

FINAL TECHNICAL REPORT

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Project Title: REACTIVITY AND COMBUSTION PROPERTIES OF COAL AND COAL DERIVED SOLID FUELS. PART A: SAMPLE PREPARATION, CHARACTERIZATION, AND REACTIVITY MEASUREMENTS.

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ABSTRACT

Using thermogravimetry-combustion methods, burning properties of a number of partially devolatilized (PD) coals and desulfurized coal-derived fuels were determined. The objective was to obtain information on the impact of reduced volatility on the combustion characteristics of the fuels.

Results obtained suggest that PD coals with comparable volatile matter content produced from the same coal but under different processing conditions had different burning characteristics. Lower preparation temperatures, higher heating rates and shorter soak times at final pyrolysis temperatures increased reactivity. PD coals with inherent volatile matter were more reactive than fuels with comparable volatile matter prepared by blending low volatile chars and the raw coal.

The major conclusions of this work are: 1) volatile matter alone may not be a valid index of reactivity; 2) the reactivity of a PD coal is highly dependent on the process through which it is produced; and 3) Thermogravimetry is a rapid and cost effective method to obtain relative burning characteristics of fuels tested under specified conditions.

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EXECUTIVE SUMMARY

Project background and objectives

Much of the coal mined in Illinois is high volatile bituminous coal with a high sulfur content. Thermal and chemical coal desulfurization processes designed to yield refinable petroleum substitutes and solid fuels for boilers reduce the fuel's volatile matter content. This reduced volatility influences combustion characteristics such as ignition temperature, flame stability and carbon burn-out in as yet unquantified ways.

One aspect of the work was to prepare sufficient quantities of an Illinois coal and three partially devolatilized coals derived from the same coal for thermogravimetry combustion studies at ISGS, fluidized-bed combustion testing at Argonne National Laboratory, and flame stability characterization in a pulverized coal burner at the University of Illinois, Urbana-Champaign. The major objective was to determine the impact of reduced volatile matter on the combustion properties of coal-derived solid fuels. The other objective of this project was to determine and compare reactivities of various desulfurized fuels produced by physical, chemical and thermal processes.

Experimental

Three partially devolatilized (PD) coals were produced from IBCSP-3 coal (volatile matter 35.7%) in the Mild Gasification pilot plant unit at United Coal Company Research Corporation (UCCRC) in Bristol, Virginia. The coal and three PD coals were subjected to a series of screening, crushing, and riffing steps at the ISGS to prepare representative sub-samples of each fuel. The three PD samples and coal were subjected to proximate and ultimate analyses, heating value determinations, and thermal analysis to determine changes that occurred during pyrolysis and how they might affect the combustibility of the fuels.

A microbalance reactor was used to prepare gram-sized PD coal samples under the following conditions: heating rates between 5 and 1200°C/min; heat-treatment temperatures between 400 and 950°C; soak times up to 4 hours. The specific surface areas of these fuels were determined by BET (N₂) and BET (CO₂) methods.

A Dupont 951 thermal analyzer was used to determine thermogravimetry-combustion reactivities of fuels. Both isothermal and nonisothermal methods were employed. Burning profiles of the coal and PD coals were obtained by heating a small sample mass (2 mg) in air at a heating rate of 20°C/min from ambient to 900°C. Isothermal reactivity tests were conducted in the temperature range between 425 and 575°C. Fuel particle sizes were -170 mesh.

Results

PD coals prepared at UCCRC had volatile matter contents (dry basis) of 11.4%, 15.4% and 23%. Volatile release data revealed that PD coals were not homogeneous but were mixtures of particles having different volatile matter content. Burning profiles (a plot of rate of carbon burn-off

against temperature) showed that at least two types of combustibles of higher and lower reactivity were present in the PD coals. The two portions of combustibles burned in two distinct stages with peak burn rates at about 500 and 550°C. The burning characteristics of the higher-reactivity portion, which was present in a larger percentage in the high volatile PD coal, was similar to that of the raw coal. The results suggested that the coal was the easiest fuel to burn followed by the high, medium and low volatile PD coals.

PD coals produced in a microbalance reactor had volatile matter contents between 2 and 30%. These fuels had different burning characteristics but exhibited a single burn profile during combustion. Lower heat-treatment temperatures, rapid heating rate and shorter soak times at peak pyrolysis temperature increased reactivity. Fuels with volatile matter contents above 10% had similar burning behavior. However, burn temperatures increased markedly with further decrease in volatile matter contents. PD coals prepared in the microbalance reactor were more reactive than their UCCRC counterparts. Fuels prepared by blending low volatile chars and the raw coal were less reactive than a PD coal with comparable volatile matter content prepared in the microbalance.

