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Work Performed Under Contract No.: DE-FC21-86MC11076

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

By
Western Research Institute
Laramie, Wyoming

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ABSTRACT

Results of mild gasification tests of minus 16-mesh Usibelli coal in an inclined fluidized-bed reactor are described in this report.

The minus 16-mesh fraction was separated from the coal by screening. The coal was dried to zero moisture content, and about 2 wt % of the volatiles was removed as gas by partial decarboxylation using a 100-lb/hr inclined fluidized-bed dryer. The dried coal was subjected to mild gasification at maximum temperatures of 1050 to 1250°F (566 to 677°C) and feed rates of 7.5 lb/hr while using a once-through flow of carbon dioxide as fluidizing gas in a 1-inch-wide, inclined fluidized-bed reactor.

Mild gasification of the dried coal resulted in production of 44 to 56 wt % of the dried coal as char, 10 to 13 wt % as liquids, 17 to 28 wt % as gas, and 8 to 21 wt % as fines. The yield of moisture- and ash-free (MAF) liquids varied from 11.4 to 14.2 wt % of the dried coal feed.

Hardgrove grindability indices were 28 for the raw coal, 49 for the dried coal, and 82 for the char. The char produced contained 16 to 22 wt % volatiles and had gross heating values ranging from 10,500 to 11,600 Btu/lb. The char equilibrium moisture content was measured at 10 wt %, whereas the raw coal contains 22 wt % moisture at equilibrium.

The liquids collected during test 64 were separated by distillation into a -700°F (-371°C) boiling distillate (40 wt %) and a +700°F (+371°C) boiling residue (60 wt %). The distillate contains 23.5 wt % alkanes, 26.2 wt % alkenes, and 22.7 wt % aromatic hydrocarbons. The distillate also contains 26.9 wt % of polar heteroatomic-containing compounds for which group-type analysis could not be made.

The distillate contains 0.4 wt % sulfur, 0.3 wt % nitrogen, and 4.1 wt % oxygen; these are relatively low values for untreated coal distillate. Extraction, caustic washing, or hydrotreating is recommended to upgrade the distillate to diesel blending stock.

The residue contains too little quinoline- and toluene-insolubles and fixed carbon to meet specifications for electrode-binder pitch. Heat treating and, perhaps, addition of soot to the +700°F (+371°C) boiling residue is recommended to produce electrode-binder pitch.

Evaluation of the char for use in production of high-purity carbon, metallurgical-grade coke, or fuel is recommended.

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1.0 INTRODUCTION

Much work has been done in the United States during the last several decades to produce fuels and feedstocks from coal. However, nearly all of the development focused on severe conditions to produce maximum yields of liquid and gaseous products. Although some of the processes have been shown to be technically feasible, the high temperatures (>1292°F/>700°C) and high pressure (>50 psig) used in these processes have resulted in high-cost processes that do not appear to be economically feasible for commercial production in the foreseeable future.

One approach to developing low-cost processes is to use mild conditions (i.e., lower temperature and pressure) to reduce the cost of producing fuels and feedstocks from coal. The use of mild conditions may produce less than maximum yields of gas and liquid products; however, it is likely that low-cost processes can produce a slate of products with marketable properties and economically acceptable yields. The focus of mild gasification is, therefore, upon developing and demonstrating processes than can be built and operated with relatively low cost on the commercial scale and will give a satisfactory return on the investment.

Cost estimates for plants using severe processing conditions show that investments of billions of dollars are needed to construct a single plant. Few organizations in the United States have the capital needed for such an undertaking and are willing to accept the enormous risk. Thus, one goal of the mild gasification work is to prove that processes can be built for a small fraction of the investment needed for severe processes, thus, significantly lowering the financial risk of constructing a mild gasification plant. Mild gasification processes must also have low operating costs to be economically feasible.

Versions of mild gasification of coal, commonly called devolatilization, are presently practiced in England, India, and South Africa and have been used commercially in many countries in the past. The development of new mild gasification processes will be based on experience with older technology combined with recent technological improvements and systems approach to optimizing the overall value of the products.

There are four factors to be considered for a successful operation of a mild gasification plant: (1) properties of the coal source, (2) gasification conditions, (3) product upgrading, and (4) the locations and sizes of markets for products. All these factors are requisite for the mild gasification process to be successful. The most important factor is markets for the products, because the operator has less control over the markets than over other factors.

2.0 BACKGROUND

Western Research Institute (WRI), in cooperation with the U.S. Department of Energy, is developing the inclined fluidized-bed (IFB) coal drying and stabilizing process. The coal is dried to near zero moisture and partially pyrolyzed in the first IFB. Then, partially pyrolyzed coal is fed into the second IFB, where it is rapidly quenched with cool carbon dioxide liberated from coal to keep the tar produced from pyrolysis on the coal particles. This tar remaining as well as carbon dioxide adsorbed stabilizes the dried coal. The IFB reactor is also an excellent classifier. Consequently, coal fines are easily separated during drying. The amount of fines separated can be controlled by fluidizing gas flow rate or gas to solid ratio.

WRI has completed testing the Usibelli coal using a 10-lb/hr bench-scale IFB. Usibelli coal is high-moisture subbituminous coal with as received moisture content and heating values of 22 wt % and 8,470 Btu/lb, respectively. The coal sample tested has lower moisture content than an average moisture content of mine-run coal (26%). More than twenty tests were performed to investigate the effects of various parameters on the dried coal characteristics (Boysen et al. 1990).

Experimental results show that the dried coal contains less than 1.5 wt % moisture based upon proximate analysis. The heating value of the product was increased from 8,470 to 11,500 Btu/lb. The solid entrainment from the IFB reactor can be kept below 10 wt % of the feed coal by reducing the fluidizing gas velocity. The dry product was less dusty than the feed coal. The equilibrium moisture of dried coal was less than 50% of feed coal equilibrium moisture. The dried coal was as stable as the raw coal and can easily be made to be briquettes without adding binders.

The dried coal provides significant economic and technical advantages, especially when the coal mining cost is relatively low (for example, Powder River Basin in Wyoming). However, the economic advantage is reduced for the coal with relatively high mining costs such as those for Usibelli coal. As a result, it will be necessary to investigate the other process operations that may produce higher value products from coal.

WRI is also developing an inclined fluidized-bed process for the mild gasification of coal for the U.S. Department of Energy. In the process, coal is dried to very low water content and is partially decarboxylated in a plug-flow, IFB dryer by contact with recycled carbon dioxide. The dried coal is then devolatilized under mild conditions in a second IFB reactor in the presence of recycled gas. Coal liquids are condensed in a series of wet scrubbers operating at successively lower temperatures to produce pitch and oil. The dirty pitch (ash content ≥ 0.35 %) will be used to treat dried coal to prevent reabsorption of moisture, reduce dustiness, and prevent spontaneous ignition. The clean pitch (ash content < 0.35%) will be used as a binder for the manufacture of anodes that are used in aluminum reduction furnaces. Pitch can also be used as a binder for briquetting char to produce metallurgical coke.

The oil will be blended with diesel fuel and used in the mine, or it will be sold as gasoline blending stock.

Char from the process will be upgraded to either anode-grade carbon or activated charcoal. The char can also be further devolatilized and pelletized using pitch as a binder. The char pellets can be partially oxidized and then calcined to produce metallurgical coke. The gas produced by mild gasification will be burned to heat recycle gas in the process.

WRI performed mild gasification tests (Merriam and Cha 1989) using a 10-lb/hr IFB reactor system with Wyodak coal from the AMAX Eagle Butte coal mine located in the Powder River Basin of Wyoming. Results of these tests were used to design a 100-lb/hr process research unit (PRU) for further development of the mild gasification process. The results were also used to select major process parameters to be used in the PRU. The PRU was designed by Riley Stoker with participation by AMAX and WRI. We have successfully completed the PRU test program. Results of the bench-scale mild gasification tests are briefly summarized here for the convenience of the reader (Merriam and Cha 1989).

WRI conducted 23 successful coal drying tests and 14 successful mild gasification tests with Wyodak coal using inclined fluidized-bed reactors. The tests in the 10-lb/hr reactors ran for four to sixteen hours with most tests maintaining steady-state conditions for eight hours. The effects of bed temperature, particle size, and drying-gas water content on the drying rates and residual moisture content of the dried coal were determined. Coal was readily dried to zero moisture, and about 1 wt % of the raw coal was driven off as carbon dioxide by partial decarboxylation at a maximum bed temperature of 575°F (302°C) using a solids residence time of five minutes. The drying rate was slightly slower using 0.050 lb of water per lb of dry carbon dioxide than when 0.030 and 0.015 lb per lb were used. Differences in particle size from 0.004 to 0.020 inch did not measurably affect the drying rate or residual moisture content of the coal.

The effects of bed temperature, heating rate, coal particle size, solids residence time, and fluidizing-gas composition on the yield of liquid products and the composition of char and gas produced were determined from the mild-gasification tests. The char contained 11 to 19 wt % volatiles, had hydrogen-to-oxygen mass ratios of 0.18 to 0.30, and had heating values of 12,333 to 12,905 Btu/lb. The volatiles content and the hydrogen-to-oxygen ratio of the char were reduced by increasing the maximum bed temperature in the mild gasification reactor from 1100 to 1200°F (593 to 649°C). The hydrogen-to-oxygen mass ratios were greater than the 0.125 value needed to supply hydrogen for formation of water, avoiding any need for makeup hydrogen in the char to carbon conversion.

Liquid products collected varied from 8.3 to 18.1 wt % of the moisture- and ash-free (MAF) coal with most of the coal liquids boiling above 700°F (371°C), a characteristic needed for electrode-binder pitch. The median hydrogen-to-carbon atomic ratio of the condensates was 1.23.

Maximum liquid yield occurred at a maximum bed temperature of about 1150°F (621°C). The yield of coal liquids increased with higher heating rates in the inlet portion of the mild gasification bed. We were not able to determine any effect of particle size on yield from 0.004- to 0.020-inch average particle size.

Gas produced had typical heating values of about 500 Btu/scf and contained 30 to 50% by volume carbon monoxide and about 3600 ppm hydrogen sulfide. A test using steam as the fluidizing gas resulted in production of gas containing about 40% hydrogen.

WRI has successfully completed five 24-hour tests and four 5-day tests using the 100-lb/hr PRU. The tests, conducted using minus 8-mesh Wyodak coal, have produced results very similar to those achieved using the bench-scale unit. During these tests, we learned that the IFB drying and mild gasification reactors in the PRU are greatly oversized with capacities estimated at about 300 lb/hr (Merriam et al. 1990).

WRI constructed a plastic cold-flow model, one-half as long and one-fourth as wide as the mild gasification reactor in the PRU. We used the cold-flow model to conduct coal throughput tests to determine the physical capacity of the PRU reactors.

An existing transparent, plastic cold-flow model (Figure 1) having a flat-plate gas distributor (Figure 2) was used to conduct cold-flow tests. Minus 16-mesh Wyodak coal from the AMAX Eagle Butte mine near Gillette, Wyoming, was floor-dried to about 25 wt % moisture content to avoid plugging the feeder with sticky coal particles. For the tests, the coal was fed to the cold-flow model at varying rates with the reactor sloped at varying inclinations from the horizontal. Gas flow was maintained constant at 12 scfm of CO_2 for the tests. The coal residence times were determined by simultaneously stopping the fluidizing gas flow and the coal feeder and dividing the weight of the coal remaining in the bed by the coal feed rate. We neglected any loss of moisture from the coal during the tests that may have introduced a slight error at low coal feed rates.

The results of the cold-flow tests (Figure 3) show that residence times decline as the feed rate is increased. The results also show that steeper slopes reduce the residence times of the coal particles.

The dashed lines at the lower-left part of Figure 3 indicate areas where the coal particles were so widely dispersed that it was not possible to identify the top of the fluidized bed. At higher feed rates (the solid lines), the top of the bed was clearly defined, and we were able to measure the depth of the bed. When using a slope of 3 degrees, the depth of the fluidized bed increased from 7/8 inches at a feed rate of 30 lb/hr to 1 1/4 inches at a feed rate of 70 lb/hr.

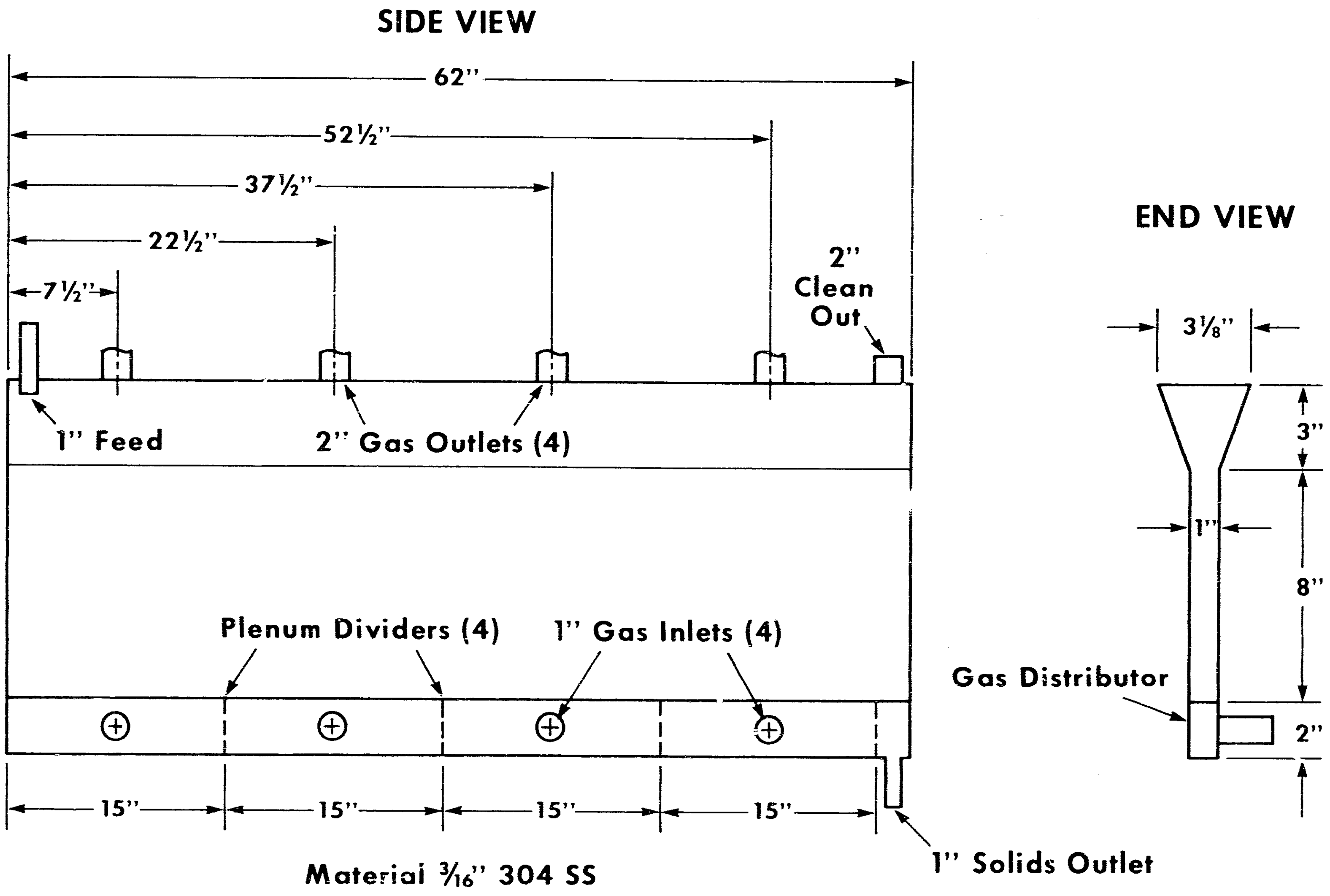
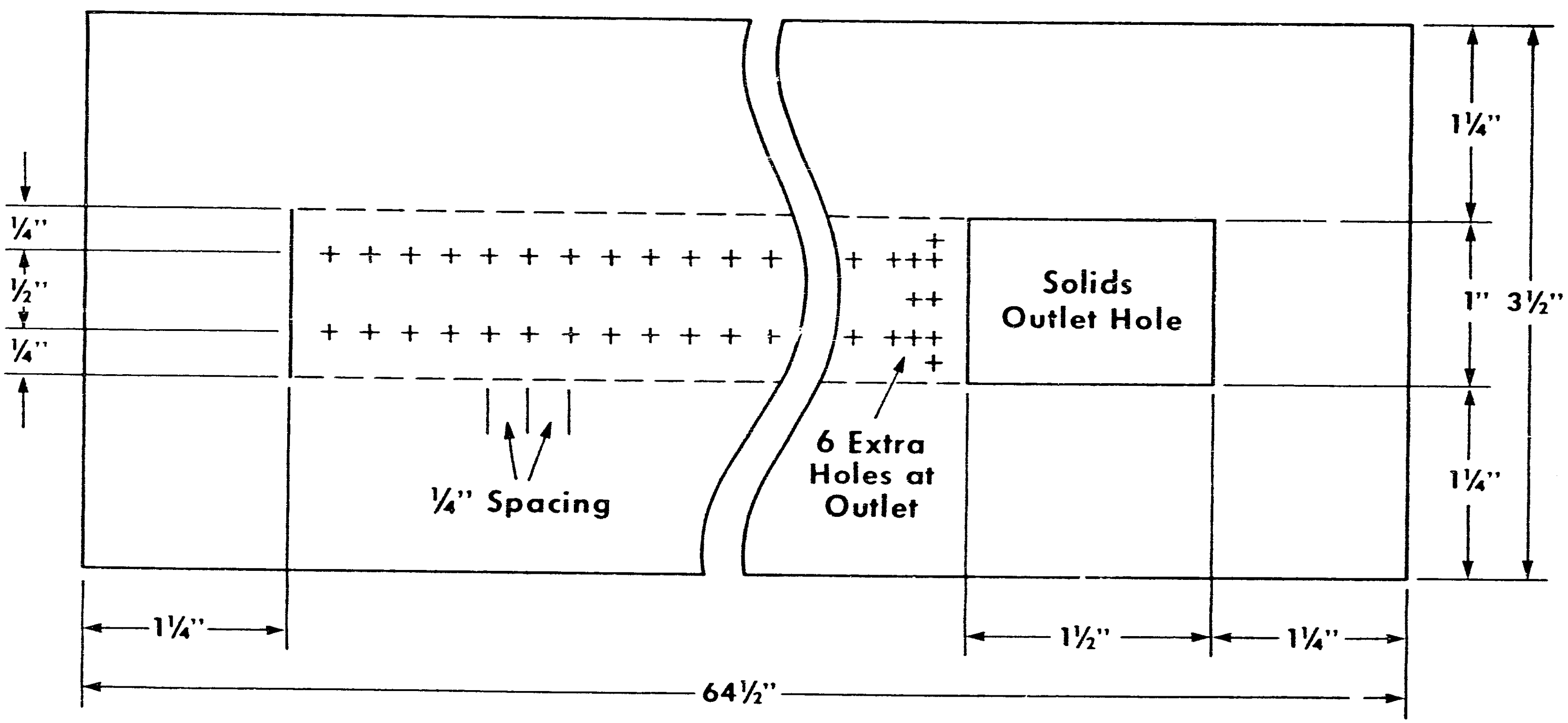


