**COMPCOALTM: A PROFITABLE PROCESS FOR PRODUCTION OF A
STABLE HIGH-BTU FUEL FROM POWDER RIVER BASIN COAL**

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COMPCOAL™: A Profitable Process for Production of a Stable High-Btu Fuel from Powder River Basin Coal

CONTRACT INFORMATION

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BACKGROUND INFORMATION

Western Research Institute (WRI) is developing a process to produce a stable, clean-burning, premium fuel from Powder River Basin (PRB) coal and other low-rank coals. This process is designed to overcome the problems of spontaneous combustion, dust formation, and readsorption of moisture that are experienced with PRB coal and with processed PRB coal. This process, called COMPCOAL™, results in a high-Btu product that is intended for burning in boilers designed for midwestern coals or for blending with other coals.

PRB coal is relatively dusty and subject to self-ignition compared to bituminous coals. Dried (or processed) PRB coal is even more susceptible to spontaneous combustion than the raw coal. Also, PRB coal dried at low temperature typically readsorbs about two-thirds of the moisture removed by drying. This readsorption of moisture

releases the heat of adsorption of the water which is a major cause of self-heating of low-rank coals at low temperature. PRB coal, and other low-rank coals, tend to be highly reactive. These reactive coals must be mixed regularly (every week or two) when fresh. However, they become somewhat more stable after they have aged for several weeks.

Low-temperature oxidation reduces the heating value of the coal, makes the coal less able to repel moisture (hydrophobicity), and is known to increase the unburned carbon remaining in the ash. Ingram and Rimstidt (1984) attribute increased moisture in naturally oxidized coals to increase in surface area caused by the physical effects of weathering and an increase in hydrophilic functional groups able to chemisorb water (organic acids are known to attract water to coal particles). Water molecules are generally thought to attach to polar oxygen sites in coal (this varies greatly with different types of coal).

Many efforts have been made to overcome these problems of dust formation and self-heating while keeping the cost of processing within the very competitive limits of the markets for coal. The University of North Dakota Energy Research Center has explored the use of various drying techniques to upgrade low-rank coals (Willson et al. 1987). They found that coals dried at low temperature readsorb moisture after cooling and return to essentially the original equilibrium moisture level. In contrast, they found that the processes using temperatures high enough to alter the structure of the coal particles resulted in reduced readsorption of moisture. They also concluded that the lowered equilibrium moisture levels resulted from the rejection of carbon dioxide by the decarboxylation reactions which occur during high-temperature drying. (The readsorption of moisture by coals dried at temperatures lower than a few hundred degrees Fahrenheit and reduction of equilibrium moisture in coals dried to about 500 to 700°F (260 to 316°C) is consistent with WRI experience, (Boysen et al. 1990).

A drying process was developed for PRB coal during the early 1980s. Initial work was done by Anaconda Minerals Co., later joined by Atlantic Richfield Co., using a 4 ton/hr pilot plant at Tucson, Arizona. The process has been licensed to Kaiser Engineers. The process uses fluidized-bed drying in conventional equipment with a proprietary product treatment step (Skinner et al. 1984). The developers conducted laboratory research to determine methods to avoid low-temperature oxidation of the product. They developed methods using cooling, controlled preoxidation, treatment with carbon dioxide, and spray application of oil or chemical solution.

Koppelman was awarded patents (U.S. Patents 4,728,339 and 5,071,477) for use of "temperatures from 200 to about 1200°F, pressures from 300 up to about 3000 psig, and residence times of 1 minute to 1 hour to process organic carbonaceous

materials to effect a desired physical and chemical modification thereof...whereby a substantial reduction in the residual moisture content...to improve physical properties including an increased heating value." The second patent describes the use of steam at high pressure to effect a controlled thermal restructuring, with the upgraded product possessing increased heating values. These patents are the basis for the K-Fuel® process.

