvent reactions may have resulted in a lower conversion. Higher conversions can be obtained by longer reaction times or higher temperatures, but minimal processing severity was desired for generating the intermediates needed for this study.

The yield of heptane solubles from the sodium aluminate-catalyzed reaction (CO/water/tetralin system) was the same (30% heptane solubles) as that obtained in uncatalyzed reactions in the same system (31% heptane solubles). Since the conversions were higher for the sodium aluminate-catalyzed reactions, the heptane-insoluble fraction is larger for the sodium aluminate-catalyzed reactions. Thus the two products do not have the same composition with respect to the solubility fractions.

Development of an economical process for liquefaction of low-rank coals requires an evaluation of the suitability of the soluble COsteam products as a feed for catalytic hydrogenation. The catalytic hydrogenation is required for depolymerization to a distillable product with higher hydrogen content and low heteroatom content. The evaluation of product quality was determined by carrying out hydrogenations with both a conventional supported cobalt-molybdenum catalyst as well as two dispersed iron sulfide catalysts. In these tests, the THF-soluble low-severity products from the sodium aluminate-catalyzed (SA-LSW) and the uncatalyzed CO/H₂O reactions (U-LSW) were catalytically hydrotreated with 10 wt% of the catalyst at 425°C for 3 hours in hydrogen (1000 psi cold). Since the compositions of the SA-LSW and U-LSW were not identical, the percent conversion was measured as the percentage of heptane insolubles converted to heptane solubles in the hydrogenation of each intermediate with each catalyst. The conversion data and product yields are given in Table 4.3-1.

The thermal (noncatalytic) hydrogenation of the SA-LSW product converted 24% of the heptane-insoluble fraction to heptane solubles. Thermal hydrogenation of the U-LSW product gave a similar conversion to heptane solubles (26%).

The supported cobalt-molybdenum catalyst was presulfided in hydrogen sulfide/hydrogen (10% H₂S). Hydrogenation of the SA-LSW with the presulfided cobalt-molybdenum catalyst resulted in a high conversion (68%) of the heptane-insoluble fraction to heptane solubles. Hydrogenation of the U-LSW with this catalyst also gave a high conversion to heptane solubles (67%).

In contrast to the molybdenum catalyst results described above, the results obtained with sulfided iron catalysts demonstrated significant differences for the hydrogenation of the low-severity products obtained from the sodium aluminate-catalyzed and the uncatalyzed reactions. An iron/alumina-pillared montmorillonite catalyst was sulfided in situ by adding elemental sulfur to the reactants. The hydrogenation of SA-LSW with this catalyst gave a 62% conversion to heptane solubles. A conversion of only 47% was obtained with the U-LSW product. The very large increase in conversion to heptane solubles in the SA-LSW experiment clearly demonstrates that the use of sodium

aluminate catalyst in the CO/water pretreatment solubilization stage had a beneficial effect on the quality of the low-severity product.

This improvement in the hydrotreatability of the low-severity product as a result of sodium aluminate catalysis was further demonstrated by a different sulfided iron catalyst. This catalyst was prepared by the impregnation of triiron complex on an acid-washed montmorillonite. Sulfidation was performed in situ with elemental sulfur, and reaction conditions were the same as before. The reaction with the SA-LSW gave an excellent conversion to heptane solubles (67%), which compared favorably with that produced by the molybdenum catalyst. As in the reactions with the pillared clay-supported iron sulfide catalyst, the reaction of this clay-supported iron catalyst gave a much lower conversion (56%) with the U-LSW.

● CO/H₂O REACTIONS OF POLYNUCLEAR AROMATIC HYDROCARBONS

Previous studies have shown sodium aluminate to be an effective catalyst for hydrogen transfer to linear polynuclear aromatics (14). Several more solid as well as soluble catalysts have been prepared and tested for the CO/H₂O hydrogenation of polynuclear aromatics. Anthracene and pyrene were used as test compounds to investigate the hydrogenation of polynuclear aromatic system by the aqueous CO system. The reactions were carried out by heating the substrate and catalyst in water at 400°C for 2 hours in the presence of 1000 psi of CO (initial cold pressure). Reaction conditions and conversion data are given in Table 4.3-2.