Figure 1. Cold-Flow Model and One-Inch Inclined Fluidized-Bed Reactor

Top View



486 Gas Inlet Holes $\frac{1}{32}$" Diameter

Figure 2. Gas Distributor for One-Inch Inclined Fluidized-Bed Reactor

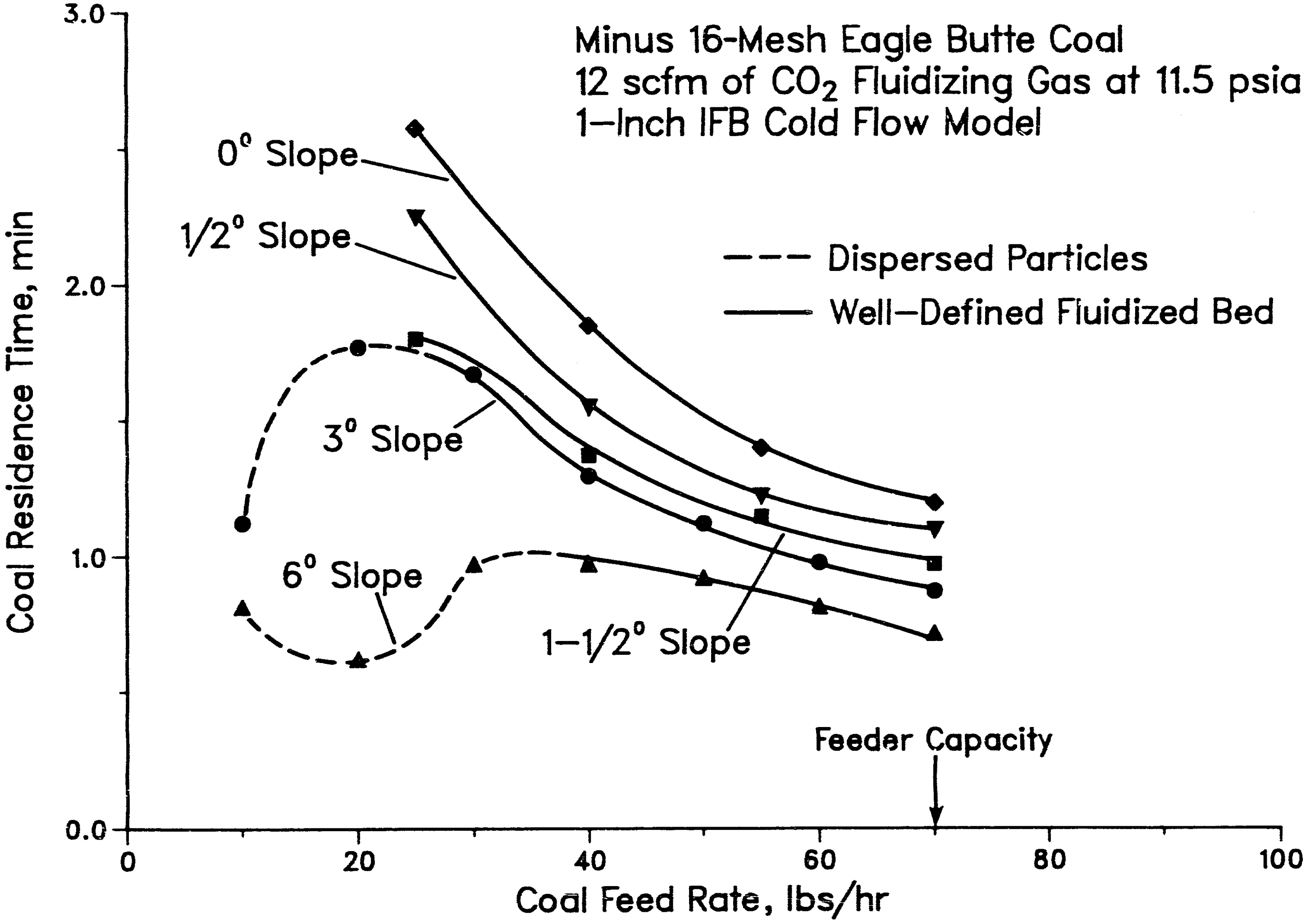


Figure 3. Results of Cold-Flow Tests Using One-Inch Fluidized-Bed Cold-Flow Model

The tests were limited by a screw feeder capacity of 70 lb/hr. The beds were well fluidized with no flooding or dead spots visible at 70-lb/hr feed rate. At a feed rate of 70 lb/hr, the throughput is three times the throughput of the 100-lb/hr PRU dryer when expressed as lb/hr per inch of bed width. The throughput is over 3.5 times the PRU throughput expressed as lb/hr per square foot of distributor area. The cold flow tests show conclusively that the IFB reactors in the PRU are physically capable of passing 300 lb/hr of coal. Hot-flow tests were conducted to determine whether or not the IFB reactors could provide sufficient residence time and heat transfer for the higher throughputs.

A series of drying tests were conducted using the 1-inch IFB reactor. This reactor is identical to the cold-flow model (Figure 1 and 2), except that the 1-inch IFB is constructed of 304 stainless steel and has solids sample collection ports and thermocouples installed in the bed. The drying system consists of a gas meter and heater, the reactor, a variable speed screw feeder, a cyclone, a dust filter, condensers, and a gas-water separator (Figure 4).

Drying tests using the 1-inch-wide IFB reactor at coal feed rates of 25 and 50 lb/hr showed that the coal feed rates and residence times agreed remarkably well with results using the cold-flow model. We also found an indication that the residence time of about 1.5 minutes used for the 50-lb/hr feed rate tests was barely adequate to dry the coal. Also, the thermal efficiency of the reactor declines at very short residence times. Unfortunately, this work was curtailed because of limited funding.

The objective of the work conducted for this project is to determine the quantity of liquid produced by mild gasification of Usibelli coal and to characterize the products from mild gasification of Usibelli coal.

3.0 TEST EQUIPMENT, PROCEDURES, AND ANALYTICAL METHODS

This section of the report describes the equipment and methods used to conduct mild gasification tests using Usibelli coal and describes the methods used to analyze the products.

3.1 Description of Equipment and Procedures

The coal used for tests 59 through 64 was screened across an inclined, rotary screen using a 16-mesh screen. The minus 16-mesh and plus 16-mesh coal fractions were stored in sealed drums. Three samples of the minus 16-mesh raw coal were analyzed by screening and ultimate analysis.

The coal used for tests 59 through 64 was dried using the drying system of the 100-lb/hr PRU (Figure 5). The procedure for operating the dryer is:

1. Purge the system using carbon dioxide.
2. Start the recycle gas blower and adjust the flow rate using a kickback valve from the blower discharge to the suction to control flow.
3. Heat the fluidizing gas until the temperatures in the dryer reach 400°F (204°C).
4. Start the coal feed at the rate of 100-lb/hr.
5. Adjust the fluidizing gas temperature to approximately 750°F (399°C) to maintain a maximum temperature in the dryer of 500 to 550°F (260 to 288°C).

The dryer outlet was piped to a dry coal receiving drum for this test.

After the data from tests 59 though 64 were analyzed, we decided to conduct tests at 1250°F (677°C) to better define the liquid yield curve. We prepared additional coal by crushing some of the remaining plus 16-mesh coal, screening it, and drying the coal using the 1-inch IFB dryer (Figure 4). Minus 16-mesh coal was dried during test 65 and the dried coal was used for test 66. We also dried some coal that was minus 16- to plus 70-mesh during test 67 and used that dried coal for test 68.

The mild gasification tests were conducted using a reactor identical to the cold-flow model shown in Figures 1 and 2. The stainless steel reactor has four pairs of independently controlled electrical heaters mounted along both sides. The reactor also has bed thermocouples and solids sample ports located at 0.125, 0.375, 0.625, and 0.875 of the reactor length. The filter bag was removed from the dust filter and replaced with an air-cooled coil and demister elements for these tests (Figure 6).

The operating procedure for the mild gasification reactor is similar to that used for the PRU dryer with several exceptions. Carbon dioxide that flows once through the reactor is used as the fluidizing gas instead of recycle gas. The bed temperatures are brought to 900°F (482°C) before the coal feed is started. A coal feed rate of 7.5 lb/hr of dried coal was used for the tests.

Self heating of Usibelli coal and chars from mild gasification was measured using an adiabatic calorimeter. The calorimeter was constructed using an old gas chromatograph for the adiabatic oven. The power proportional GC oven provides good temperature control. This permits the air bath surrounding the sample holder to be held very near to the temperature of the interior of the sample. Increases in temperature in the interior of the sample holder and the surrounding air bath are compared by a thermopile built into the sample holder. The increase in temperature in the sample holder due to self heating is monitored by two thermocouples above and below the controlling thermopile (F.A. Barbour, WRI, personal communication, November 16, 1990).