Lien (1991) discusses the problems and progress AMAX has experienced with a McNally Pittsburgh dryer at the AMAX Belle Ayr mine. In this process, coal is dried by contact with a hot stream of fluidizing gas. The gas is comprised partly of flue gas from combustion of coal dust with air and partly from recycled gas. The hot drying gas contains less than 5% oxygen. The dried coal, which contains 12 to 13 wt % moisture, enters the cooler at a temperature of 180 to 190°F (82 to 88°C) where it is cooled to about 100°F (38°C) by contact with air. The cooled product is mixed with 2 to 4 gallons of number 6 fuel oil per ton to control product dustiness and help inhibit readsorption of moisture. Lien (1991) discusses the problems of upsets in the process caused by loss of feed and the experience with degradation of particles in the dryer. He also states that a major concern has been the stability of the product.

The Syncoal process is used at a Clean Coal I demonstration plant located at Western Energy Company's Rosebud mine near Colstrip, Montana. In the process, coal is passed through two vibrating fluidized-bed reactors where it is contacted by hot gas to dry the coal and remove carboxyl groups and volatile sulfur compounds. The dried coal is further desulfurized by pneumatically stratifying the product to separate pyrite-rich ash (Western Energy Company 1992).

The Carbondry process (Simmons and Simmons 1992) has been tested at the pilot-plant scale at Carbontec's facility at Bismarck, North

Dakota. The process involves a hot oil first stage drying unit and a flue gas drying unit. The process uses a coating of oil on the surface of particles to protect against readsorption of moisture and spontaneous heating. Published data indicate that the product made from PRB coal using the process contains about 6 to 10 wt % moisture and has a heating value ranging from 11,200 to about 11,700 Btu/lb.

The ENCOAL LFC process is used at a commercial demonstration facility located at Triton Coal Company's Buckskin mine north of Gillette, Wyoming (McPherson 1992). In the process, coal is roasted to drive off moisture, coal liquids, and sulfur compounds. The plant, which was built using an award from Clean Coal III, produces a crude coal liquid and solid process derived fuel.

Numerous mechanical treatments are available for stabilizing coal products by reducing the surface contact with air. These include briquetting,

pelletizing, and extruding with or without an added binder. An excellent list of references describing the use of a binder in pelletizing is given in U.S. Patent 4,615,712 (Wen), which describes the production of humic acid from oxidation of coals or leonardite and the use of the humic acid as a binder.

It is relatively easy to develop a process to drive the moisture from PRB coal. It is considerably more challenging to develop a process which can remove the moisture from the coal, alter the coal structure to minimize readsorption of moisture, and prevent oxidation and spontaneous combustion of the finished product. We have dried coal and done partial decarboxylation in our past work (Merriam et al. 1990). Drying minus 8 mesh PRB coal in a fluidized-bed reactor at atmospheric pressure results in all of the moisture being removed when the temperature of the coal in the bed reaches 350°F (177°C) (Figure 1).

Figure 1. Drying Curve for Minus 8 Mesh PRB Coal Using Various Flow Rates of Fluidizing Gas

Continued heating of the coal as it moves along the cross-flow bed results in the partial decarboxylation, which removes oxygen from the coal in the form of carbon dioxide and carbon monoxide along with some methane (Figure 2). This removal of oxygen increases the heating value of the product and it has been reported to reduce the susceptibility of the coal to spontaneous heating (Tomuro et al. 1985). However, our experience with PRB coal treated in this manner is that the coal is highly reactive and is frequently observed to ignite spontaneously. The coal is most susceptible to self-ignition when it has been freshly processed. Dried coal which has been aged for several weeks (and which has contacted air) is less likely to self-ignite.

Early attempts at WRI to stabilize dried coal (Boysen et al. 1990) were focused upon heating the coal to a slightly higher temperature to reduce the tendency to readsorb moisture (Figure 3). This work, which was done using minus 28 mesh PRB and Usibelli coals in a fluidized-bed reactor, indicates that the equilibrium moisture can be reduced to about 13 wt % by heating the coal to about 700°F (371°C) (Thomas, K.P., personal communication, memorandum dated December 16, 1991). However, it is necessary to heat the coal to about 1100°F (593°C) to reduce the equilibrium moisture to about 10 wt %. The coal tars become mobile in PRB coal at temperatures just above 600°F (316°C). So much loss of liquids would occur if the coal is heated to 1100°F (543°C) in the presence of fluidizing gas.