TABLE 4.3-2

Catalytic Hydrogenation of Polynuclear Aromatic Hydrocarbons

Reaction Temp. = 400°C, Reaction Time = 2 hr Reductant (CO) = 1000 psi			
Catalyst (mmol/g substr)	Substrate (mmol)	Conv. (%)	Major Products (mmol)
SA (0.50)	Anthracene (2.80)	44	9,10-Dihydroanthracene (1.20) Tetrahydroanthracene (0.02)
TMAAlO ₂ (0.50)	Anthracene (2.86)	83	9,10-Dihydroanthracene (2.21) Tetrahydroanthracene (0.19)
Magnetite (0.50)	Anthracene (2.92)	74	9,10-Dihydroanthracene (2.04) Tetrahydroanthracene (0.12)
Magnetite (0.50)	Pyrene (2.47)	2	Dihydropyrene (0.04)

Reaction of anthracene with soluble aluminosilicate (tetramethylammonium salt) gave only 44% conversion of the substrate to hydroanthracenes. The product was mostly 9,10-dihydroanthracene plus a small amount of tetrahydroanthracene. Compared with sodium aluminate (82% conversion), soluble aluminosilicate showed considerably lower hydrogen transfer activity.

Tetramethylammonium aluminate gave slightly higher conversion (83%) of anthracene than sodium aluminate. Product distribution was similar to that obtained with the sodium aluminate-catalyzed reduction of anthracene (14, 15). Thus the tetramethylammonium aluminate must function similarly to sodium aluminate, and the cation is probably not involved in the mechanism.

Reduction of anthracene in $\text{CO}/\text{H}_2\text{O}$ was also investigated using an insoluble (solid) catalyst. Magnetite (nonsulfided) gave a significantly lower conversion (74%) than the sodium aluminate-catalyzed hydrogenation of anthracene. The major product was 9,10-dihydroanthracene, and a small amount of tetrahydroanthracene was also formed. The reaction of magnetite with pyrene gave a very poor conversion (2%), and dihydropyrene was the only product. These data are consistent with sodium aluminate-catalyzed $\text{CO}/\text{H}_2\text{O}$ reduction of pyrene (15). Magnetite is a good catalyst for the water gas shift reaction. It appears that whatever complex forms between magnetite and CO , it is unable to transfer either hydrogen or electrons to anthracene very effectively.

● $\text{CO}/\text{H}_2\text{O}$ HYDROTREATMENT OF COALS

During our previous study of homogeneous catalysts for first-stage coal liquefaction, catalysts for improving the conversion and product quality of liquefactions carried out in aqueous systems were investigated. However, these reactions generated very high operating pressures. In order to reduce the operating pressures, a mixed solvent system consisting of 10 g of tetralin and 6 g of water was used. Since the first stage liquefaction product is used as a feed for the subsequent catalytic hydrotreatment, use of tetralin will give a soluble first-stage product that can be directly used for second-stage reaction. Furthermore, the product work-up is also simplified. The reaction conditions and yields data are given in Table 4.3-3.

Previous results have shown that the addition of sodium aluminate to the $\text{CO}/\text{H}_2\text{O}$ system improves the conversion of Wyodak subbituminous coal to distillate and soluble products at 400°C (14). Since high conversions to THF solubles are easily obtained at 400°C without any promoter or catalyst with the low-rank coals, the conversion to oils, asphaltenes, and distillate was accurately determined to evaluate the activity of sodium aluminate. The composition of the distillate, oil, and asphaltene product obtained after first-stage liquefaction in aqueous CO was determined for comparison with that obtained in organic solvents with CO or with hydrogen. These studies have indicated that the volatile first-stage product from aqueous liquefaction contained large amounts of phenolics rather than hydrocarbons, as for organic solvent liquefaction. As a consequence, the distillate can be removed and used elsewhere, so that hydrogen is not wasted in deoxygenation of phenols.

TABLE 4.3-3

Catalytic Liquefaction of Wyodak Coal

Reaction Temp. = 400°C, Reaction Time = 30 min Reductant gas (CO) = 1000 psi (at room temp.)					
Catalyst, mmol/g coal	Coal, as-received, g	Solvents, g	Conv. *, %	Products, % Hept-I Hept-S	
None	Wyodak, 10	Tetralin, 10 Water, 6	64	32	32
NaAlO ₂ , 0.5	Wyodak, 10	Tetralin, 10 Water, 6	73	37	36
AS, 0.5	Wyodak, 5.0	Tetralin, 5 Water, 3	69	40	29
TMAAlO ₂ , 0.5	Wyodak, 10.0	Tetralin, 10 Water, 6	63	35	28
Magnetite, 0.5	Wyodak, 5.0	Tetralin, 5 Water, 3	88	64	24

* = Conversions are based upon the amount of initial coal (maf).