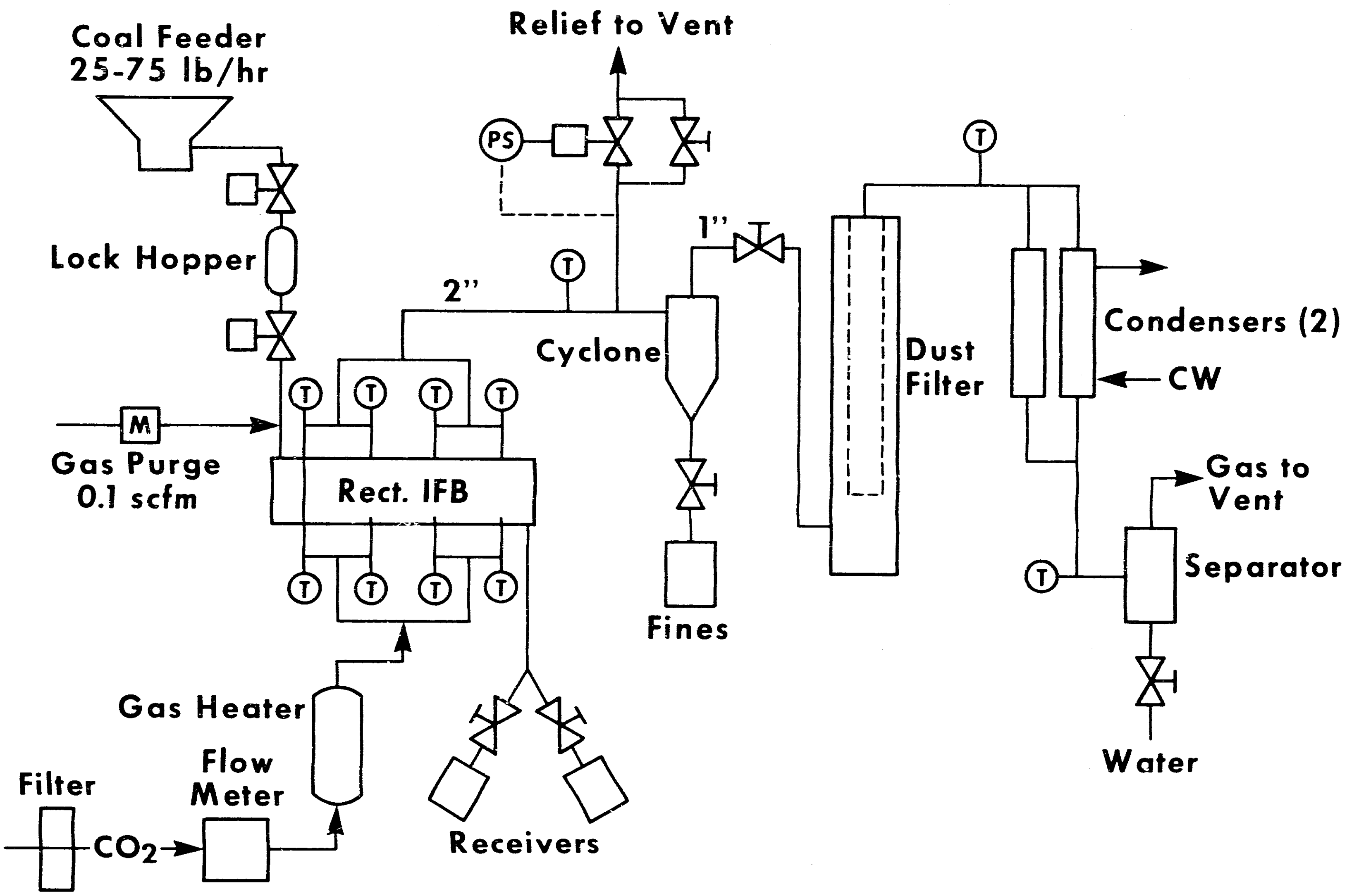


Figure 4. Process Flow Diagram for One-Inch Inclined Fluidized-Bed Drying System

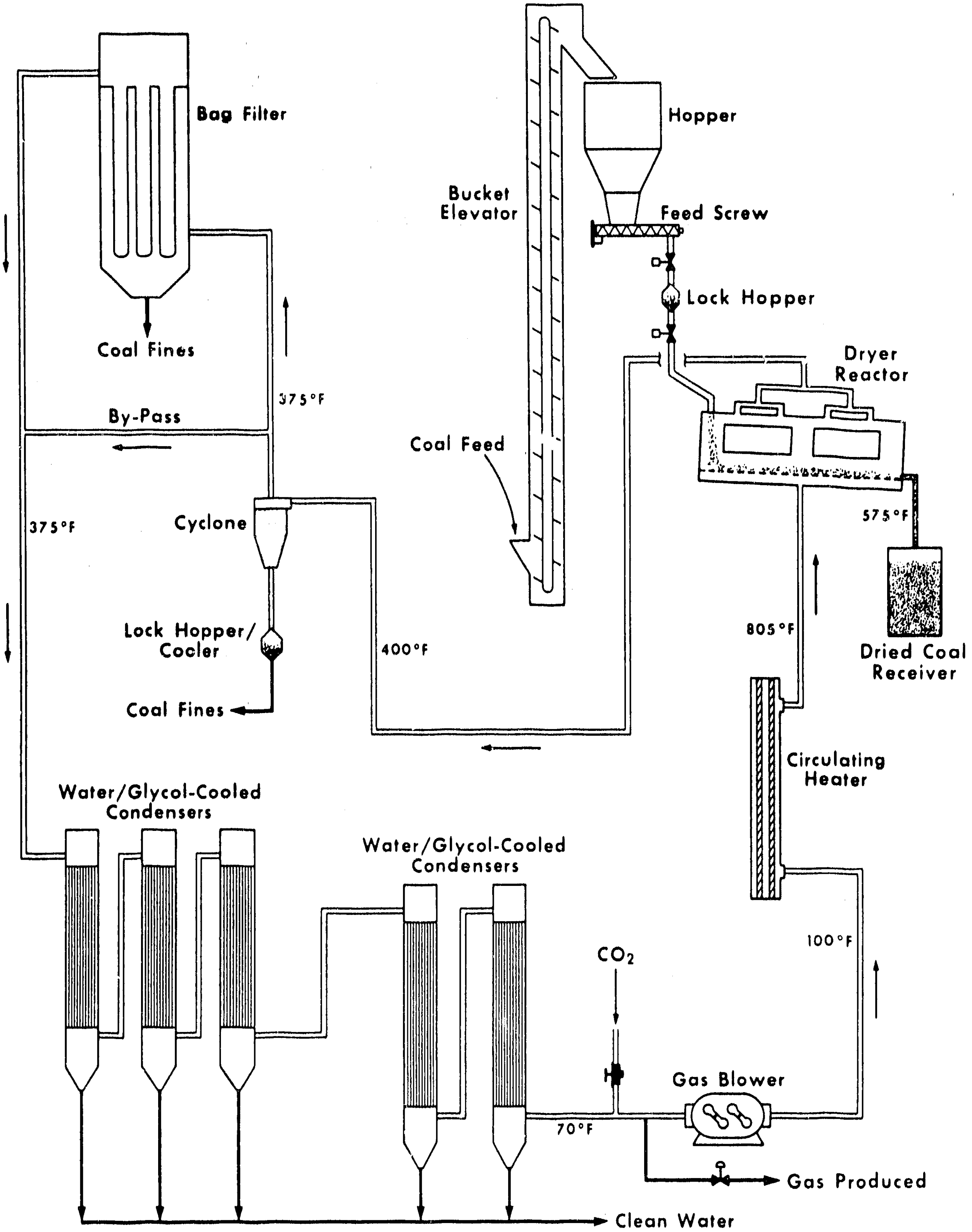


Figure 5. PRU Drying System Used to Dry Usibelli Coal

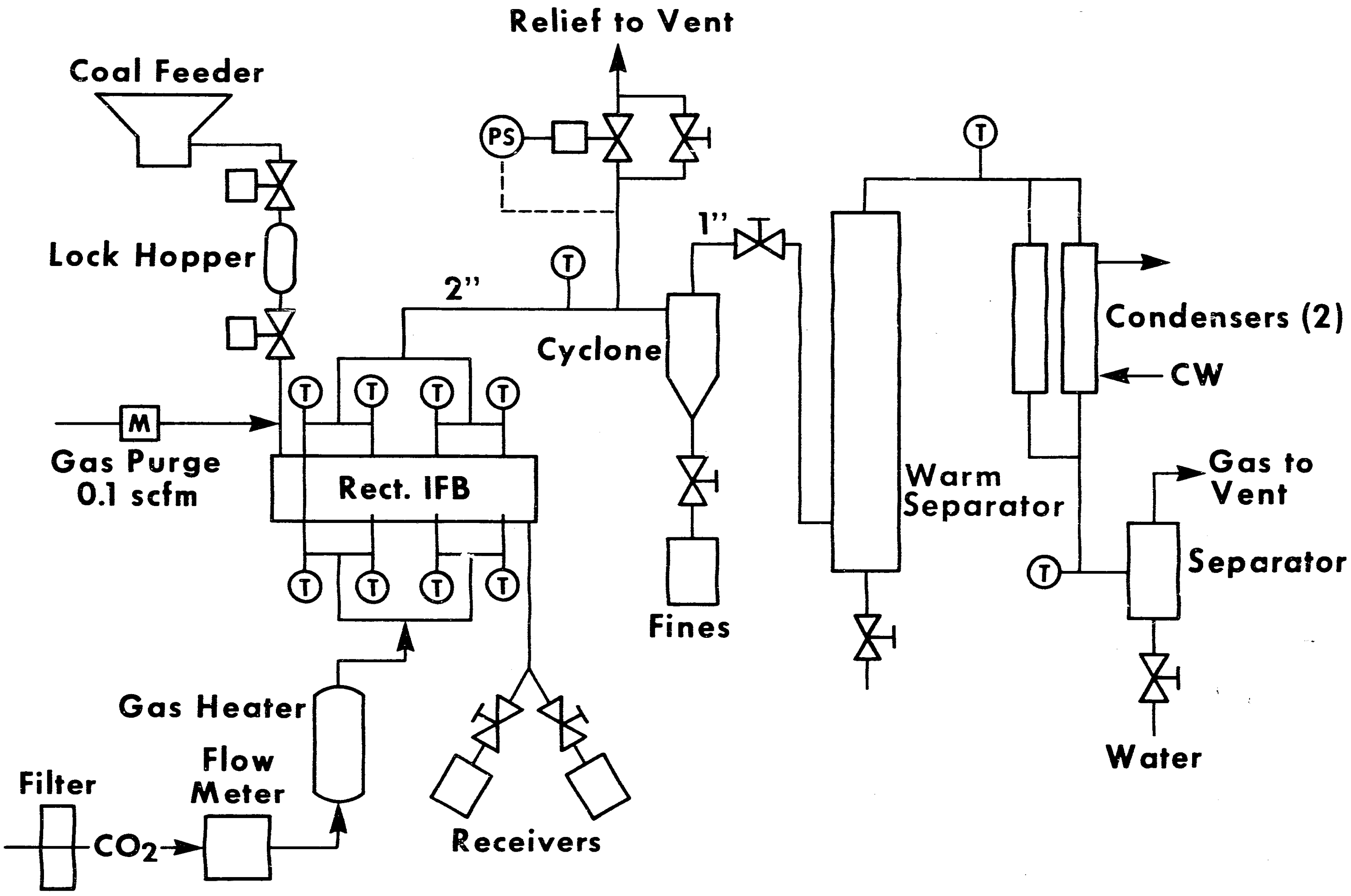


Figure 6. System Used for Mild Gasification Tests

The sample holder was constructed from 0.75-inch stainless steel tubing. Eighteen holes were drilled into the tubing for thermocouples that were inserted through the tubing wall. The positions of the two sensing thermocouples and the sixteen controlling thermocouples are shown in Figure 7. The four controlling thermocouples were spot welded in such a manner to create a thermopile with sixteen thermocouples inside the sample holder and sixteen thermocouples outside the sample holder. When both the coal bed inside the sample holder and GC oven are at the same temperature, the voltage across the thermopile is zero. With this configuration, only a coal bed temperature higher than the oven temperature will activate the GC oven temperature programmer and increase the oven temperature. Preliminary tests suggested that the temperature difference between the coal bed and the GC oven needed to activate the controller is less than 0.4°F (0.2°C).

The two sensing thermocouples are located above and below the controlling thermopile. The lower thermocouple is located at the coal-gas interface near the bottom of the sample holder. The upper thermocouple is located about one inch above the thermopile.

Pure oxygen was used for the oxidant for these tests. Moisture was added to the gas stream prior to entering the sample holder by using a sparger at room temperature. The moist oxygen was then preheated in the GC oven to very near the temperature of the oven. The preheating was accomplished by passing the oxygen through a 10-ft length of copper tubing packed with glass balls and wrapped around the interior of the GC oven.

A starting temperature of 122°F (50°C) was selected for the calorimeter tests. The selection of this temperature was based on similar tests previously done at AMAX on coals dried in the IFB. The following criteria were used as guidelines for self heating.

- Starting temperature between 122-149°F (50-65°C)
- Oxygen oxidizer
- Inflection point indicating an increase in heating rate at a point before 5 hours (300 min)

When sand was tested in the adiabatic calorimeter, no increase in temperature was detected after temperature equilibrium had been reached. The sample was allowed to run over night. The data from this run suggested that the whole sample holder reaches temperature equilibrium in about 30 minutes.

3.2 Analytical Methods

All analyses were conducted using either ASTM (ASTM 1985) or standard WRI procedures. The screen analyses, Hardgrove grindability index, and equilibrium moisture of the coal and char were measured using ASTM methods D 410, D 409, and D 1412, respectively.

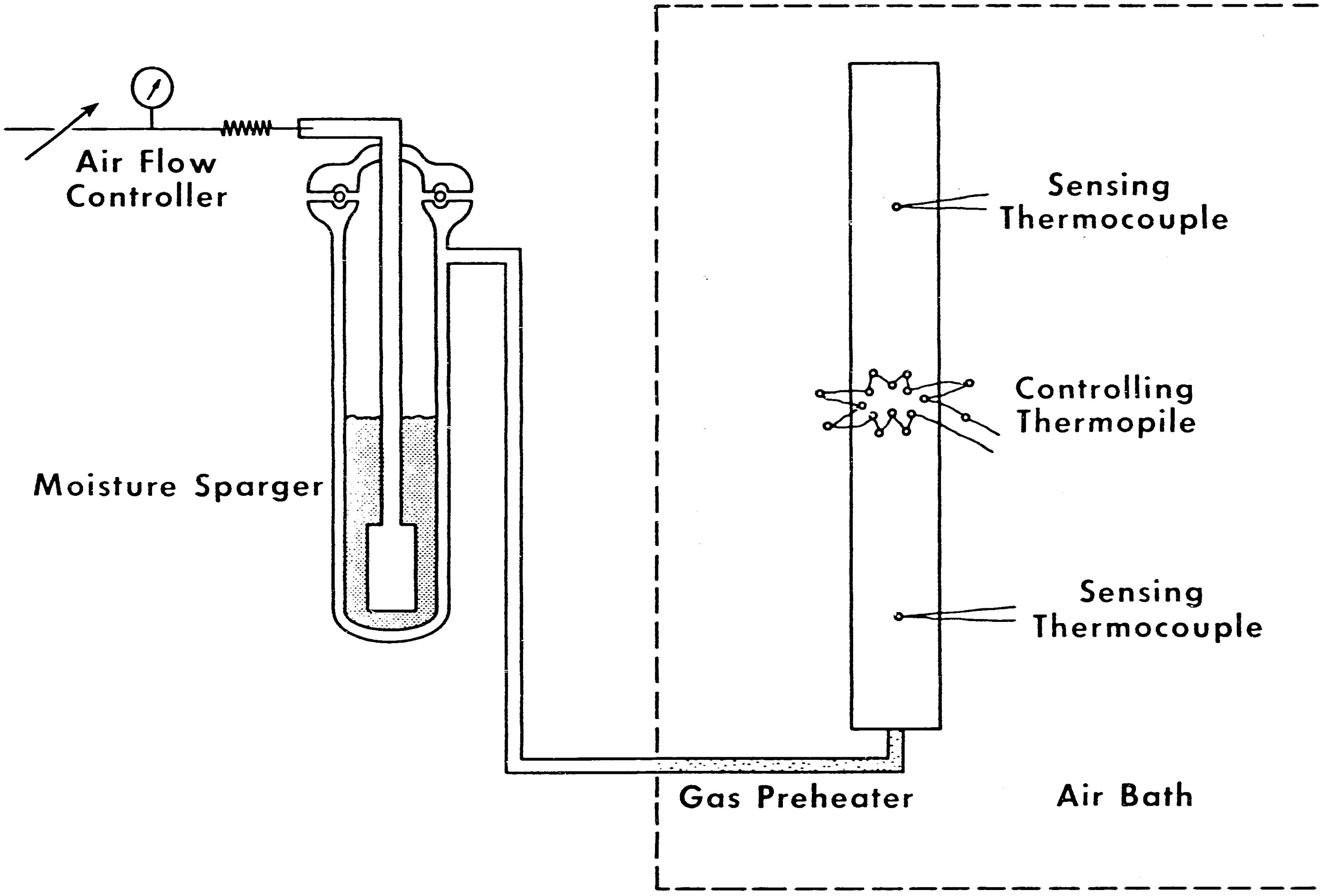


Figure 7. Adiabatic Calorimeter Used for Self-Heating Tests

The coal liquid from test 64 was distilled to produce two fractions: an IBP-700°F (IBP-371°C) distillate and a +700°F (+371°C) residue. The distillation was conducted by a commercial laboratory using ASTM method D 1160. The samples were then returned to WRI blanketed with nitrogen. A modification of ASTM method D 2318 was used to determine the quinoline and toluene insolubles. Instead of using Celite as a filter aid with a Buchner funnel to collect the insolubles, the quinoline and toluene insolubles were collected on a 10- to 15-μm fritted-glass funnel. Beta resins comprise the difference between the toluene insolubles and the quinoline insolubles. The moisture, ash, volatiles, and fixed carbon were measured using D 3172. In addition, the ash was determined by combusting the distillation residue in a muffle furnace set at 1000°F (538°C), and the water was determined by azeotropic distillation using toluene. The values obtained by the different methods were within experimental error.

Carbon, hydrogen, and nitrogen were measured using a Perkin-Elmer 2400 CHN elemental analyzer; sulfur was determined using a Fisher sulfur analyzer; and oxygen was determined by pyrolysis with quantification of the active species using a Coulometrics coulometer. Viscosity and specific gravity were determined using a Brookfield viscometer and ASTM method D 70, respectively. Heating values of liquids were determined using ASTM method D 240 whereas ASTM method D 2015 was used for chars. The distillate range of the IBP-700°F (IBP-371°C) distillate was determined using ASTM method D 2887, and the distillate range of the +700°F (+371°C) residue was determined using a standard WRI procedure, WRI-075. This WRI method relies on an external standard to determine the response factor. The data obtained using ASTM method D 2887 was mathematically converted to a ASTM method D 86 format.

Hydrocarbon-group types were determined using WRI method WRI-069. This is a proprietary gas chromatographic/mass spectral (GC/MS) method used with a Hewlett-Packard 5985B GC/MS system. The method uses parent molecular ions to identify the individual hydrocarbon-group types and sums of diagnostic fragment ions for quantification. Hydrocarbon-type concentrations are determined using internal standards, and sensitivity factors are developed for individual compounds and classes of compounds. The hydrocarbon fraction was obtained for GC/MS analysis by chromatographic separation of the distillate on neutral alumina. The first 50 mL eluting from the column with benzene as the solvent is defined as the hydrocarbon fraction.

The neutral fraction generated by chromatographic separation over neutral alumina was further evaluated by analysis with combined gas chromatography/mass spectrometry. The raw mass spectra were processed using the computer programs available with the system. The processing included background subtraction, quantitative measurement of the gas chromatographic peak areas, and library search to identify the individual compounds. Compounds that were not identified through the library search were identified by comparison of the spectra with spectra available from the literature and by interpretation of the unknown spectra.

4.0 RESULTS

Results of tests are presented in this section.

4.1 Coal Preparation

Coal received from Usibelli Coal Mine Inc. near Healy, Alaska, in June 1990 was screened (Table 1) through a 16-mesh screen. The minus 16-mesh coal was dried in the drying section of the 100-lb/hr PRU. The dried coal was then subjected to mild gasification using the 1-inch IFB reactor. The screened coal, which was dried using the 100-lb/hr PRU, was the feed for tests 59 through 64. Some of the remaining plus 16-mesh coal was crushed, screened, and dried using the 1-inch IFB drying system. The coal dried using the 1-inch IFB (Tests 65 and 67) became the feed for mild gasification tests 66 and 68, respectively.

The average particle size of the coal actually being subjected to mild gasification for tests 59-64 is considerably larger than the size of raw coal shown in Table 1 because particles smaller than minus 100 mesh are quickly removed from the dryer by elutriation. The fines have a very large affect upon the calculated average particle size. The three samples contain an average of 9.9 wt % of minus 100-mesh coal particles that were elutriated from the dryer. The coal dried during test 67 and used for mild gasification test 68 produced only 2.6 wt % fines during drying.

WRI analyses of the raw coal (Table 2) agree fairly well with analyses provided by Usibelli with the exception of ash content. We can find no measurable difference in composition between the coal provided by Usibelli and the minus 16-mesh coal used for testing.