Figure 2. Partial Decarboxylation of Minus 8 Mesh PRB Coal in a Fluidized-Bed Dryer

Figure 3. Equilibrium Moisture Content of Coals Subjected to Mild Pyrolysis

We later added a stabilization reactor to the pyrolysis reactor to coat char with the high-boiling fraction of the coal liquids driven from the coal in the pyrolysis reactor (Merriam and Sethi 1992). This work showed that we could further depress the equilibrium moisture to about 8 wt %. (Most of the increase in temperature that starts low-temperature oxidation is caused by the heat of adsorption of water upon the coal particles.)

PROJECT DESCRIPTION

In the COMPCOAL process, sized coal is dried to zero moisture content and additional oxygen is removed from the coal by partial decarboxylation as the coal is contacted by a stream of hot fluidizing gas in the dryer (Figure 4). The hot, dried coal particles flow into the

pyrolyzer where they are contacted by a very small flow of air. The oxygen in the air reacts with active sites on the surface of the coal particles causing the temperature of the coal to be raised to about 700°F (371°C) and oxidizing the most reactive sites on the particles. This "instant aging" contributes to the stability of the product while only reducing the heating value of the product by about 50 Btu/lb. Less than 1 scf of air per pound of dried coal is used to avoid removing any of the condensable liquid or vapors from the coal particles. The pyrolyzed coal particles are mixed with fines from the dryer cyclone and dust filter and the resulting mixture at about 600°F (316°C) is fed into a briquettor. Briquettes are cooled to about 250°F (121°C) by contact with a mist of water in a gas-tight mixing conveyor. The cooled briquettes are transferred to a storage bin where they are accumulated for shipment.

Figure 4. Identification of Stream Flows and Conditions Used to Size Equipment for the COMPCOAL Process

An important feature of the process is the avoidance of pyrolysis in the dryer and use of the onset of pyrolysis in the pyrolyzer to stabilize the particles. In the dryer, where the gas flow rate is high, the coal remains below the temperature at which liquids and vapors are formed. In the pyrolyzer, the temperature is raised to form liquids in the coal particles, but the gas flow is kept low to avoid stripping liquids out of the coal. In this manner, a high flow rate of gas can be used to carry heat into the dryer and subsequently, in the pyrolyzer, the tars in the coal may be melted and refrozen without producing a substantial loss of liquid or vapors from the coal.

A recycle gas stream is used to carry heat into the dryer while limiting the temperature at which fluidizing gas enters the dryer. Heat for drying is produced by burning coal using a low NO_x burner. Vapors from the pyrolyzer are incinerated in the burner. The flue gas is mixed with recycled gas to lower the temperature at which the fluidizing gas enters the dryer. The water is removed from the dryer effluent gas by condensation in air-cooled condensers supplying a nearly dry stream for sulfur removal. The water from the condensers is sprayed onto the hot COMPCOAL briquettes in the cooling conveyor where the water is converted into steam.

The process we describe herein is not yet optimized. For example, if we can tolerate a wet gas stream into the sulfur removal unit, then one of the air-cooled condensers is not needed and only the recycle portion of the dryer effluent gas needs to be cooled.

WRI has experience with the drying portion of the process using minus 8 mesh PRB coal at feed rates of 90 to 150 lb/hr in tests lasting from 24 to 120 hours (Merriam et al. 1990). The pyrolysis (stabilization) portion of the process is presently being developed using a batch, laboratory-scale reactor. We plan next to conduct tests using a continuous-flow, bench-scale reactor.

RESULTS

This section describes work conducted during the early part of 1993 by WRI to develop an effective method to stabilize dried coal.

Self-Heating and Oxidation

We conducted numerous tests to determine how much various treatments affect the self-heating and low-temperature oxidation tendencies of raw and processed PRB coal. Samples were evaluated by contacting the coal or processed coal with oxygen saturated with water vapor at a temperature of 122°F (50°C) in an adiabatic chamber (Figure 5). The test results are evaluated graphically by plotting the temperatures in the samples versus time. The intersection of the slope of the initial heating curve and the slope of the curve after the temperature has started to rise is used as the time to ignition. Tests are continued until the inflection point in the heating curve is defined or until the test has continued for 24 hours. Our experience has shown that an inflection point in the heating curve rarely develops after 24 hours of heating using this method. The results of the self-heating tests (Table 1) are used to compare the effectiveness of different processing conditions.