Heptane solubles are by difference, also includes water and gas.

AS = Soluble aluminosilicate.

TMAAlO₂ = Tetramethylammonium aluminate.

Reaction of Wyodak coal was carried out by heating a well-mixed slurry of coal in aqueous sodium aluminate plus tetralin (10 g of as-received coal/10 g of tetralin/6 g of water/2.5 mmol of sodium aluminate) for 30 minutes at 400°C in the presence of 1000 psig initial CO pressure. Compared with the CO/water system, CO/water/tetralin gave somewhat lower conversion (73%) to THF-soluble products, with 37% being heptane-insoluble and 36% heptane-soluble (oils). Similar reaction in the absence of sodium aluminate gave 63% conversion of the coal to THF-soluble products, with 32% heptane-insoluble and 32% heptane-solubles (oils). These data indicate that sodium aluminate promotes the liquefaction of low-rank coals in aqueous as well as water/tetralin solvent systems.

Studies were also initiated to investigate other catalysts for aqueous-CO liquefaction of coal. Reaction of Wyodak coal in the water/tetralin system was carried out using tetramethylammonium aluminate under reaction conditions identical to the sodium aluminate-catalyzed reaction. Tetramethylammonium aluminate gave a little lower conversion to THF-soluble and lower conversion to heptane-soluble products, so it is probably inactive as a catalyst. The reaction of Wyodak coal was also carried out with soluble aluminosilicate in the water/tetralin solvent system under the above conditions. This catalyst also gave lower conversion (69%) to THF-soluble product than sodium

aluminate, and the conversion to heptane solubles (oils) was significantly lower. These attempts to modify the catalyst structure were not successful.

The liquefaction of Wyodak was also carried out in tetralin/water using a high surface area solid catalyst (magnetite). This catalyst gave very high conversion (88%) to THF-soluble material. However, the conversion to heptane-soluble was only 24%. These data indicate that magnetite reacts differently than sodium aluminate, but there is no good explanation for this behavior.

The liquefaction product quality was determined by GC analyses of the oil fraction. Products in the oils were oxygenated compounds, such as methanol, 2-propanol (from acetone), and phenolics. In addition, there were hundreds of hydrocarbon components that are typically found in coal-derived products. Total phenolics amounted to about 5% of the starting maf coal. The ratio of tetralin to naphthalene was 25, indicating that approximately 4% of tetralin was converted into naphthalene. A large number of alkyl tetralins and naphthalene were also formed. Consequently, hydrogen transfer from tetralin also occurs during liquefaction. Based on the retention time of the components, it is concluded that sodium aluminate produces lower molecular weight products than the rest of the catalysts used in these investigations.

● CO/H₂O REDUCTION OF ANTHRACENE

The second priority in our program was to understand the mechanism of the sodium aluminate catalysis. Sodium aluminate could probably activate CO for hydride reduction as well as sodium carbonate does, perhaps better. But does it also activate CO so that hydrogenation of hydrocarbons occurs? Can it lower activation energies for cleavage of bonds such as in ether and carboxylate groups? In order to investigate the mechanism of NaAlO₂-catalyzed reduction of polynuclear aromatics in the CO/H₂O system, a series of reactions of a 1:1 mixture of anthracene and anthracene-d₁₀ was conducted. The reactions were carried out with and without catalyst at 400°C for 2 hours and 1000 psi of CO (initial pressure) to determine any differences in the isotope effects exhibited by the catalyzed reactions. Reactions of anthracene were also carried out with and without catalyst in D₂O for comparison with reactions carried out earlier in H₂O. Reaction conditions and analytical data are given in Table 4.3-4.

The results of the reactions of anthracene in D₂O exhibit a substantial decrease in conversion compared with those carried out in H₂O earlier in the project. The conversion of anthracene in the CO/H₂O system was 79% without NaAlO₂ catalyst and 82% with NaAlO₂. The lower conversions in D₂O (19% and 22% for uncatalyzed and catalyzed reactions, respectively) are expected for a reaction that formed hydrogen via a water gas shift reaction followed by addition of hydrogen to anthracene. The results are consistent with the normal isotope effects observed in hydrogen addition reactions. Although inverse isotope effects are observed for the water gas shift reaction that forms the hydrogen (16), the overall reduction in reaction rate for the CO/D₂O reactions is mainly determined by the normal isotope effect operating during the slower hydrogen addition step. A reaction involving donation of hydrogen from a formate intermediate to the anthracene might be expected to exhibit an inverse isotope effect similar to that found in the water gas shift reaction, but we are not aware of any evidence that has established this effect as fact.