Table 1. Size Distribution of Minus 16-Mesh Usibelli Coal Used for Tests

Mesh[a]	Percent Retained			
	Used for Tests 59-64			Test 68[b]
6	0	0	0	0
8	0	0	0	0
20	14.6	14.0	12.7	5.7
40	49.8	46.3	42.6	66.1
70	24.5	24.3	23.5	22.4
100	4.7	6.2	7.1	4.6
140	2.9	3.8	6.2	0.4
200	1.0	1.2	2.1	0.2
Pan	2.5	4.3	5.8	0.5
<u>Average Particle Size, inches</u>				
Surface Mean	0.0134	0.0111	0.0094	0.0176
Weighted Average	0.0252	0.0241	0.0225	0.0232

[a] U.S. Standard Testing Sieves
[b] Average of four analyses

Table 2. Analyses of Raw Usibelli Feed Coal, wt %

	Whole Coal				Minus 16 Mesh		
Proximate (AR)							
Moisture	24.23	24.53	25.6	25.4	21.9	24.6	24.4
Ash	9.25	9.05	10.0	11.3	10.3	10.2	10.5
Volatiles	35.23	35.14	34.3	34.2	35.8	33.7	34.2
Fixed Carbon	31.29	31.28	30.0	29.2	32.1	31.5	30.9
Ultimate (dry basis)							
Carbon			67.1	69.2	67.4	68.2	68.9
Hydrogen			5.5	5.7	5.5	5.6	5.7
Nitrogen			1.0	0.8	0.8	0.8	0.8
Sulfur			0.6	0.6	0.5	0.5	0.5

Note: First two proximate analyses from the left by Usibelli. All other analyses by WRI.

4.2 Coal Drying

We dried 1163 lb of minus 16-mesh Usibelli coal using the PRU dryer at a feed rate of 95 lb/hr (Table 3) and a recycle gas flow of 76 scfm at 700°F (371°C) as fluidizing gas (tests 101 and 102). The flow rate of 76 scfm is somewhat higher than what is needed to fluidize the minus 16-mesh coal, but this rate was used to be sure that we carried a sufficient flow of heat into the dryer. The high gas flow rate relative to the small particle size contributed to the high production of fines from the dryer (Table 4). (We typically produce 5 to 7 wt % of the raw coal as fines when drying minus 8-mesh Wyodak coal. The fines production is the minus 100-mesh fraction in the feed coal.)

The coal was quickly dried to zero moisture content in the dryer (Figure 8). The drying curve is quite different from drying curves of minus 8-mesh Wyodak coal containing about 30 wt % moisture. In those curves we see a plateau on the temperature curve at 140 to 160°F (71°C) followed by a rapid increase in temperature when zero moisture content is reached.

We also dried an additional 150 lb of minus 16-mesh coal (test 65) and 150 lb of minus 16-mesh to a plus 70-mesh coal (test 67) using the 1-inch IFB dryer at feed rates of 23 and 30 lb/hr, respectively. Carbon dioxide that flows once through the dryer was used as fluidizing gas. Tests 65 and 67 produced less water than the tests conducted using the PRU. This is because some water was lost while crushing and screening the coal, and the recovery of water from the once-though system is not as efficient as the recycle gas system used for the PRU dryer. Production of fines from test 67 is low because fines were separated from the feed coal used for test 67 by screening.

Table 3A. Conditions Used for Drying Usibelli Coal in the 100-lb/hr PRU

Fluidizing Gas		
Flow, scfm	76	
Temperature, °F	700	
Average Coal Rate Feed, lb/hr	95	
Bed Temperature, °F		
Zone 1 (0.16)*	210	
Zone 2 (0.48)	354	
Zone 3 (0.79)	531	
Coal Composition, wt %	Moisture	Volatiles (Dry basis)
Zone 1 (0.28)	5.7	45.5
Zone 2 (0.59)	0.0	43.2
Zone 3 (0.91)	0.5	42.5
Dried Coal Residence Time, min	~3	

*Fraction of bed length listed in parentheses. Bed thermocouples and sample ports are placed at different locations in the PRU.

Table 3B. Conditions Used for Drying Usibelli Coal in the 1-Inch IFB Dryer

Test	65	67
Fluidizing Gas		
Flow, scfm	6.8	6.8
Temperature, °F	807	815
Coal Rate Feed, lb/hr	23	30
Bed Temperature, °F		
Zone 1 (0.125)	144	136
Zone 2 (0.375)	247	264
Zone 3 (0.625)	290	272
Zone 4 (0.875)	410	371
Coal Moisture Content, wt %		
Zone 1 (0.125)	14.2	-
Zone 2 (0.375)	11.7	-
Zone 3 (0.625)	4.7	-
Zone 4 (0.875)	0.8	1.4

Fraction of bed length listed in parentheses

Table 4. Material Balances for Drying Minus 16-Mesh Usibelli Coal

	PRU		1-Inch IFB	
Test:	101	102	65	67
Weight, lb				
Wet Coal Feed	636.9	526.6	150.0	150.0
Dried Coal	404.7	332.0	93.7	110.6
Water	158.7	141.5	31.6	31.7
Fines	59.4	48.2	17.2	2.5
Dust from Filter	0.5	-	1.4	1.4
Gas Produced[a]	14.3	11.8	0.8	0.8
Total Out	637.6	533.5	144.7	147.0
% of Feed				
Wet Coal Feed	100.0	100.0	100.0	100.0
Dried Coal	63.5	63.0	62.5	73.7
Water	24.9	26.9	21.1	21.1
Fines	9.3	9.2	11.5	1.7
Dust from Filter	0.1	-	0.9	0.9
Gas Produced[a]	2.3	2.3	0.5	0.5
Total Out	100.1	101.4	96.5	97.9

[a] Estimated from volatiles balance

We did not calibrate the PRU dryer to determine the residence time of the coal in the dryer for this test. However, we know that the residence time is approximately 3 minutes when using minus 8-mesh coal with a 3 degree slope, 76 scfm gas flow at 700°F (371°C), and 95-lb/hr feed rate. Only about one-half of the residence time in the dryer is needed to completely remove moisture from the coal. However, additional devolatilization (gas removal) did occur in the last one-half of the bed (Table 3). The 0.5 wt % water in the sample from zone 3 is water which was reabsorbed on the sample after the sample was taken. (We have data from other tests that show there is no moisture detectable by proximate analysis remaining on coal at the conditions existing in zone 3.)

4.3 Mild Gasification Tests

We conducted six 8-hour tests, one 6-hour test, and one 24-hour test at a dry-coal feed rate of 7.5 lb/hr, which is equivalent to a wet-coal feed rate of 10 lb/hr (Table 5). The tests were conducted using maximum bed temperatures of 1050, 1100, 1150, 1200, and 1250°F (566, 593, 621, 649, and 677°C). Test 63 is a duplicate of the conditions used for test 60, and tests 61 and 64 are also duplicates.

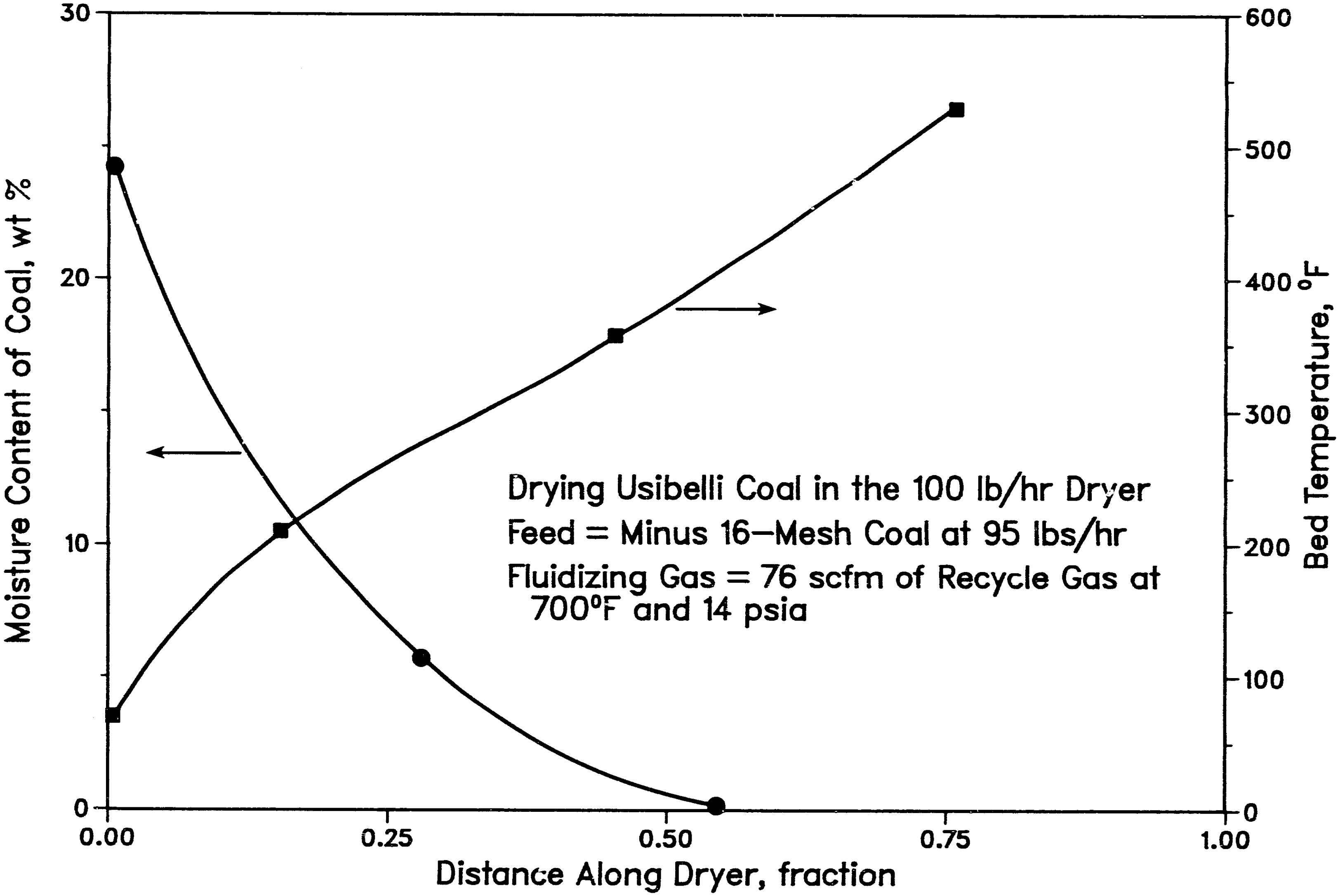


Figure 8. Drying Rate Curve for Usibelli Coal

We set the reactor at a slope of zero degrees expecting to achieve char residence times of 5 minutes. We chose to use a dry-coal feed rate of 7.5 lb/hr to minimize the cost of crushing and screening coal. Also, we knew that the mild gasification reactor system did not have sufficient heating capacity to reach 1200°F (649°C) at feed rates of 25 lb/hr or higher. Unfortunately, residence times are not predictable at such low feed rates (Figure 3). Char residence times were determined by dividing the bed weight by the average char production rate.

Tests conducted using the cold-flow model show that at feed rates less than about 30 lb/hr using a 6 degree slope and about 25 lb/hr using a 3 degree slope, the fluidized bed is represented by scattered groups of fluidized particles with no discernible top. Correlations for residence time with slope and feed rate are poor at the lower feed rates. We think the bed instability at low feed rates caused most of the variation in residence times listed in Table 5.

Table 5. Conditions Used for Mild Gasification of Usibelli Coal (Average of Test Duration)

Test:	59	60	61	62	63	64	66	68
Bed Temperatures, °F								
Zone 1 (0.125)	740	854	895	887	810	844	1032	1050
Zone 2 (0.375)	1032	1083	1125	1150	1065	1125	1220	1230
Zone 3 (0.625)	1040	1094	1131	1154	1088	1137	1243	1250
Zone 4 (0.875)	1049	1099	1151	1196	1101	1149	1247	1251
Dried Coal Feed Rate, lb/hr	8.1	7.7	7.7	7.3	7.5	7.5	7.4	7.2
Fluidizing Gas								
CO_2 Flow, scfm	6.4	6.5	6.6	6.8	6.7	6.7	6.8	6.8
Temperature, °F	1090	1145	1205	1230	1120	1180	1312	1348
Char Residence Time, min	1.0	1.4	1.4	11.8	4.0	7.0	-	1.3
Test Duration, hr	8	9	8	8	8	24	6	8

Fraction of reactor length listed in parentheses

A coal devolatilization curve from test 64 (Figure 9) shows that all of the devolatilization takes place in the first one-half of the bed. This curve shows that the residence time was more than adequate to achieve the desired volatiles removal. All of the four bed samples are taken within a few minutes. However, the char sample is taken from the char receiver after the test is over. The different time at which samples are taken, detects variation in the volatiles content of the char produced during the test.

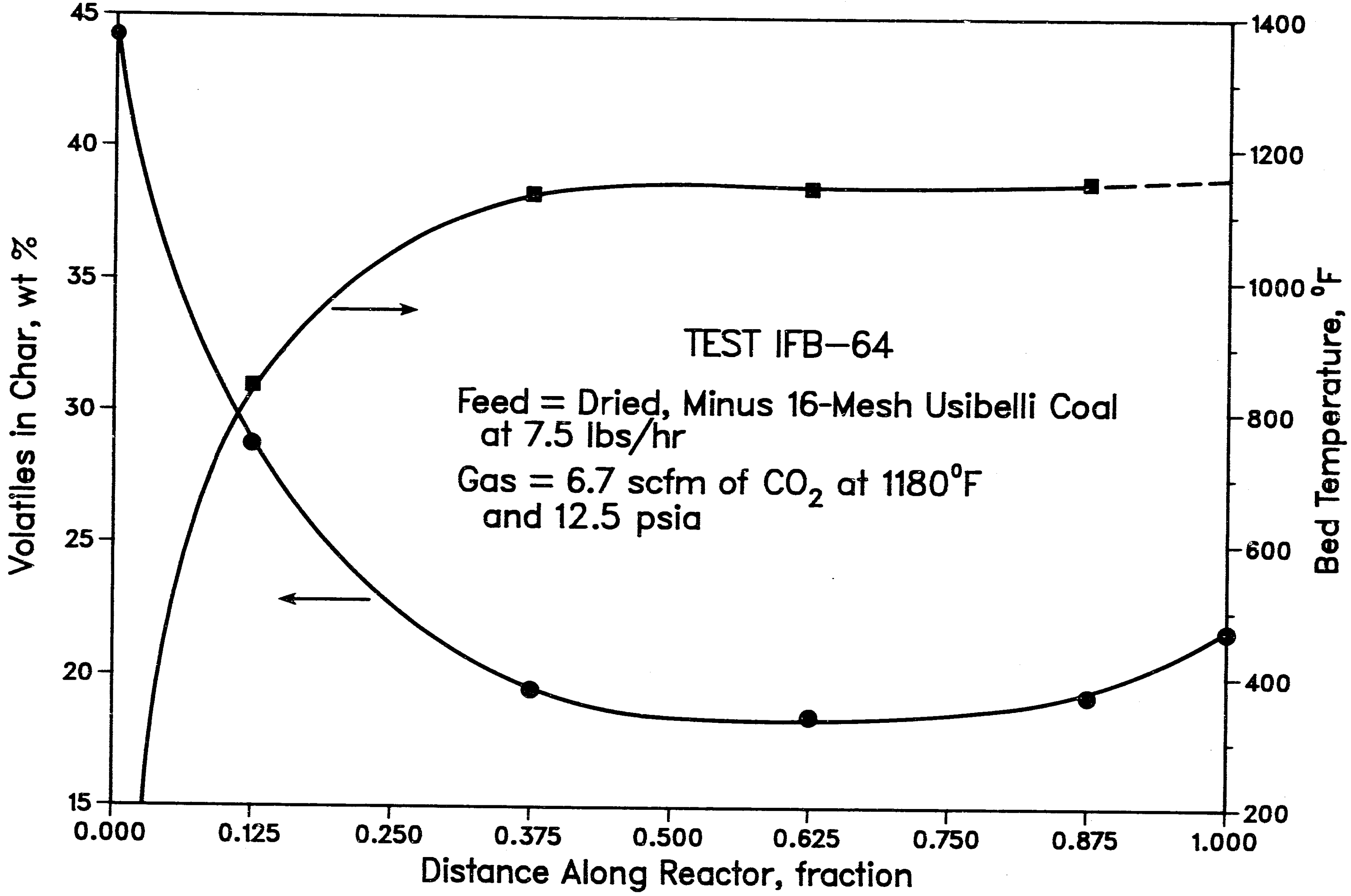


Figure 9. Devolatilization Curve for Usibelli Coal

Char samples are taken from the reactor using 1/2-inch pipes having valves at the reactor and at the outlet end of the pipes. This arrangement permits us to let the char samples cool in a nonoxidizing environment. When the sample ports are flushed before collecting samples, the coal char is collected in an open container. We observed that the char in the open container oxidizes quickly. Glowing particles could be seen in the char 10 to 15 minutes after the char was put into the open container. Our experience with chars is that char fresh from the reactor oxidizes on the surface of the pile quickly while aged char oxidizes more slowly.