The tests to study the effects of temperature and oxygen on the self-heating of dried PRB coal were conducted using a small, stirred autoclave which is heated by immersion in a heated bed of fluidized sand (Figure 6). Samples of coal, which had been dried in a fluidized bed to 550°F (288°C) were split into 50-gram aliquots inside a nitrogen filled glove box to avoid contact with air. The aliquots were transferred into the reactor inside the glove box. The autoclave was then assembled and the gas pressure was cycled from 0 to 60 psig three times to flush unwanted gas from the reactor. The autoclave was then lowered into the heated sand for 35 minutes, including about 10 minutes at the desired maximum temperature.

Upon completion of the test the autoclave was removed from the sand bath and immersed in water to rapidly cool the treated coal. Gas samples were obtained for analysis by transfer into

evacuated containers. The treated coal was removed from the autoclave in the nitrogen filled glove box and samples were placed in containers under a nitrogen blanket for further analyses.

Figure 5. Apparatus Used to Determine the Susceptibility of Coal to Self-Heating and Oxidation

The data in Table 1 show several characteristics and trends which we have used to guide our development of the COMPCOAL process. The section of Table 1 showing "coal dried at various conditions" indicates that coal moved into and out of the drying oven five times (which was incidentally exposed to air) and the sample dried in air both show relatively long ignition times. This pattern of data is an indication that exposure of dried coal to air at 220°F (104°C) results in some resistance to self-heating relative to the coal samples dried in nitrogen.

The samples dried in nitrogen and carbon dioxide show reduced ignition times with

increasing temperature over the range of temperatures from 220, 550, 565, and 658°F (104, 288, 296, and 348°C). We therefore conclude that heating the dried coal in inert gas increases the susceptibility to self-heating as the temperature is increased in the range studied. The dried coal which is heated in a small amount of air (at a starting pressure of 0.8 atmospheres at our laboratory) indicates a trend opposite to that shown by heating in nitrogen. The dried coal which is heated in air shows increased resistance to self-heating (longer ignition times) as the temperature is increased from 585 to 703°F (307 to 373°C). The trend when heating in air using a starting pressure of 0.8 atmospheres is not strong, but appears to be real.

Table 1. Time to Ignition for Minus 16 Mesh Raw, Dried, and Processed Coal, hr

	Temperature °F	Duplicate Tests	
Raw Eagle Butte Coal		>24	>24
Coal Dried at Various Conditions			
N ₂ , 5 times @ 1 hr each	220	17	>24
N ₂ , 1 time for 5 hr	220	6	8
Air, 1 time for 6 hr	220	24	24
Fluid Bed, CO ₂ , 5 min (A)	550	4	5
Dried Coal from (A) Heated in N ₂			
Batch in Stirred Reactor	565	4	4
Batch in Stirred Reactor	658	2	3
Dried Coal from (A) Heated in 0.8 Atm Air			
Batch in Stirred Reactor	586	4	5
Batch in Stirred Reactor	675	6	5
Batch in Stirred Reactor	692	10	>24
Batch in Stirred Reactor	723	7	8
Dried Coal from (A) Heated in 3.4 Atm Air			
Batch in Stirred Reactor	565	4	6
Batch in Stirred Reactor	675	4	5
Batch in Stirred Reactor	691	14	9
Batch in Stirred Reactor	697	7	8
Batch in Stirred Reactor	708	>24	>24
Batch in Stirred Reactor	732	>24	>24

Figure 6. Stirred-Batch Reactor Used to Perform the "Accelerated Aging" Stabilization of Dried PRB Coal

The dried coal which is heated using more air available to react with the coal (a starting air pressure of 3.4 atmospheres) shows a strong and definite trend of increasing resistance to self-heating and oxidation. This last trend is also very sensitive to the temperature of the coal in the stirred bed when the oxygen is reacting with the dried coal (Figure 7). The pattern between the groups (heating in inert gas, heating in 0.8 atmospheres of air, and heating in 3.4 atmospheres of air) also shows a consistent trend of increasing resistance to self-heating and oxidation as the quantity of oxygen available to react with the dried coal is increased.