TABLE 4.3-4

Reduction of Anthracene

Reaction Temp. = 400°C, Reaction Time = 2 hrs Solvent (D ₂ O or H ₂ O) = 2 g, Reductant (CO) = 1000 psi			
Catalyst, mmol/g substr	Substrate, mmol	Conv., %	Major Products, mmol
None*	Anthracene 2.87	19	Dideutroanthracene 54 Tetradeutroanthracene trace
NaAlO ₂ * 0.50	Anthracene 2.86	22	Dideutroanthracene 0.60 Tetradeutroanthracene trace
None	Anthracene 0.56	20.5	Dihydroanthracene 0.11
	Anthracene-d ₁₀ 0.53	20.7	Dihydroanthracene-d ₁₀ 0.11
NaAlO ₂ 0.50	Anthracene 0.56	22.2	Dihydroanthracene 0.12
	Anthracene-d ₁₀ 0.53	26.2	Dihydroanthracene-d ₁₀ 0.14

* = D₂O solvent.

The conversion in D₂O was somewhat better with than without the NaAlO₂ catalyst, as was the case with H₂O. A comparison of the magnitudes of the isotope effects do not allow us to reach a definitive conclusion about the catalytic mechanism.

A small inverse secondary isotope effect was observed for the reduction of anthracene compared with perdeuteroanthracene in the uncatalyzed CO/H₂O system. Furthermore, the NaAlO₂-catalyzed reaction showed an even greater inverse secondary isotope effect with respect to the aromatic substrate. These results were not expected. Since perdeuteroanthracene has a lower electron affinity (more negative reduction potential) than anthracene, one might expect a normal isotope effect for the reduction reaction, and previous results with various aromatics indicated that the electron affinity is a major factor in determining the reactivity of aromatics in the CO/H₂O system. The inverse isotope effect results indicate that the transition state involved in the reactions must occur later than it does in an electrode reduction. However, the observed results may have been caused by a reverse reaction of the dihydroanthracene products, which depletes the nondeuterated product with respect to the deuterated product via a primary isotope effect. Further work is needed to understand these results.

● REACTIONS OF DIPHENYLPROPANE (DPP)

The mechanism by which iron oxoaluminate catalyzes the reduction of anthracene in tetralin is unknown. It was obvious that the hydrogen atoms required for the reduction can come from the tetralin solvent, but how does iron oxoaluminate aid in the transfer of the hydrogens? 1,3-Diphenylpropane was used to investigate hydrogen transfer catalysis mechanisms of iron oxoaluminate. The reactions were carried out at 400°C for 2 hours in the presence of 1000 psi of carbon monoxide. The reaction conditions and analytical data are given in Table 4.3-5.

The thermal reaction of diphenylpropane in decane (no anthracene) occurred with the expected radical transfer/cleavage reaction to give mainly toluene and styrene in low conversion (18%). Addition of iron oxoaluminate tetraisopropoxide to the reaction of diphenylpropane with no anthracene in decane resulted in a significant increase in the conversion (28%) of the diphenylpropane, indicating that the iron oxoaluminate is assisting in the transfer of hydrogen atoms between the diphenylpropane and the radical intermediates. A substantial part of the styrene was reduced to ethylbenzene, with the hydrogen donated from the isopropyl groups released from the decomposing oxoaluminate. Addition of anthracene to the thermal diphenylpropane/decane system with no catalyst had no effect on the conversion of diphenylpropane (18%). Addition of anthracene to the catalyzed reaction of diphenylpropane resulted in a large increase in conversion of the diphenylpropane. This result suggests that an iron intermediate is also assisting in transferring hydrogen atoms to the anthracene. The resulting anthracenyl radicals must also be involved in the radical-chain carrying process that results in cleavage of the diphenylpropane. Further experiments are in progress with recovered iron oxoaluminate (which has lost the isopropoxide groups) to elucidate the capabilities of this iron form in sustaining radical transfer reactions.