The coal balances from the tests (Tables 6 and 7) are affected by the use of once-through carbon dioxide. The large flow of noncondensable gas relative to the small flow of condensables makes the partial pressure of condensables very low in the effluent gas stream. Thus, we expect that much of the water and low-boiling coal liquid produced by mild gasification will pass through the collection system. These substances will be recovered by using a recycle gas stream because the low-boilers accumulate to give higher partial pressures.

In earlier tests, using Wyodak coal fluidized by a once-through flow of carbon dioxide, the water content of collected liquids was negligible (Merriam and Cha 1989). However, when we conducted tests using a recycle gas system with the 100-lb/hr PRU, we collected water equivalent to 4.6 to 6.9 wt % of the dried coal feed to the mild gasification reactor (Merriam et al. 1990). We also determined that the water produced during mild gasification of dried coal (not the same water found by proximate analysis of raw coal) increased slightly with the temperature used for mild gasification. We think that the pyrolysis water is mostly formed by chemical reaction with lesser amounts resulting from destruction of mineral hydrates in the coal. If we add 5.7 (the median between 4.6 and 6.9 wt % water produced) to the average closure in Table 6, the average closure will be 99.3%. Thus, the losses from the coal are mostly water and lesser amounts of low-boiling coal liquids.

We consider balance closures of about 97 to 102% to be good for this type of work. Closures of 90 to 105% are fair, whereas those below 90 or above 105% we consider poor.

In tests using recycle gas, we also collect a small amount of low-boiling tar acids in the water from the PRU. The condensed water and low-boiling coal liquid contains a higher concentration of sulfur compounds and a lower concentration of nitrogen compounds than the higher-boiling condensates.

Table 6. Coal Balances for Mild Gasification Tests, lb

Test	59	60	61	62	63	64	66	68
Dried Coal In	60.0	60.0	60.0	60.0	60.0	180.0	47.4	59.6
Char	33.5	31.0	28.0	30.7	30.0	92.7	14.7	25.9
Fines from Cyclone	0.7	0.2	7.0	4.9	5.9	18.3	8.7	9.1
Material from Warm Separation	4.1	6.3	1.8	0.1	2.3	4.2	1.5	0.4
Liquid Collected	6.3	6.0	6.6	7.7	6.9	20.2	5.2	3.5
Gas Produced[a]	11.5	10.8	11.7	12.5	10.3	33.0	11.3	16.9
Samples from Bed	0.6	0.8	0.9	2.3	0.8	0.9	0.9	0.8
Total Out	56.7	55.1	56.0	58.2	56.2	169.3	42.3	56.6
Closure, %	94.5	91.8	93.3	97.0	93.7	94.1	89.2	95.0

[a] Calculated from volatiles balances

Table 7. Coal Balances for Mild Gasification Tests, wt %

Test	59	60	61	62	63	64	66	68
Dried Coal In	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Char	55.8	51.7	46.1	51.2	50.0	51.5	31.0	43.5
Fines from Cyclone	1.1	0.3	11.7	8.1	9.9	10.2	18.4	15.3
Material from Warm Separation	6.8	10.5	3.0	trace	3.9	2.3	3.2	0.7
Liquid Collected	10.5	10.0	11.1	12.8	11.5	11.2	11.0	5.9
Gas Produced	19.2	18.0	19.5	20.8	17.2	18.3	23.8	28.4
Samples from Bed	1.1	1.3	1.6	3.8	1.4	trace	1.9	1.3
Maximum Bed Temp, °F	1050	1100	1150	1200	1100	1150	1250	1250

Test 66 was terminated at 6.4 hours when the timer that controls the lockhopper valves malfunctioned. In addition to the shortened test and the uncontrolled shutdown, test 66 resulted in poor closure of the coal balance (Table 6) and an exceptionally high fines production rate (Table 7). Therefore, we decided to repeat test 66 as test 68. The difference between the two tests was that we screened the fines out of the coal that was dried and used as feed for test 68.

In the recently completed tests using Wyodak coal in the 100-lb/hr PRU, the fines produced by mild gasification were essentially the same composition as the dried coal feed to the reactor. The similar composition of the feed coal and fines led us to conclude that the fines were elutriated from the bed before devolatilization could take place.

This suggests that fines were not formed during mild gasification. We have seen just the opposite effect from tests using Usibelli coal in the 1-inch IFB reactor. Fines produced during tests 62, 64, 66, and 68 contain 23.4, 23.5, 22.9, and 21.3 wt % volatiles, respectively, and are similar to the composition of the char. The devolatilization of the fines during mild gasification suggests that the fines were formed after being devolatilized or that devolatilization takes place in the cyclone.

Figure 10 shows the distribution of products from Table 7, after adjustments, plotted versus maximum bed temperature for each of the tests. The weights of material from the warm separator are split as follows. For all tests except 63 and 64, 100% of the weight is added to the fines; for test 63, 75% of the weight is added to the fines, and 25% is added to the liquid; and for test 64, 90% of the weight is added to the liquid, and 10% to the fines. (Table 19 lists the composition of the material collected from the warm separator.)

Results of the expected trends for the components show that our estimate of gas production from test 59 is probably high. The weight of solid products (char, fines, and bed samples) from test 62 is probably high. (Our records do show that numerous sample port flushes were made during test 62, so the apparently high weight of bed samples is probably correct.)

The distribution of products from tests conducted above 1150°F (621°C) shows contradictory results (Figure 10). Test 62 resulted in a too-high carbon balance closure (Table 8) and doubtful char composition (Table 14). Test 66 resulted in low closure of the coal balance (Table 6) and very low char production (Table 7). Very little liquid was collected from test 68 (Table 7). We can, however, use other data to test the plausibility of the product distribution.

First, the trend of decreasing volatiles content of chars (Table 14) with increasing test temperatures (Table 5) shows that the data point from test 68 for char, fines, and bed samples is very likely near the correct trend line for solid products. (The char values from test 62 are not sufficiently accurate for use in this analysis.) The char analyses show that the trend toward driving more volatiles from the char at higher temperatures is roughly constant throughout the temperature range that we tested.

Second, we know from other work that the liquid yield curve for Wyodak coal (Merriam and Cha 1989) and subbituminous coals, in general, (Edwards et al. 1983) has a maximum near 1150°F (621°C). It is reasonable to expect Usibelli coal to have a similar maximum.

The sum of the three curves must equal 100% minus losses; therefore the gas curve must exhibit an increasing slope above 1150°F (621°C), if the solids and liquids curves are generally correct. Increase in the production of gas at higher temperatures is also consistent with other work.

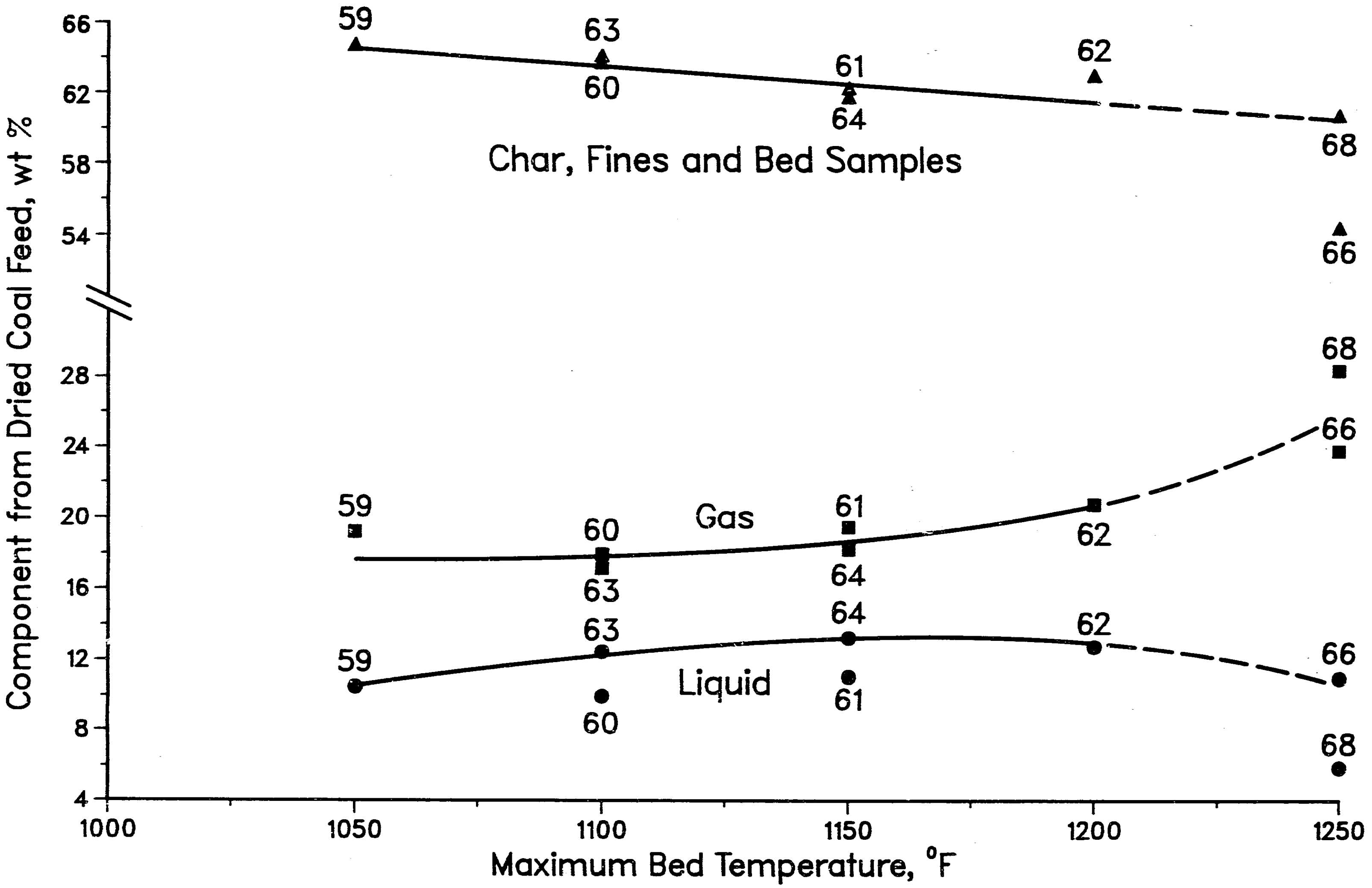


Figure 10. Distribution of Char, Gas, and Liquid Produced from Usibelli Coal

The material collected from the warm separator during all tests except 63 and 64 was coal dust. Obviously, the cyclone was not performing at a high level of efficiency, probably because the cyclone is larger than we prefer to use for the tests. The oversized cyclone results in a low inlet velocity and low separation efficiency. (This cyclone is the smallest we have.)

Significantly, the material collected from the warm separator during tests 63 and 64 contains high concentrations of volatiles. After test 63, we removed a hard agglomerate containing 56 wt % volatiles and 8 wt % ash. After test 64, we removed a hard, black, shiny substance that is brittle at room temperature. The substance contains 77 wt % volatiles and 1 wt % ash; it has the appearance of a frozen liquid.

Elemental balances for the tests (Tables 8, 9, 10, 11, and 12) are based on the analysis of the dried coal feed. The composition of char was normalized to bring the total of the elements plus ash to 100%. Actual composition of fines was used for tests 62 and 64. The average composition of fines from tests 62 and 64 was used for other tests. The samples are subtracted from the feed. Coal liquid composition is from actual measurement, except for the average composition used for test 66. Composition of the water in the coal liquid is estimated from water analyses from tests using Wyodak coal. Material from the warm separator is combined with the liquids collected.

Table 8. Carbon Balances for Mild Gasification Tests, lbs C

Test:	59	60	61	62	63	64	66	68
Dried Coal	36.51	36.39	36.33	35.47	36.39	110.09	28.58	36.09
Char	21.65	20.11	17.85	21.63	19.20	61.44	9.90	17.92
Fines	0.48	0.14	4.78	3.12	4.03	11.41	5.95	6.31
Liquid	8.22	9.70	6.67	6.01	7.17	19.63	5.05	2.95
Gas Produced	4.47	3.75	3.93	6.59	4.38	11.25	3.93	5.92
Total Out	34.83	33.70	33.23	37.35	34.78	103.74	24.83	33.10
Closure, %	95.4	92.6	91.5	105.3	95.6	94.2	86.9	91.7

Table 9. Hydrogen Balances for Mild Gasification Tests, lb MAF H

Test:	59	60	61	62	63	64	66	68
Dried Coal	3.09	3.08	3.07	3.00	3.08	9.31	2.42	3.05
Char	0.97	0.84	0.78	0.71	0.84	2.41	0.34	0.67
Fines	0.02	0.00	0.17	0.12	0.14	0.48	0.21	0.22
Liquid	0.88	1.05	0.70	0.68	0.77	2.33	0.48	0.31
Gas Produced	0.42	0.23	0.20	0.78	0.50	0.60	0.21	0.35
Total Out	2.29	2.10	1.86	2.28	2.26	5.82	1.24	1.55
Closure, %	74.1	68.2	60.4	75.9	73.4	62.5	51.2	50.8

Table 10. Nitrogen Balances for Mild Gasification Tests, lb N

Test:	59	60	61	62	63	64	66	68
Dried Coal	0.54	0.53	0.53	0.52	0.53	1.62	0.42	0.53
Char	0.30	0.34	0.25	0.31	0.27	0.84	0.15	0.23
Fines	0.01	0.00	0.07	0.06	0.06	0.20	0.08	0.09
Liquid	0.00	0.21	0.11	0.08	0.13	0.17	0.09	0.06
Gas Produced	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total Out	0.39	0.55	0.43	0.45	0.45	1.21	0.32	0.38
Closure, %	73.0	103.3	80.1	85.9	86.4	74.8	76.2	71.7

Table 11. Sulfur Balances for Mild Gasification Tests, lb S

Test:	59	60	61	62	63	64	66	68
Dried Coal	0.12	0.12	0.12	0.11	0.12	0.35	0.09	0.12
Char	0.08	0.08	0.10	0.11	0.09	0.35	0.05	0.08
Fines	0.00	0.00	0.02	0.02	0.02	0.04	0.02	0.02
Liquid	0.05	0.05	0.03	0.03	0.04	0.10	0.03	0.01
Gas Produced	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total Out	0.14	0.13	0.12	0.15	0.15	0.37	0.10	0.11
Closure, %	117.4	109.2	129.4	136.0	129.7	105.9	111.1	91.7

Table 12. Oxygen Balances for Mild Gasification Tests, lb O

Test:	59	60	61	62	63	64	66	68
Dried Coal	12.82	12.78	12.76	12.46	12.78	38.67	10.04	12.67
Char	3.96	3.41	3.16	2.83	3.48	10.67	1.43	2.46
Fines	0.07	0.02	0.73	0.65	0.61	2.33	0.90	0.95
Liquid	1.07	1.28	0.88	0.98	1.06	2.15	0.75	0.47
Gas Produced	6.62	6.82	7.57	5.13	5.42	21.15	7.15	10.65
Total Out	11.72	11.54	12.35	9.60	10.57	36.30	10.23	14.53
Closure, %	91.4	90.3	96.8	77.0	82.7	93.9	101.9	114.7

The carbon balance closures agree well with the closures from coal balances suggesting that the carbon balances for all tests except 62 are reliable. Hydrogen balance closures are consistently low suggesting that the hydrogen content measured in the feed coal is high or a systematic loss of hydrogen has occurred in all tests. We did not measure nitrogen-containing compounds in the gas or water (such as ammonia, cyanide, or nitriles); therefore, we expect low closures on nitrogen balances. Also, the small quantities of nitrogen and sulfur present make those balances susceptible to large variations in closures. High closures for the sulfur balances, especially because we did not measure the sulfur species in the gas, suggest that sulfur analysis of the dried coal is high. Closures of some of the oxygen balances are remarkably good considering that oxygen balances are typically very difficult to close.

4.4 Properties of Products

The grindability indices (Table 13) show that we should expect that drying the coal will increase pulverizer capacity. Partial devolatilization of the char should further increase pulverizer capacity.

Table 13. Grindability Indices for Coal, Dried Coal, and Char

Material	Hardgrove Grindability Index	Moisture Content, wt %
Minus 16-mesh Feed Coal	28	22.42
Dried Coal	49	0.52
Char from Test 64	82	0.0

The char produced during the mild gasification tests contains a relatively high amount of volatiles (Table 14). We expect the char to be highly reactive. Although we did not measure the reactivity of the char, we know that char produced from Wyodak coal under similar conditions is highly reactive. Also, on several occasions, we did observe that the char removed from reactor sample ports oxidizes rapidly when left in an open container.