Tests with air in the stirred, batch reactor with an initial pressure of 3.4 atmospheres show a change in the quantity and composition of gas produced (Figure 8) in the temperature range of the tests. At the lower temperatures a small amount of gas composed of predominantly carbon dioxide, with lesser amounts of carbon monoxide and traces of methane is produced. The volatiles removed at the higher temperatures are mostly noncondensable gases. In the upper part of the temperature range the volume of gas produced is increased greatly and the concentration of the methane and the ethane in the gas increases.

Figure 7. The Effects of Temperature and Oxidation on the Self-Heating Characteristics of Dried PRB Coal

Significantly, no oxygen is detected in the effluent gas, indicating that the oxygen in the air at the start of the tests is completely reacted with the coal. However, the consumption of the oxygen from the air by the coal is more than offset by the

oxygen that is removed from the coal by the processing (Figure 9). The carbon dioxide and carbon monoxide emitted from the coal contain many times as much oxygen as is consumed from the air in the reactor.

Figure 8. The Change in Composition of Gas Produced at Temperatures Below and Above the Onset of Stabilization

Figure 9. The Oxygen Released from the Coal is Many Times the Oxygen Taken Up by the Accelerated Aging

Readsorption of Moisture

The tendency of processed coal to readsorb moisture is an important characteristic which must be considered as a determinant of the quality of any dried or pyrolyzed coal. We have used the test for equilibrium moisture (ASTM D1412) as a measure of the maximum quantity of water which coal and processed coal can adsorb. The test is actually intended to measure the water content which a coal seam can contain. In the test, coal is crushed to minus 28 mesh and soaked in deionized water for 3 hours. The excess water is then removed from the coal by filtration and the coal is held in a sealed container at 98% relative humidity for 48 hours. The water content of the coal is then determined. We think this test may represent conditions which are somewhat more severe than processed coal may typically be exposed to, but we use it because it is an accepted ASTM procedure, and the test does not appear to overstate the readsorption characteristics of the coal by a large amount.

We use equilibrium moisture as an indication of the stability of the products from the various processing conditions we have tested. Low equilibrium moisture is indicative of a stable processed coal.

The results of our tests (Table 2) show that coal dried to 550°F (288°C) is less susceptible to readsorption of moisture than the raw coal. (However, dried coal, when untreated, is more susceptible to oxidation than raw coal.) Forming the dried coal into briquettes reduces the tendency to readsorb moisture even further, while the accelerated aging at 793°F (423°C) reduces the equilibrium moisture still more.

We have not yet tested the obvious combination of briquettes made from coal treated in the "accelerated aging" process. The beads and sand are included to show that materials having no porosity and nonpolar surfaces have an equilibrium moisture content of about zero.

Table 2. Equilibrium Moisture Content of Eagle Butte Coal, Dried Coal, Briquettes, and Treated Coal, wt %

	Duplicate Tests	
Eagle Butte Feed Coal	25	26
Dried in Air, 6 hr, 220°F	22	22
Fluid Bed Dried in CO ₂ to 550°F	17	17
Briquettes Made from Dried Coal	13	9
Briquettes-Dried Coal-10% Fines	14	14
Dried Coal Heated in 3.4 Atm Air and 793°F	10	11
One Millimeter Glass Beads	1	1
Ottawa Sand	0	0

Characteristics of Stabilized Coal

The stabilized coal produced by reacting dried PRB coal with air using the stirred batch reactor

contains 35 to 40 wt % volatiles and has heating values of 12,000 to 12,700 Btu/lb (Table 3 and Figure 10).

Table 3. Characteristics of the COMPCOAL Product

Test	11	10	12	6
Temperature, °F	565	691	697	708
Volatiles, wt %	40.2	36.7	35.4	34.5
Heating Value, Btu/lb	12,009	12,439	12,600	12,725

Figure 10. Volatile Content and Heating Value of the COMPCOAL Product

FUTURE WORK

Our report, "COMPCOALTM: A PROFITABLE PROCESS FOR PRODUCTION OF A STABLE HIGH-BTU FUEL FROM POWDER RIVER BASIN COAL" (WRI-93-R008) describes the bench-scale tests which we conducted to prove the process concept. We are presently seeking support to continue development of the process.

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