● CONCLUSIONS

The low-severity products from CO/H₂O reactions obtained with and without sodium aluminate were compared in hydrogenation tests with three catalysts as well as the thermal noncatalytic reaction. The thermal reaction gave poor conversions to heptane solubles for both low-severity products. A significant difference in the conversions of the two low-severity products to heptane solubles was found for two clay-supported iron catalysts. The sodium aluminate-catalyzed CO/H₂O reaction gave a product with much higher potential for hydrotreating than that obtained from the uncatalyzed CO/H₂O reaction. In contrast, a commercial cobalt-molybdenum catalyst gave about 68% conversion for both low-severity products. Thus the very effective hydrogen-activating molybdenum sulfide catalyst was able to compensate for the lower quality of the uncatalyzed reaction product. If the economics of coal liquefaction and catalyst recovery demand the use of the inexpensive and disposable iron catalysts, the use of sodium aluminate in a pretreatment solubilization step will be very important in increasing the yields obtained in the subsequent catalytic hydrogenation step.

TABLE 4.3-5
Reactions of Diphenylpropane

Reaction Temp. = 400°C, Reaction Time = 2 hr Reductant (CO) = 1000 psi				
Catalyst, mmol/g substr	Substrate, mmol	Solvent, g	Conv., %	Major products, mmol
None	2.60	<i>n</i> -Decane, 1.01	18	Toluene, 0.36 Ethylbenzene, 0.07 Styrene, 0.21 Benzene, 0.01 Indane, trace Bibenzyl, 0.01
IOAl, 0.10	2.55	<i>n</i> -Decane, 2.04	28	Toluene, 0.67 Ethylbenzene, 0.30 Styrene, 0.18 Indan, 0.01 Bibenzyl, 0.01
None	2.55	<i>n</i> -Decane, 1.0 Anthracene, 90.10	18	Toluene, 0.38 Ethylbenzene, 0.09 Styrene, 0.19 Anthracene, 0.56
IOAl, 0.10	2.55	<i>n</i> -Decane, 1.0 Anthracene, 0.1	54	Toluene, 1.13 Ethylbenzene, 0.52 Styrene, 0.13 Anthracene,
Recov. IOAl, 0.10	2.25	<i>n</i> -Decane, 1.0		Toluene Ethylbenzene Styrene Anthracene

● FUTURE WORK

Further efforts to understand the nature of the catalytic effects of NaAlO₂ are planned. These include reinvestigations of the hydrogen isotope effects in CO/H₂O reductions of coals and selected model compounds.

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APPENDIX 4.1-1
ASTM PROCEDURES

ASTM PROCEDURES

Currently five ASTM procedures are used to address the physical stability of the coal or coal-derived product. ASTM procedure D1412-86 to determine equilibrium moisture is an adequate procedure to assess moisture readsorption for LRCs and upgraded LRCs, provided that the test is carried out over sufficient time to ensure that the sample has indeed equilibrated, which sometimes can exceed a week's duration. For determination of the handleability of coal and coal-derived products in terms of dust generation, ASTM D547-41 dusting index, ASTM D441-45 tumbler method, ASTM D409-71 Hardgrove index, and ASTM D440-49 drop-shatter test are used.

● DROP-SHATTER TEST

This method of drop-shatter test covers the determination of the relative size stability and its complement, the friability, of sized coal. It affords a means of indicating the ability of coal to withstand breakage when subjected to handling at the mine and during transit to the consumer. The test is useful for ascertaining the similarity of coals in respect to size stability and friability rather than for determining values within narrow limits in order to emphasize their dissimilarity. This method is considered applicable for testing a selected size of different coals, for testing different single sizes of the same coal, and for mixed sizes of the same or different coals.

This test appears best-suited for measuring the relative resistance to breakage of the larger sizes of coal when handled in thin layers such as from loader to mine car, from loading boom to railroad car, and from shovel to chute. While it may not be so well adapted for measuring the liability to breakage of coal when handled in mass, it is believed that the test method will serve also to indicate the relative size stability of composite sizes of coal where, in commercial handling, the smaller-sized pieces have a cushioning effect that tends to lessen the breakage of the larger pieces of coal.