As expected, the char produced at higher temperature has the lowest volatiles, hydrogen, and oxygen contents. The char produced at the lowest temperature (test 59) has the highest hydrogen and oxygen contents. The nitrogen and sulfur contents of chars change very little with changing production temperature in the temperature range we tested. We expect to remove the pyritic sulfur and leave most of the organic and sulfate sulfur in the char at the test conditions.

The heating values of chars from these tests agree with the calculated values, except for the char from test 64. Within the range of temperatures we tested, we expect to produce a smaller portion of the products as char at higher temperatures. We also expect the char produced at higher temperature to have higher heating value because more oxygen is driven from the char at higher temperatures.

We measured the equilibrium moisture content of as-received Usibelli coal and char produced during test 62 (Table 15). The equilibrium moisture is a measure of the maximum moisture content the coal (or char) can absorb from the water vapor in the surrounding air. The equilibrium moisture (ASTM D 1412) is determined by soaking the coal in water for 2 hours, removing the excess water by filtration, and then storing the coal in a desiccator for 48 hours. The humidity in the desiccator is controlled to have a vapor pressure of water of 30 mm Hg at 86°F (30°C) (greater than 97% relative humidity).

These results show that the char has a reduced capacity for adsorbing moisture from humidity in the air. The data from earlier tests is included to show that larger particle sizes of the raw coal supplied for mild gasification tests have adsorption capacities similar to minus 28-mesh coal. We did not crush the char used for adsorption tests because we did not want to alter the characteristics of the char. However, we think the adsorption capacity is independent of particle size within the size range of coals and chars tested.

A sample of the Usibelli feedstock was evaluated for self-heating tendencies using the same conditions that we used for the dried products. No self-heating tendencies were detected. The oven temperature came into equilibrium at 122°F (50°C) and stayed there for about four days. At this time, the test was terminated.

Table 14. Composition of Chars Produced by Mild Gasification of Usibelli Coal, wt %

Test:	59	60	61	62	63	64	66	68
Volatiles	21.5	22.7	20.8	15.7	22.0	22.0	19.7	19.3
Ash	19.5	20.1	20.8	16.7	20.4	18.5	19.2	17.5
Fixed Carbon	59.0	57.4	58.3	67.6	57.6	59.6	61.1	63.2
Carbon	64.6	64.8	63.8	70.4	64.0	66.2	67.3	69.2
Hydrogen	2.9	2.7	2.8	2.3	2.6	2.6	2.4	2.6
Nitrogen	0.9	1.1	0.9	1.0	1.0	0.9	1.1	0.9
Sulfur	0.3	0.3	0.4	0.4	0.4	0.3	0.4	0.3
Oxygen (by difference)	11.8	11.0	11.3	9.2	11.6	11.5	9.6	7.7
Hydrogen/Oxygen (mass)	0.246	0.245	0.248	0.250	0.224	0.226	0.250	0.338
Hydrogen/Carbon (atomic)	0.535	0.496	0.523	0.389	0.484	0.468	0.428	0.451
Gross Heating value Btu/lb								
Measured[a]	10,726	10,851	10,466	11,619	10,776	9,969	10,976	11,153
Calculated[b]	10,692	10,666	10,549	11,400	10,468	10,798	10,965	11,433

[a] Measured using adiabatic bomb calorimeter (ASTM D 2015)

[b] Calculated using the Boie Equation (Boie 1952):

$$\Delta H_c = 15{,}120[C] + 49{,}977[H] + 2700[N] + 4500[S] - 4770[O]$$

where ΔH_c is the gross heating value in Btu/lb, and C, H, N, S, and O are weight fractions of elements

Table 15. Equilibrium Moisture Content of Coal and Char, wt %

Material	Equilibrium Moisture
Minus 28-mesh Usibelli Coal from earlier drying test	21.8 22.2 21.8
Raw Usibelli Coal supplied for these mild gasification tests	22.8 22.7
Char from test 62	9.6 10.6

A sample of char taken from the zone 4 sample port during test 64 was substituted for product char because we had no char remaining from test 64. Char from the sample port was cooled and collected in a jar under air, whereas the product chars were collected under a CO_2 atmosphere. Apparently, the zone 4 sample-port char from test 64 was not a representative sample.

Four of the char samples showed self-heating tendencies that were nearly identical. A typical thermogram for one of these samples is shown in Figure 11. The samples all started to generate heat, which was indicated by an increase in the oven temperature set point, before temperature equilibrium was reached between the oven and the lower thermocouple. The self heating continued until the oven maximum temperature was reached and shut off the oven heater. Sample combustion was determined by the crossing of the oven and the lower thermocouple temperatures. At this point, the lower thermocouple temperature was increasing at a high rate and exceeded the recording capability of 482°F (250°C) for an extended time. When the samples were removed from the sample holder, there was a noticeable amount of ash at the bottom of the holder as a result of the combustion (F.A. Barbour, WRI, personal communication, November 16, 1990).

Four of the products (IFB 59, IFB 60, IFB 61, and IFB 63) were extremely reactive. Table 16 lists data from the self-heating tests of these products and the coal feedstock. Three of the four chars that are quite reactive exhibited combustion within one and one-half to two hours. The forth reactive product (IFB 61) reached combustion within 3 hours. These are all capable of spontaneous combustion, as described by the previously mentioned criteria.

The product from IFB 64 was not very reactive. The material started to exhibit self-heating tendencies just like the other char products. However, the heating rate never increased and stopped after about 500 minutes, reaching a temperature of 153°F (67°C). There was no evidence of combustion when the sample was removed from the holder. The product from IFB 62 was also less reactive; it took approximately twice as long for combustion to start as it did for most of the other products. IFB 64 is not capable of spontaneous combustion, as described by the criteria mentioned earlier, whereas IFB 62 is borderline.

There are obvious trends of increases in heating time, time to start combustion, and the temperature of combustion with increases in the temperature at which the char was produced (Table 16). The char produced at the lowest temperature (test 59) is the most reactive.

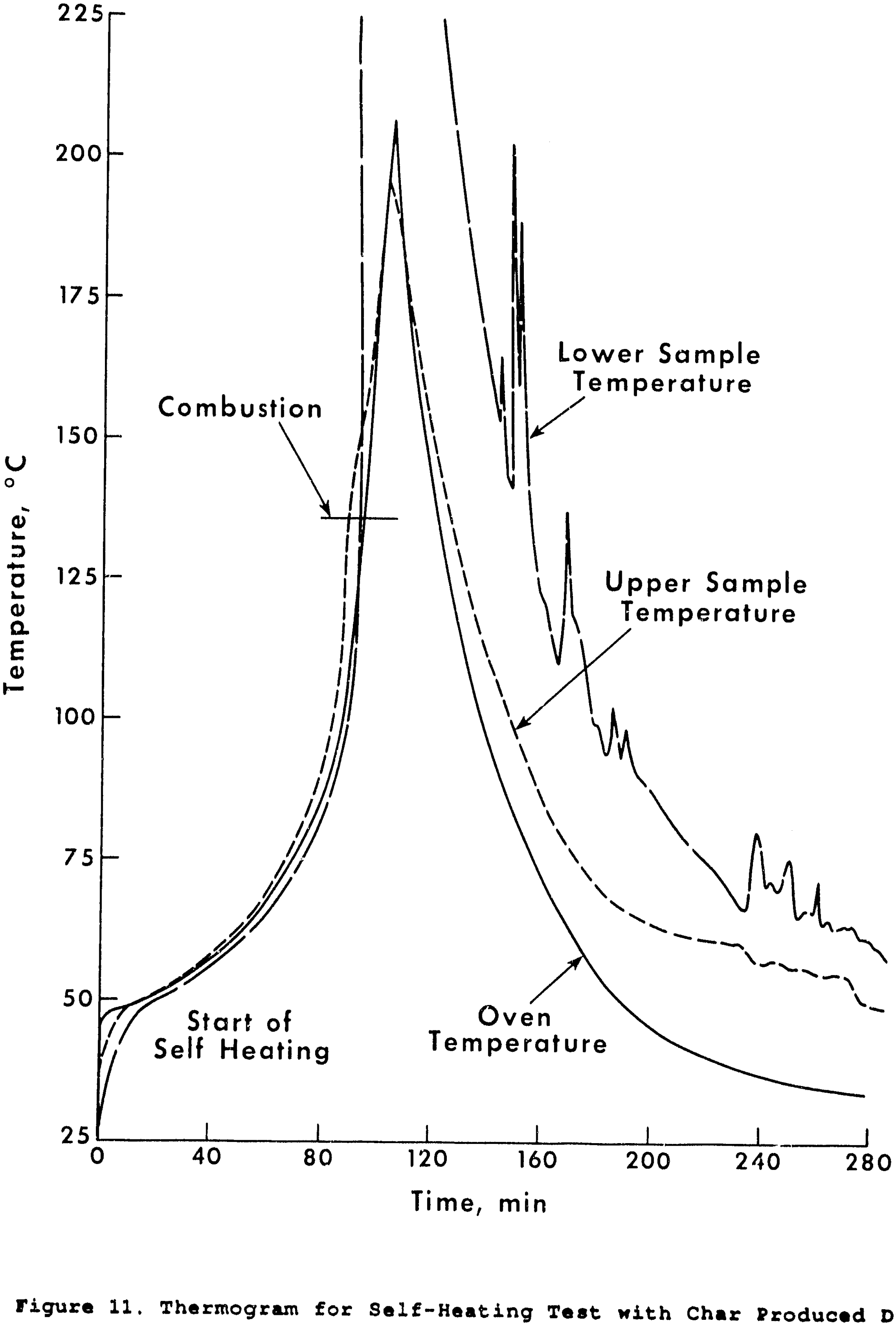


Figure 11. Thermogram for Self-Heating Test with Char Produced During Test 59

The composition of the gas produced during mild gasification tests (Table 17) is approximate because the carbon dioxide produced from the coal is the small difference between two large numbers. Carbon dioxide that flowed once through the reactor was used as fluidizing gas. Carbon dioxide is consumed by the char-carbon dioxide reaction in the bed of hot char. Carbon dioxide is also produced from the coal during mild gasification. To determine the composition of the gas produced from the coal, we subtract the carbon dioxide injected as fluidizing gas from the gas flowing from the system. The gas produced from the coal is approximately 5 vol % of gas flowing from the reactor. Thus, an error of only a one-tenth of 1% in measurement of the gas flow results in a 2 vol % change in carbon dioxide content of the gas produced. The relative portions of the components of the gas, other than carbon dioxide, are much more accurate.

The absence of any carbon dioxide in the gas from test 62 suggests that more carbon dioxide was consumed by reaction with char than was produced from the coal, which is not likely. We expect that the gas produced at the highest temperature (tests 66 and 68) will have the lowest carbon dioxide content. We also expect that the gas produced at the lowest temperature (test 59) will have the highest carbon dioxide content. We did not find this which suggests an error in our estimate of the composition of gas produced during test 59.

Table 16. Self-Heating Test Data for Chars from Usibelli Coal

Test:	IFB 59	IFB 60	IFB 61	IFB 62	IFB 63	IFB 64	Coal Feed
Starting of Self Heating[a]	20	22	22	28	19	26	b
Increase in Heating Rate[a]	82	112	146	315	82	c	b
Combustion[a]							
Time	95	118	155	327	91	c	b
Temp, °F	275	280	291	387	250	c	b
Test Temp, °F	1049	1099	1151	1196	1101	1149	

[a] Calorimeter values are time in minutes from the start of the self-heating test

[b] The coal feedstock never started to exhibit self heating

[c] Product from IFB 64 started to heat up but quit after 500 minutes and 153°F

Table 17. Approximate Composition of Gas Produced, vol %

Test:	59	60	61	62	63	64	66	68
CO	25.7	19.8	19.8	65.7	18.6	21.4	24.6	23.2
CO_2	48.1	62.8	65.5	-	52.1	63.4	60.0	60.9
CH_4	19.9	12.9	10.5	26.2	12.5	10.7	11.0	10.6
C_2H_6	2.6	1.0	1.1	2.6	1.4	1.2	1.1	1.4
C_2H_4	1.1	1.6	0.9	1.2	0.7	1.0	1.6	1.8
C_3H_8	2.2	1.4	1.1	4.3	14.4	1.2	1.1	1.3
C_4	0.5	0.4	0.3	Tr	0.4	0.4	0.4	0.6
Gross Heating value, Btu/scf	419	285	241	649	597	257	276	287

It is not possible to actually produce a gas having zero carbon dioxide or 65 vol % carbon monoxide content because the reaction between carbon dioxide and char decreases as the concentration of carbon dioxide decreases. From a recently completed series of tests using Wyodak coal (that is similar in composition to Usibelli coal) using a recycle gas system which permits accurate determination of gas composition we determined (Merriam et al. 1990):

- Hydrogen, which was not detected during tests using a once-through flow of carbon dioxide, increased from 4 vol % at 950°F (510°C) to 13 vol % at 1150°F (621°C).
- Carbon monoxide increased from 18 to 23 vol % over the same range of temperatures.
- Methane increased from 23 to 34 vol % over the same range of temperatures, whereas gross heating value increased from 550 to 600 Btu/scf.
- Carbon dioxide concentration decreased from 42 vol % at 950°F (510°C) to 25 vol % at 1150°F (621°C).

Usibelli coal has a lower moisture content than Wyodak coal (24.3 wt % versus 30.7), a higher ash content (9.2 wt % versus 4.9), and a higher volatiles content (35.2 wt % versus 33.7). However, the fixed carbon and the carbon, hydrogen, nitrogen, and sulfur contents of the two coals are almost identical. Thus, we expect that the gas produced by mild gasification of these two coals will be similar in composition. Also, a shift in the composition of gas produced toward more hydrocarbons will improve the hydrogen balances.

The composition of the liquids collected (Table 18) during the tests is very similar. The compositions of the distillate and the residue from liquid produced during test 64 are listed in Table 22. We did not analyze a sample of the crude liquid. The oxygen content of the MAF liquids is measured directly.

Table 18. Composition of Liquids Collected, wt %

Test:	59	60	61	62	63	64	66	68
Elemental (MAF)								
Carbon	80.0	79.4	79.9	80.2	79.9	-	-	79.3
Hydrogen	8.5	8.3	8.3	8.5	8.4	-	-	8.1
Nitrogen	0.8	1.7	1.3	1.1	1.5	-	-	1.7
Sulfur	0.5	0.4	0.4	0.4	0.5	-	-	0.2
Oxygen	9.8	9.8	10.1	9.5	10.0	-	-	-
Total	99.6	99.6	100.0	99.7	100.3	-	-	-
H/C Ratio	1.28	1.25	1.25	1.27	1.26	-	-	1.23
Water	0.74	0.80	0.59	3.97	2.05	1.89	2.19	2.20
Ash	0.76	0.31	0.10	0.22	0.14	0.05	0.44	2.53

We operated the condensers in the liquid collection system as a compromise between low temperatures to collect more liquid and warm temperatures to avoid plugging the condensers. The increased water content of the liquids from tests 62 through 68 shows that the liquid collection was more efficient during these latter tests than during tests 59 thru 61.

The H/C atomic ratio of the coal liquids is higher than the ratio typically produced from other reactors. Merriam and Cha (1989) report similar high ratios in liquids produced from Wyodak coal. We think that this high hydrogen content of the liquids is caused by the IFB reactor. In most reactors, the vapors from the coal are exposed to particles in the reactor where conditions cause cracking and coking. This reduces the hydrogen content of the liquid and produces more gas. In the IFB reactor, the vapors are quickly swept from a shallow bed before substantial cracking or coking can occur.

The high H/C ratio is very desirable for the production of diesel fuel. However, a low H/C ratio is needed for electrode-binder pitch. Some commercial operations use heat treating and/or air-blowing to reduce the hydrogen and oxygen content of coal liquids used for binder pitch. The treatments also increase the specific gravity and carbon content of the liquids.

The material collected from the warm separator (Figure 6) changed during the series of tests (Table 19). The material consisted of fines or partially devolatilized fines from all tests except 63 and 64. The material from test 63 was a mixture of fine coal particles and volatiles. Test 64 resulted in mostly condensed liquid that was collected from the warm separator.