The physical dimensions of the box that holds the coal are 18 inches in width, 28 inches in length, and approximately 15 inches in depth, supported above a mounted cast-iron steel plate not less than $\frac{1}{8}$ " thick. The inside of the bottom should be 6 feet above the plate. Round screens 8, 6, 4, 3, 2, 1 $\frac{1}{2}$, 1, $\frac{3}{4}$, $\frac{1}{2}$, $\frac{1}{4}$, $\frac{1}{8}$ inches will be used to size the coal. The accepted particle size for procedure D440-49 is 4- to 6-inch coal. 50-lb samples of coal are loaded into the box and dropped twice. Two separate trials are conducted, with acceptable results when within 2% error. Friability is defined in a manner similar to the tumbler test.

● DUSTINESS TEST

The ASTM procedure designates that a 5-foot dust cabinet cell (6 ft³ volume) be used to study the dust generated from dropping a coal sample 4 feet. The top foot of the cell is used to load 50 lb of the air-dried test coal onto a top slide plate. No size for the coal is specified for this test. Once the coal has been loaded, the top slide plate is removed. After a 5-second delay, two lower slide plates are inserted at the 2-foot level. The first slide plate is removed after 2 minutes. The amount of material that has settled on the slide plate is weighed and multiplied by an estimated density of the coal. This material is called the coarse dust. After 10 minutes, the second slide plate is removed and weighed. Again, the weight is multiplied by the density, categorized, and called float dust. The

results are then reported as coarse and fine dust ratings. Average results for the test coals are determined with acceptable results when they fall within 20%.

● TUMBLER TEST

The tumbler test covers the determination of the relative friability of a particular size of sized coal. It affords a means of measuring the liability of coal to break into smaller pieces when subjected to repeated handling at the mine or subsequently by the distributor or by the consumer. The test is useful for ascertaining the similarity of coals in respect to friability due to abrasion. This method also may serve to indicate the relative extent to which sized coals will suffer size degradation in certain mechanical feed devices. The test may be employed for differentiating between certain ranks and grades of coal, and therefore the method is of service for coal classification purposes.

The tumble test involves using a cylindrical steel cell with internal diameters of 7.25 inches by 7.25 inches in depth and $\frac{1}{4}$ inch thick. An insert with three ledges is used to aid the tumbling or mixing of the coal. The dimensions of the insert are $6.5 \times \frac{3}{4} \times \frac{1}{8}$ inch with $\frac{1}{8}$ -inch clearance between their outer edge and the outside ring. This unit is designed for 1000 grams of 1.5×1.06 -inch coal sample. For tumbling, the jar is laid in a horizontal position in a suitable support or rack and rotated about its cylindrical axis at the rate of 40 rpm for 60 minutes, or 2400 total revolutions. The coal is tumbled, then sized using wire screens of various sizes, ranging from 1.06 to 0.75 inch. Calculations are based upon size distributions and the amounts that collect on each screen. From the screen analysis, the friability index and dust index are calculated to report the durability of the coal material. The dust index is determined by the weight percent which is below 50 mesh, while the friability index is calculated using screening data and a size factor (calculated by various weight fractions from the screening results.)

● HARDGROVE GRINDABILITY

The Hardgrove grindability test is a standard procedure that is utilized in evaluating coals for the dust program. It is the most widely used measure for ascertaining the relative ease of size reduction of coals and is determined by comparing size-reduction characteristics in laboratory test apparatus of specified design. Grindability is used for determining how much energy input is required for grinding and/or pulverizing coals. The index is beneficial for analyzing the dustiness of the selected coals.

Briefly the procedure is as follows: a 50-gram sample of coal, 1.18×0.6 mm in size (16 x 30-mesh), is prepared and placed in the standard Hardgrove test apparatus. The test machine is designed to subject the sample to the grinding action of eight 25.4-mm (1-inch) steel balls, which revolve in a lower stationary container and are driven by an upper rotating ring carrying a weight of 29.1 kg (64 pounds). The upper ring is rotated for 60 revolutions. The sample is then removed from the Hardgrove machine and screened on a 75-micron (200-mesh) screen. The Hardgrove grindability index is based on the amount of minus 75-micron material produced. Under standard procedure, this quantity is calculated by difference between the weight of sample placed in the test apparatus (50 grams) and the weight of material retained on the 75-micron screen.

● EQUILIBRIUM MOISTURE

ASTM D1412 equilibrium moisture procedure consists of first slurring the coal sample in water and mixing the slurry for 3 hours. The mixture is then dewatered and placed in a cabinet where conditions are maintained under vacuum at 30°C and 96% to 97% relative humidity. The humidity is maintained by a saturated potassium sulfate (K_2SO_4) solution. The final moisture at "equilibrium" is an average of three samples, determined by weight loss at 105°C. The standard test recommends an incubation period of 72 hours (3 days) for lignitic and subbituminous coals.