Table 19. Material from the Warm Separator, wt %

Test:	59	60	61	62	63	64	66	68
Material	Fines	Fines	Fines	Fines	Mixed	Liquid	Fines	Fines
Proximate								
Moisture	0	-	1.2	0	0.3	0.5	3.0	-
Volatiles	36.3	-	38.5	0	56.2	76.8	33.4	-
Ash	19.0	-	12.8	-	8.4	1.1	18.7	-
Fixed Carbon	54.6	-	47.5	-	35.4	21.6	44.9	-
Toluene Insolubles						20.2		
Quinoline Insolubles						8.3		
Ultimate (MAF)								
Carbon	77.8	-	-	-	-	76.9	-	-
Hydrogen	4.0	-	-	-	-	7.1	-	-
Nitrogen	1.1	-	-	-	-	1.0	-	-
Sulfur	0.2	-	-	-	-	0.5	-	-

The yield of coal liquids is adjusted by adding 25% of the material collected from the warm separator during test 63 and 90% of the material from test 64 to the weight of crude liquid. This adjusted yield shows a maximum MAF yield near 1150°F (621°C) (Figure 12). The MAF yield is based upon moisture and ash-free weight of the liquid products divided by the moisture and ash free weight of the coal feed to the mild gasification reactor (Table 20). (We estimate that the material from the warm separator from test 63 is 25 wt % condensed liquids based upon the volatiles content using a dry basis. We estimate that the material from test 64 is 90 wt % condensed liquid based upon ash content.)

Two factors contribute to the unplanned variation in liquid yields: (1) the relatively low elutriation of fines during tests 59 and 62, increased the liquid yields from those tests; and (2) the low collection efficiency reduced the yields from tests 59, 60, and 61. An indication of the variation in liquid yields caused used by uncontrolled factors can be seen by comparing the yields from test 60 with 63 and test 61 with 64. Test 63 resulted in a 14.0 wt % MAF yield, whereas test 60 produced 11.4 wt % although the tests were conducted at the same temperature. Tests 61 and 64 resulted in 12.7 and 15.1 wt % MAF yields, respectively.

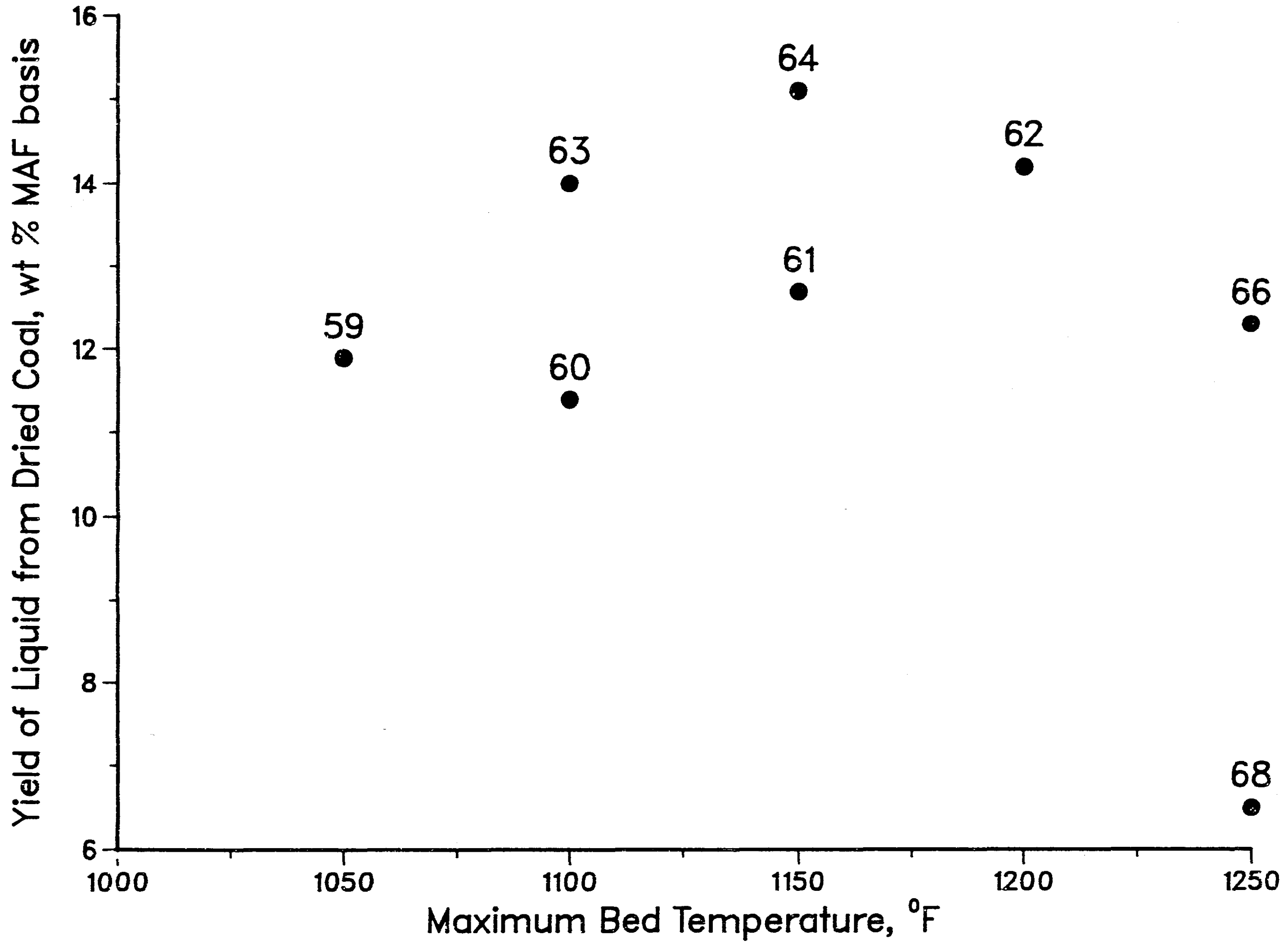


Figure 12. MAF Yield of Liquid Products versus Maximum Bed Temperature Used During Tests

Table 20. Yield of Coal Liquids from Mild Gasification Tests

Test:	59	60	61	62	63	64	66	68
Dried Coal Feed (MAF), lb	52.0	52.0	52.0	52.0	52.0	156.0	41.1	51.7
Crude Liquid Collected, lb	6.30	6.01	6.64	7.69	7.50	24.01	5.2	3.5
Ash in Liquid, lb	0.048	0.019	0.007	0.017	0.059	0.052	0.023	0.088
Water in Liquid, lb	0.047	0.048	0.039	0.305	0.142	0.382	0.114	0.077
MAF Liquid, lb	6.21	5.94	6.59	7.37	7.30	23.58	5.06	3.34
Yield, wt % MAF Feed to MG	11.9	11.4	12.7	14.2	14.0	15.1	12.3	6.5
wt % Wet Coal to Dryer	7.5	7.2	8.0	9.0	8.8	9.5	7.7	4.8

The narrow range of liquid yields and the small difference in yields between tests causes the uncontrolled variations in liquid yield to have a large effect upon the relative results.

A majority of the coal liquid produced during test 64 was sent to a commercial laboratory for distillation to produce a distillate, IBP-700°F (IBP-371°C), and a residue, +700°F (+371°C). Unfortunately, the residue did not meet the distillation specification in that it contained 14.6 wt % distilling below 700°F (371°C). The amount of water recovered during the distillation was 2.02 wt % of the feed. The loss during the distillation was 0.34 wt %. In a separate analysis conducted at WRI on the remaining portion of the coal liquid, the water was 1.89 wt % of the sample. This sample also contained 0.05 wt % ash. The coal liquid also contained 1.61 wt % of unconverted coal. In this case, unconverted coal is defined as the material not soluble in toluene and pyridine and includes the ash.

The results of simulated distillation analyses of the distillate and residue are listed in Table 21. As expected, the distillate is 100% distillable below 1000°F (538°C) having an initial boiling point (IBP) of 280°F (138°C) and a final boiling point (FBP) of 750°F (399°C). Oil distilling in this temperature range is commonly the feedstock for the production of gasoline, jet fuel, diesel fuel, and kerosene. However, more than 70% distills in the temperature range that is commonly used for the production of jet fuel and diesel fuel. As mentioned earlier, the residue contains 14 wt % distilling below 700°F (371°C). The specification limit for pitch suitable for the production of electrodes is a maximum of 5 wt %. Distillation to a higher maximum temperature or a more efficient separation will produce a product that meets this specification.

The distillate was evaluated as a feedstock for the production of transportation fuel. The chemical and physical properties of the distillate are in Tables 22 and 23, respectively. The sulfur, nitrogen, and oxygen contents of the distillate are fairly low, 0.4, 0.3, and 4.1 wt %, respectively. The H/C ratio is fairly high, 1.61, and the heating value is about 18,100 Btu/lb. A similar distillate produced from coal from the Eagle Butte mine of Wyoming by our mild gasification process had 0.8 wt % sulfur, 0.6 wt % nitrogen, and 8.5 wt % oxygen. In addition, the H/C ratio of this distillate was 1.32. The 420-700°F (216-371°C) distillate from the test using Wyodak coal was evaluated by Oak Ridge National Laboratory as a blending stock with diesel fuel for the production of substitute fuel. It was concluded that blends up to about 25% produced a marginal fuel. However, these results are tentative at this time (Daw et al. 1990).

Table 21. Results of Simulated Distillation Analysis of the Products from Test 64, wt %

Property	Distillate (IBP-700°F) D 2887	Distillate (IBP-700°F) D 86	Residue (+700°F) WRI-075
IBP-200°F	0	0	0
200-300°F	1.6	0	0
300-400°F	11.5	4.6	0
400-500°F	37.4	46.5	0.2
500-600°F	36.0	41.5	3.6
600-700°F	10.8	7.4	10.8
700-800°F	2.7	0	14.9
800-900°F	0	0	19.5
900-1000°F	0	0	10.5
Residue	0	0	40.5

Note: The distillate represents 33.8 wt % of the coal liquid produced during test 64.

The residue was evaluated as a pitch that would be used as the binder for the manufacture of electrodes. The chemical and physical properties of the residue are listed in Table 22. In addition, Table 22 lists some of the commercially available specifications that a pitch must meet in order for it to be used for the manufacture of electrodes. The quinoline and toluene insolubles and the fixed carbon are below the specification values. Quinoline insolubles and toluene insolubles are tests used to characterize a family of highly aromatic resins in coal tars. These resins have low H/C ratios, high specific gravity and viscosity, and form a coke-like residue having good binding properties when heated. This value, of course, will increase if the excessive amount of light ends distilling below 700°F (371°C) is removed but not enough to satisfy the specification. The excessive amount of distillate is only 9.5 wt %. The percentage of moisture is slightly high, and the percentage of ash is below the maximum allowed for a pitch. The moisture, in this case, probably represents evaporative loss of light ends. The viscosity of the residue is probable lower than normal, and the specific gravity is less than the required minimum of 1.31 at 77°F (25°C).

The approximate composition of a blend of the material collected from the warm separator during test 64 (Table 19) with the +700°F (+371°C) residue and subsequent reduction of the <700°F (<371°C) fraction by distillation is listed in column 4 of Table 22. This blend is the feedstock for the production of pitch. Heat treating is needed to remove most of the oxygen and hydrogen, increase the carbon, fixed carbon and insolubles content, and increase the specific gravity. Possibly, the addition of some soot will be used in combination with heat treating (or air blowing) to make specification-grade binder pitch (Gemmeke et al. 1978; Alscher et al. 1987).

Table 23 lists the results of the hydrocarbon-group-type analysis of the IBP-700°F (IBP-371°C) distillate. The distillate contained 26.9 wt % material that was not analyzed by the GC/MS because it was removed during the chromatographic separation to produce the hydrocarbon fraction. The material not recovered from the chromatographic column is very polar and contains a majority of the heteroatom-containing compounds. The hydrocarbon fraction is composed of primarily alkanes, alkenes, and indanes/tetralins. If this distillate is considered as a feedstock for the production of transportation fuel, hydrotreatment to reduce heteroatom content and to saturate alkenes may be necessary. However, research at WRI suggests that blending the distillate with diesel fuel may produce a fuel that can be used on the plant site as a transportaion fuel. In addition, caustic extraction of the distillate to remove phenols and other heteroatom-containing compounds will increase the percentage of the distillate being incorporated into the blend. To date, compatibility and stability tests have not been conducted by WRI on such blends.

Table 22. Comparison of the Properties of the Products from Test 64 with Commercially Available Pitch Specifications

Property	Specification	Distillate (IBP-700°F)	Residue (+700°F)	Residue + Warm Separator (Calc)
Quinoline Insolubles, wt %	12-17	-	0.7	2.7
Toluene Insolubles, wt %	26 min	-	11.0	14.3
Beta Resins, wt %	15 min	-	10.3	11.6
Fixed Carbon, wt %, MAF	54 min	0.0	11.4	15.0
Moisture, wt %	0.2	-	0.3	0
Ash, wt %	0.35 max	-	0.2	0.45
Carbon, wt %	-	84.4	80.8	80.0
Hydrogen, wt %	-	11.4	8.5	8.2
Atomic C/H Ratio	1.70 min	0.62	0.80	
Sulfur, wt %	0.6 max	0.4	0.4	0.4
Nitrogen, wt %	-	0.3	0.9	0.9
Oxygen, wt %	-	4.1	8.8	
Total, wt %	-	100.6	99.4	
Viscosity, cP				
221°F	10,000 max	-	638	
302°F	5,000 max	-	36.9	
Specific Gravity, 77°F	1.31 min	0.8989	1.103	
Specific Gravity, 60°F	-	0.9050	1.106	
Heating Value, Btu/lb	-	18,134	16,164	
Distillate, wt % <700°F	5.0 max	97.3	14.7	5.0

Table 23. Results[a] of the Hydrocarbon-Group-Type Analysis of the IBP-700°F Distillate from Test 64, wt %

Saturate Hydrocarbons		Aromatic Hydrocarbons	
Alkanes	23.5	Alkylbenzenes	4.3
Alkenes	26.2	Indanes/Tetralins	15.5
Monocyclic Alkanes	0.1	Naphthalenes	2.4
Dicyclic Alkanes	0.1	Fluorenes	0.3
Tricyclic Alkanes	0.5	Anthracenes	0.2
Total Saturate Hydrocarbons	50.4	Total Aromatic Hydrocarbons	22.7

[a] 26.9 wt % of sample not analyzed by GC/MS

The results of a detailed GC/MS analysis of the IBP to 700°F (IBP to 371°C) distillate from test 64 are listed in Table 24. These results include the gas chromatographic retention time, the identity of the compound, and the area percentage that compound represents of the total gas chromatographic peak area. Several of the gas chromatographic peaks could not be identified because their intensity was too low to record reliable mass spectra or the peaks contained more than one component. In these cases the identity of the peak is labeled unknown.

Examination of these results shows that the sample is composed primarily of normal alkanes, 1-alkenes, and aromatic hydrocarbons. The normal alkanes and 1-alkenes represent a large fraction of this sample, as shown in the results of the hydrocarbon-group-type analysis. The normal alkanes and 1-alkenes are predominantly in the 13 to 27 carbon number range. Cetane (C_{16}) is the alkane used to characterize diesel fuel. Alkanes in the C_{13} to C_{27} range are desirable components of diesel fuel. Alkenes (olefins) are not desirable components of fuels because the double bond is highly reactive making the fuel unstable during storage. Diesel fuel can contain up to 20% aromatics and still meet specifications for good performance.

Several oxygenated compounds such as substituted benzofurans were identified in this sample. The presence of these compounds is expected in the neutral fraction because these compounds do not have strong functionalities and will easily elute from the alumina column with benzene. Oxygen-containing compounds are susceptible to polymerization, which causes formation of gum in fuels.