The applicability of the suggested 3-day period was evaluated by extending the incubation period an additional 24 hours to determine whether further weight loss occurred. After 72 and 96 hours of incubation, the sample weight and weight loss were determined. The final moisture content was determined according to normal procedure only after 96 hours.

● MODIFIED ASTM EQUILIBRIUM MOISTURE

1. Ten samples of near equal weight (~5 grams each) were prepared and then weighed to the nearest ten-thousandth of a gram.
2. The moisture contents of two samples were determined by heating to constant weight in a 105°C oven. An average moisture content was calculated from these two samples. The initial moisture contents of the remaining eight samples were assumed to be equivalent to this average. The solid contents (mass) for each of the remaining eight samples were calculated using the average moisture value. The solids mass in each of these samples was assumed to be unchanged during subsequent incubation.
3. The remaining eight samples were incubated for 72 hours at 30°C and 96% to 97% relative humidity, the humidity being maintained by a saturated potassium sulfate solution. All eight samples were weighed to determine mass loss gain, and a new moisture content was calculated assuming the mass change was due to moisture loss/gain only. An average moisture content was determined from these eight samples; this average value was called the "calculated" moisture content. The actual moisture contents of two samples were determined by heating to constant weight in a 105°C oven. An average moisture content was determined from these two samples; this average value was called the "measured" moisture content.
4. The remaining six samples were incubated for an additional 48 hours, resulting in a cumulative incubation period of 120 hours (5 days). Again calculated and measured moisture contents were determined. This procedure was repeated after 168 hours (7 days) and 240 hours (10 days) of cumulative incubation. The entire test procedure was done on day 10 as the last two samples were consumed during measurement of the final moisture content. Calculated and measured moisture contents were determined after each of these additional incubation periods.

APPENDIX 4.1-2
SAMPLE CALCULATIONS

CALCULATION OF REDUCTIONS AND RECOVERIES

1. Total Material Recovery, wt% = $\left[\frac{M_{dc} + M_c}{M_{rc} + M_w} \right] 100$
2. Water Recovery, wt% = $\left[\frac{M_c + (M_{dc} \times DC_m)}{M_w + (M_{rc} \times RC_m)} \right] 100$
3. Solids Recovery, wt% = $\left[\frac{M_{dc}(1 - DC_m)}{M_{rc}(1 - RC_m)} \right] 100$
4. Btu Recovery, % = $\left[\frac{M_{dc}(1 - DC_m)DC_{hv}}{M_{rc}(1 - RC_m)RC_{hv}} \right] 100$
5. Dry Coal Recovered, lb/100 lb raw coal = $\left[\frac{M_{dc}}{M_{rc}} \right] 100$
6. Moisture Reduction, wt% = $\left[\frac{1 - (M_{dc} \times DC_m)}{M_{rc} \times RC_m} \right] 100$

where

M_{rc} = mass of raw coal charged, grams
 M_{dc} = mass of dried coal recovered, grams
 M_w = mass of water charged, grams
 M_c = mass of condensate recovered, grams
 RC_m = raw coal moisture content, wt%/100
 DC_m = dried coal moisture content, wt%/100
 RC_{hv} = raw coal mf heating value, Btu/lb
 DC_{hv} = dried coal mf heating value, Btu/lb

Example, using results from Knife River hot-water dried at 300°C:

M_{rc} = 2000 g	RC_m = 36.73/100
M_{dc} = 1408 g	DC_m = 15.69/100
M_w = 2000 g	RC_{hv} = 10,384 Btu/lb
M_c = 2394 g	DC_{hv} = 11,056 Btu/lb

$$1. \text{ Total Material Recovery, wt\%} = \left[\frac{1408 + 2394}{2000 + 2000} \right] 100$$

$$= 95.1 \text{ wt\%}$$

$$2. \text{ Water Recovery, wt\%} = \left[\frac{2394 + (1408 \times 0.1569)}{2000 + (2000 \times 0.3673)} \right] 100$$

$$= 95.6 \text{ wt\%}$$

$$3. \text{ Solids Recovery, wt\%} = \left[\frac{1408(1 - 0.1569)}{2000(1 - 0.3673)} \right] 100$$

$$= 93.8 \text{ wt\%}$$

$$4. \text{ Btu Recovery, \%} = \left[\frac{1408(1 - 0.1569)11,056}{2000(1 - 0.3673)10,384} \right] 100$$

$$= 99.9\%$$

$$5. \text{ Dry Coal Recovered, lb/100 lb raw coal} = \left[\frac{1408}{2000} \right] 100$$

$$= 70.4 \text{ lb/100 lb raw coal}$$

$$6. \text{ Moisture Reduction, wt\%} = \left[\frac{1 - (1408 \times 0.1569)}{2000 \times 0.3673} \right] 100$$

$$= 69.9 \text{ wt\%}$$

U.S. DEPARTMENT OF ENERGY
FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT

1. Program/Project Identification No. DE-FC21-93MC30087		2. Program/Project Title 4.0 Advanced Fuel Forms and Coproducts		3. Reporting Period 4-1-93 through 6-30-93	
4. Name and Address Energy and Environmental Research Center University of North Dakota P.O. Box 9018 Grand Forks, ND 58202-9018 (701) 777-5000				5. Program/Project Start Date 1-12-93	
				6. Completion Date 1-11-98	
Milestone ID. No.	Description	Planned Completion Date	Actual Completion Date	Comments	
TASK 4.1	BENEFICIATION FOR ADVANCED SYSTEMS				
Subtask 4.1.1	Physical Stability Testing				
(1)	Identify equipment for apparatus	4/30/93	3/30/93		
(2)	Design and assemble stability apparatus	6/30/93	6/30/93		
(3)	Test various parent and product coals	12/31/93			
Subtask 4.1.2	Oil Agglomeration				
(1)	Assessment of deolling techniques for oil recovery	3/31/93	6/30/93		
(2)	Assessment of agglomerate stability	6/30/93			
(3)	Performance of preliminary plant design and process economics	10/31/93			
(4)	Assessment of drop-tube furnace combustion characteristics	1/31/94			
Subtask 4.1.3	Size Aggregation				
(1)	Tableting scoping tests on four coals	4/30/93		Deleted no funding	
(2)	Developing cold briquetting parameters (moisture, particle size, binder)	9/30/93			
(3)	Developing hot briquetting techniques	12/31/93			
(4)	Preliminary pelletizing survey/development	12/31/93			
TASK 4.2	COPRODUCTS				
Subtask 4.2.1	Char Upgrading				
(1)	Develop gas and aqueous adsorption procedures	3/31/93			
(2)	Char properties as a function of time, temperature, and ash level	10/31/93			
(3)	Char properties as a function of activation	12/31/93			

U.S. DEPARTMENT OF ENERGY
FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT

1. Program/Project Identification No. DE-FC21-93MC30097		2. Program/Project Title 4.0 Advanced Fuel Forms and Coproducts		3. Reporting Period 4-1-93 through 6-30-93	
4. Name and Address Energy and Environmental Research Center University of North Dakota P.O. Box 9018 Grand Forks, ND 58202-9018 (701) 777-5000				5. Program/Project Start Date 1-12-93	
				6. Completion Date 1-11-98	
Milestone ID. No.	Description	Planned Completion Date	Actual Completion Date	Comments	
Subtask 4.2.2	Liquids Upgrading				
(1)	Effect of temperature and pressure on liquid and gas yields during coal carbonization	9/30/93			
(2)	Characterization of carbonization products	9/30/93			
(3)	Effect of catalyst on liquid and gaseous product	12/31/93			
Subtask 4.2.3	Denitrification of Coal Liquids				
(1)	Adsorbent condition and recovery	8/31/93		Deleted no funding	
(2)	Adsorbent lifetime	10/31/93			
TASK 4.3	EXPLORATORY STUDIES ON LRC LIQUEFACTION				
Subtask 4.3.1	Aqueous/CO Liquefaction of LRC Using Sodium Aluminate				
(1)	Effect of reaction time	7/31/93			
(2)	Effect of CO pressure	8/31/93			
(3)	Effect of coal structure	9/30/93	5/30/93		
(4)	Mechanism of reduction	11/30/93			
(5)	Coupling to second-stage processing	11/30/93	5/30/93		
(6)	Catalytic upgrading of LRC pyrolysis products	12/31/93			
(7)	Laser light scattering studies of coal particles and colloids	12/31/93			
(8)	Colloidal dispersion of ion-exchangeable catalysts	12/31/93			

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