Table 24. Compounds Identified in the IBP-700°F Distillate from Test 64 by Detailed Analysis Using Gas Chromatography/Mass Spectrometry

Retention Time, min	Compound or Compound Type	Area Percent
1.8	Benzene	0.07
7.4	1,2,4-Trimethyl-benzene	0.22
7.8	1-Decene	0.10
8.3	1,3,5-Trimethyl-benzene	0.32
8.5	1-Methyl-3-propyl-benzene	0.21
9.0	1-Ethynyl-4-methyl-benzene	0.13
10.6	1-Ethyl-2,4-dimethyl-benzene	0.10
11.1	Methyl(1-methylethynyl)-benzene	0.23
11.6	7-Methyl-benzofuran	0.08
11.8	2-Methyl-benzofuran	0.38
12.3	1,2,4,5-Tetramethyl-benzene	0.31
12.9	2,3-Dihydro-4-methyl-indene	0.18
13.4	1-Methyl-indene	0.86
13.6	3-Methyl-indene	0.96
14.8	Naphthalene	0.66
15.1	2,3-Dihydro-1,6-dimethyl-indene	0.39
15.5	2,3-Dihydro-4,7-dimethyl-indene	0.30
16.1	4,7-Dimethyl-benzofuran	0.22
16.4	Unknown	0.83
16.5	C_1 substituted Tetralin	0.56
16.7	C1 substituted Tetralin	0.25
16.9	n-Dodecane	0.40
17.3	1,3-Dimethyl-5-(1-methylethyl)-benzene	0.14
17.5	6-Methyl-dodecane	0.28
17.9	1,2-Dihydro-3-methyl-naphthalene	0.23
18.1	1,2-Dihydro-6-methyl-naphthalene	0.33
18.3	1,1-Dimethyl-indene	0.88
18.6	Methyl-dihydro-naphthalene	0.18
19.2	2,3-Dihydro-4,7-dimethyl-indene	0.45
19.4	1-Ethyl-2,4,5-trimethyl-benzene	0.25
19.8	2-Methyl-naphthalene	1.08
20.3	1-Ethyl-2,3-dihydro-1-methyl-indene	0.32
20.5	1-Methyl-naphthalene	0.87
20.8	1-(1-Methylethynyl)-benzene	0.30
21.0	1-Tridecene	1.57
21.2	n-Tridecane	0.49
21.5	Unknown	0.06
22.0	1-Methyl-4-(1-methylethylindene)-cyclohexane	0.06
22.2	1,3,5-Trimethyl-2-(1,2-propanynyl)-benzene	0.13
22.7	1,2,3,4-Tetrahydro-1,6,8-trimethyl-naphthalene	0.60
22.9	Methyl-anthracene	0.54
23.7	1-Chloronaphthalene (internal standard)	7.21
23.8	Unknown	1.10

Table 24. Compounds Identified in the IBP-700°F Distillate from Test 64 by Detailed Analysis Using Gas Chromatography/Mass Spectrometry (Continued)

Retention Time, min	Compound or Compound Type	Area Percent
24.1	C_3 substituted Tetralin	0.07
24.5	C_3 substituted Tetralin	0.22
24.7	1,5-Dimethyl-naphthalene	0.52
24.9	Unknown	0.53
25.5	1,8-Dimethyl-naphthalene	3.42
25.7	1,2,3,4-Tetrahydro-1,5,8-trimethyl-naphthalene	0.19
26.0	n-Tetradecane	1.34
26.2	2,7-Dimethyl-naphthalene	0.28
26.7	Dimethyl-naphthalene	0.26
27.1	1,4-Dimethyl-2-(2-methylpropyl)-benzene	0.08
27.3	Unknown	0.29
27.6	1,2-Dihydro-acenaphthylene	0.41
28.0	1,2,3,4-Tetrahydro-1,5,7-trimethyl-naphthalene	0.83
28.2	Unknown	0.45
28.4	2,3-Dihydro-3,3,4,5-tetramethyl-1H-indene-1-one	0.34
28.6	4,6-Dimethyl-tetradecane	0.92
28.8	C_3-substituted Naphthalene	0.23
29.0	1,5,5,6-Tetramethyl-1,3-cyclohexadiene	0.94
29.1	Unknown	0.14
29.2	Dibenzofuran	0.14
29.5	2,3-Dihydro-3,3,4,7-tetramethyl-1H-indene-1-one	1.14
29.7	1-Pentadecene	1.45
30.1	n-Pentadecane	1.16
30.3	Unknown	0.15
30.5	2,3,6-Trimethyl-naphthalene	0.45
31.0	2-(1-Methylethyl)-naphthalene	0.68
31.2	1,6,7-Trimethyl-naphthalene	0.54
32.1	1,3,6-Trimethyl-naphthalene	2.42
32.2	Methyl-acenaphthylene	0.27
32.5	Biphenylene	0.08
33.1	Unknown	0.18
33.6	1-Hexadecene	1.54
34.0	n-Hexadecane	1.82
34.3	Unknown	0.13
35.0	1-Methyl-7-(1-methylethyl)-naphthalene	0.07
35.5	C_5-substituted naphthalene	0.59
35.9	Unknown	0.73
36.3	1-Methyl-9H-fluorene	0.15
36.5	1H-Phenalene	0.11
36.8	Unknown	0.05
37.4	1-Heptadecene	2.23
37.8	n-Heptadecane	1.78
38.0	7-Methyl-nonadecane	0.47

Table 24. Compounds Identified in the IBP-700°F Distillate from Test 64 By Detailed Analysis Using Gas Chromatography/Mass Spectrometry (Continued)

Retention Time, min	Compound or Compound Type	Area Percent
39.0	Unknown	6.41
39.4	Unknown	3.65
39.9	Unknown	0.32
40.2	Unknown	0.26
40.5	Unknown	0.20
41.0	1-Octadecene	1.98
41.4	n-Octadecane	1.89
41.7	Unknown	0.35
42.7	Unknown	0.19
44.4	1-Nonadecene	1.97
44.7	n-Nonadecane	2.44
45.1	Unknown	0.02
46.8	Unknown	0.46
47.4	Unknown	0.63
47.6	1-Eicosene	2.06
47.9	n-Eicosane	2.26
50.7	1-Heneicosene	1.86
51.0	n-Heneicosane	2.70
51.3	Unknown	0.19
52.7	Unknown	0.17
53.6	1-Docosene	1.89
53.9	n-Docosane	2.47
54.2	Unknown	0.16
56.4	1-Tricosene	1.44
56.7	n-Tricosane	2.20
59.2	1-Tetracosene	1.70
59.4	n-Tetracosane	1.49
61.7	1-Pentacosene	0.60
61.9	n-Pentacosane	1.34
64.2	1-Hexacosene	0.68
64.4	n-Hexacosane	0.55
66.6	Unknown	0.19
66.8	n-Heptacosane	0.35
68.9	Unknown	0.22
69.1	Unknown	0.16

5.0 DISCUSSION OF RESULTS

The drying produced the expected results. All of the moisture measured by proximate analysis was removed from the coal. The coal was partially decarboxylated with 2.3 wt % of the raw coal removed as gas. The minus 100-mesh fraction of the raw coal was elutriated as fines from the dryer. All of the moisture was essentially removed from the coal in the first one-half of the dryer. Most of the decarboxylation occurred in the first one-half of the dryer.

The residence time measurements from the mild gasification tests (Table 5) are very inconsistent. In retrospect, we could have obtained better residence time measurements if we had conducted the tests at feed rates of 20-lb/hr or higher (Figure 3). However, the cost would have increased, and we would have needed to construct a higher-capacity fluidizing gas heater. The residence time used for test 64 was sufficient to devolatilize the coal to a residual level fixed by the bed temperature (Figure 8).

The quantity of fines produced during the mild gasification tests is unexpectedly high. There are several possible causes for the high fines production. We may have had more severe fluidization conditions in the mild gasification reactor than we used in the dryer. Handling the dried coal, especially feeding the dried coal through a screw feeder, may have generated more fines. The volatiles contents of the fines suggests that they formed by degradation of coal in the mild gasification reactor.

More gas is produced from the Usibelli coal during mild gasification than we typically produce when using Wyodak coal. Also, the gas contains more oxygen (in carbon monoxide and carbon dioxide) than gas produced by mild gasification of Wyodak coal. The higher oxygen content of the Usibelli coal produces more oxygen-containing gases. A more accurate determination of the composition and quantity of the gas product can be made if tests are conducted using recycle gas.

The 92 to 97% closures of coal balances suggest a systematic error in the data. We undoubtedly lost some of the water generated in the mild gasification reactor. This is water formed by chemical reactions or water released from hydrates that decompose at temperatures used in the mild gasification reactor. The low partial pressure of liquids in the effluent gas stream permits some high-vapor-pressure liquids to pass through the collection system. We expect that the loss of coal liquids through the collection system is small because the coal liquids produced are predominately high-boiling liquids. We produced MAF yields from Wyodak coal of 12 to 15 wt %. These values are almost identical to the yields from Usibelli coal. Perhaps yields from Usibelli coal could have been 0.5 wt % higher, if a recycle gas system had been used (i.e., 14.5% instead of 14.0).

The char oxidizes readily when it is exposed to ambient temperature air shortly after the char is taken from the reactor. We have observed that chars (Usibelli and Wyodak) do not oxidize as readily in air after the chars have been aged under inert gas for several days. The Usibelli char produced during test 62 does not contain as much moisture at equilibrium as raw coal contains.

The heating values of the chars produced during the tests (Table 14) are similar except for the heating values of chars from tests 62, 64, and 68. The chars from tests conducted at higher temperature (62, 64, and 68) have lower oxygen contents than chars from the other tests.

Thus, the high heating value for char from test 62 is consistent with the conditions used for that test. The low heating value for char from test 64 is not consistent with other conditions and probably is the result of an error in sampling or measurement.

There are several possible markets for the char: (1) conversion to high-purity carbon for sale as electrode-grade carbon or carbon black, (2) conversion to activated charcoal, (3) conversion to metallurgical-grade coke, or (4) use as boiler fuel. Char produced from Wyodak coal under similar conditions is highly reactive to both hydrogenation and oxidation. The low sulfur content of the char is an attractive characteristic for both metal production and fuel uses. The high reactivity of the char is a desirable characteristic for use in conversion processes, but it will be a problem for transportation of untreated char. The susceptibility to oxidation and the high volatiles content available for ignition should make the char an excellent fuel. If the char is converted to coke some of the liquid may be used as a binder.

The carbon dioxide content of the gas produced during the mild gasification tests (Table 17) is an approximate estimation for reasons discussed previously. We did not measure the content of sulfur-containing gases during these tests. The heating value of the gas may be about 200 to 500 Btu/scf. The gas has value for use in supplying heat to a processing unit or for combustion in a gas turbine to produce electrical power. The gas can also be converted to synthesis gas for use in processing.

The liquid produced by mild gasification of Usibelli coal is a heavy, tarry substance with about 60 wt % of the dry, coal liquid boiling above 700°F (371°C). The production of heavy liquids is a characteristic of the IFB reactor when using both coal and oil shale. The minimization of cracking and coking in the shallow, fluidized-bed reactor results in a high yield of heavy liquid having a high hydrogen content and a low yield of gaseous products.

The range of liquid yields (Table 20) is narrower than we expected to produce from the variation in temperatures used during the tests. The range of yields from these tests using Usibelli coal is in the center of a broader range of yields determined from previous bench-scale tests using Wyodak coal (Merriam and Cha 1989).

The material collected in the warm separator at about 250°F (121°C) varies considerably. The material collected during all tests except 63 and 64 is coal dust with a volatiles content lower than the dried coal feed. The material collected in the warm separator during test 63 is an agglomerate of coal dust and volatiles that contains 56 wt % volatiles and 8 wt % ash. The material collected during test 64 is a hard, black, shiny substance that has the appearance of a frozen liquid. It contains 77 wt % volatiles and 1 wt % ash. Some of the coal liquids produced in the reactor during tests 63 and 64 were collected in the warm separator.

About 60 wt % of the dry coal liquid from test 64 boils in the range needed for electrode-binder pitch. About 35 wt % boils in the range needed for diesel fuel, with the remaining 5 wt % boiling in the gasoline range (Table 21).

The +700°F (+371°C) boiling residue has an acceptable sulfur and ash content for use in electrode binder-pitch (Table 22). The low fixed-carbon content can be increased by heat treating the residue to drive off hydrogen and oxygen. Heat treating results in condensation of the organic structure, thus, producing a more aromatic material. The material collected from the warm separator during test 64 contains 77.2 wt % volatiles, 1.1 wt % ash, and 21.7 wt % fixed carbon, which will significantly raise the fixed-carbon content of the residue. The increase in fixed-carbon content of the liquid and removal of hydrogen and oxygen will increase the quinoline and toluene insolubles and specific gravity of the residue.

The distillate from test 64 (Tables 21 and 22) contains more hydrogen than is typical in liquids produced by gasification of coal. The high hydrogen content is desirable for use of the distillate as blending stock for diesel fuel, whereas the high oxygen, sulfur, and nitrogen contents are undesirable. We expect that the oxygen is concentrated in tar acids, which typically comprise about one-third of the low-boiling coal liquids. Tar acids can be removed from the neutral oil by methanol-water extraction, caustic wash or hydrotreating. In some instances, untreated distillates have been successfully burned in diesel engines as blends with diesel fuel. The coal-derived fuels generally perform best in low-speed diesel engines.

The 0.4 wt % sulfur content of the distillate exceeds the present specification of 0.25 wt % maximum sulfur in diesel fuel. Also, the U.S. EPA proposed a reduction of the maximum sulfur content of diesel fuel to 0.05 wt % by 1993. The typical method for sulfur removal, hydro-desulfurization, is an expensive process. However, the high hydrogen content of the distillate should reduce the cost of hydrotreating.

Other possible markets for the distillates include conversion to gasoline, jet fuel, kerosene, or solvents. Market evaluation and further technical evaluation are needed to determine the most likely combination of products to achieve a commercially successful operation.

6.0 CONCLUSIONS AND RECOMMENDATIONS

We have drawn the following conclusions from the results of tests described in this report:

- Usibelli coal can be successfully dried to zero moisture content and partially decarboxylated using the conditions described in this report.

- Mild gasification of dried Usibelli coal results in production of about 50 wt % char, 20 wt % gas, 11 wt % coal liquids, and 11 wt % fines.

- Char produced by mild gasification contains about 20 wt % volatiles, has a hydrogen-to-oxygen mass ratio of 0.24, and has a gross heating value of about 10,800 Btu/lb. The char does not contain as much moisture at equilibrium as the raw coal.

- The coal liquid collected is a heavy, tarry, substance that contains about 5 wt % boiling in the gasoline range, about 35 wt % in the diesel-fuel range, and about 60 wt % in the electrode-binder-pitch range.

- The MAF yields of dry, hydrocarbon liquids of the coal feed to the mild gasification reactor vary from 11.4 to 15.0% under the conditions tested.

We recommend that the following work be done to test the suitability of the products for selected markets.

- The char should be tested for use as a source of high-purity carbon, metallurgical-grade coke, or fuel depending upon the most promising market.

- The distillate portion of the liquid should be tested for use in diesel fuel. Upgrading tests such as extraction, caustic washing, or hydrotreating should be conducted as part of the evaluation.

- The residue portion of the liquid should be upgraded to meet specifications for electrode-binder pitch or tested for use as a binder in briquetting green coke.

- The composition of the gas should be more accurately determined by using a recycle gas system to conduct mild gasification tests. This can be done by using the 100-lb/hr PRU or by adding a recycle gas system to the 1-inch reactor.

- Tests should be conducted using conditions that permit more accurate determination of char residence time.

- Sufficient quantities of materials should be produced to permit large-scale tests of product use. The 100-lb/hr PRU system is well suited for this purpose.

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8.0 DISCLAIMER

Mention of specific brand names, models of equipment or processes is for information only and does not imply endorsement of any particular brand.

9.0 REFERENCES

Alscher, A., W. Gemmeke, F. Alshmeier, and W. Boenigh, 1987, Evaluation of Electrode Binder Pitches for the Production of Prebaked Anodes Using a Bench Sale Process, Light Metals, p. 483-490.

ASTM, 1952, ASTM--IP Petroleum Measurement Tables, American Society for Testing Materials: Philadelphia, PA.

Boie, W., 1952, Wissenchaftliche Zeitschrift der Technischen Hochschule Dresden, 2: 687.

Boysen, J.E., C.Y. Cha, F.A. Barbour, R.F. Turner, T.W. Kang, M.H. Berrgren, R.F. Hogsett, and M.C. Jha, 1990, Final Report for Development of an Advanced Process for Drying Fine Coal in an Inclined Fluidized Bed. Laramie, WY, Western Research Institute Report to DOE, Pittsburgh Energy Technology Center, WRI-90-R031.

Daw, C.S., R.L. Graves, R.P. Krishnan, B.H. West, A.L. Compere, and W.L. Griffith, 1990, Mild Gasification Product Characterization--1990 Results. Proceedings of Tenth Annual Gasification and Gas Stream Cleanup Systems Contractor Review Meeting, U.S. DOE, Morgantown, WV.

Edwards, J.H., I.W. Smith, and R.J. Tyler, 1983, The CSIRO Flash Pyrolysis Project: Compendium of Data. North Ryde, NSW, Austrailia, Investigation Report 140.

Gemmeke, W., G. Collin, and M. Zander, 1978, The Characterization of Binder Pitch (II), Light Metals, p. 355-367.

Merriam, N.W., and C.Y. Cha, 1989, Development of an Advanced, Continuous Mild Gasification Process for the Production Of Co-Products, Topical Report for Task 2, Mild Gasification Tests. Laramie, WY, Western Research Institute Report to DOE, WRI-91-R018.

Merriam, N.W., C.Y. Cha, T.W. Kang, and M.B. Vaillancourt, 1990, Development of an Advanced, Continuous Mild Gasification Process for the Production of Co-Products, Topical Report for Task 4, Mild Gasification Tests - System Integration Studies. Laramie, WY, Western Research Institute Report to DOE, WRI-91-R023.

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