The results of isothermal reactivity tests showed that the relative available pore surface area changed with conversion during combustion. The extent of surface area development was higher for fuels prepared at lower temperatures. The reactivities of fuels were closely related to the surface area development during combustion. Arrhenius-type plots were made to determine activation energies for a selected number of PD coals. The activation energy was 31 kcal/mole in all cases. However, a PD coal prepared at 600°C was three times more reactive than a char produced at 950°C.

The burning characteristics of the partially desulfurized fuels were determined by non-isothermal TG-combustion methods. The burning characteristics of a physically cleaned coal was similar to that of its parent coal. Desulfurized chars prepared by steam desulfurization at 700°C and hydrodesulfurization at 850°C were less reactive than the coal they were derived from. Again, heat-treatment temperature was the major factor dictating burning characteristics.

In Part B of this work, the combustion characteristics of the raw coal and three PD fuels prepared at UCCRC were investigated in fluidized-bed combustion tests at Argonne National Laboratory (ANL). The results of the fluid-bed experiments were in agreement with the thermogravimetric measurements of combustion reactivity.

Conclusions

The major conclusions drawn from this research were:

- o Volatile matter alone can not be used as an index of reactivity
- o Burning characteristics of a PD coal depend on the process through which it is produced

- o Lower heat treatment temperature, rapid heating rate and shorter soak time at maximum heat-treatment temperature favor reactivity
- o Fuels with inherent volatile matter are more reactive than those with comparable volatile matter prepared by blending low volatile chars with coal
- o Thermogravimetry is a rapid and cost effective technique to obtain information on the compositional and combustion properties of solid fuels

Recommendations

Future research efforts should be directed to determine the interrelationship between volatile matter and particle size and their effects on combustion characteristics. It would be desirable to obtain carbon loss data in a drop tube furnace type reactor under conditions representative of a coal-fired boiler. It is highly recommended that a process scheme for producing PD coals be identified prior to combustion tests. Finally, the potential of thermogravimetry to predict high temperature burning characteristics of fuels should be studied.

OBJECTIVES

A major emphasis of this work was to determine the effect that varying levels of volatile matter in a fuel have on the subsequent combustion properties of this fuel. The specific goals of the project were as follows:

1. Prepare pound quantities of three partially devolatilized (PD) coals from an Illinois coal.
2. Determine the impact of reduced volatile matter on the combustion characteristics of fuels.
3. Determine combustion properties of partially desulfurized fuels.
4. Determine how well thermogravimetry-combustion can predict combustion behaviors of fuels in two types of larger reactors (fluidized-bed combustor, pulverized coal burner).

INTRODUCTION AND BACKGROUND

Much of the coal mined in Illinois is high volatile bituminous coal with a high sulfur content. Concerns over air pollution and acid rain currently discourage the continued use of this resource in both industrial and utility steam boilers. It would be highly beneficial to the Illinois Coal Industry if processes were developed to convert the high-sulfur coal into environmentally acceptable feedstocks.

Thermal and chemical coal-desulfurization processes designed to yield solid fuels for boilers reduce the fuel's volatile matter content. This reduced volatility influences combustion characteristics such as ignition temperature, flame stability, and carbon burn-out in as yet unquantified ways. This study was undertaken to determine combustion characteristics of partially devolatilized fuels.

Literature Review

Numerous reactivity studies have been conducted by various investigators on a variety of coal chars under widely varying experimental conditions (Jenkins et al., 1973; Dutta and Wen, 1977; Knight and Sergeant, 1982-1983; Radovic et al., 1983-1984; Katta and D. L. Keairns, 1984; Wells et al., 1984). Several comprehensive reviews on the combustion (Essenhigh, 1981; Smith, 1982) and gasification (Dutta and Wen, 1977; Laurendeau, 1978; Johnson, 1981) of coal chars have also been published. On the basis of information available from these studies, it can be concluded that the reactivity of a char is related to its parent coal, the conditions under which it is prepared and its mineral matter composition and distribution.

Lower rank coals release many volatile compounds which open up internal pore surface area. In contrast, higher rank coals have very little volatile matter to release and their pores remain very small, virtually impervious to the reactant gas during combustion or gasification. Some of the important process parameters that affect the reactivity are pyrolysis

environment, heating rate, maximum heat treatment temperature, soak time at peak temperature, pressure, preoxidation and particle size. These factors extensively influence the pore structure, active surface area, accessibility of the gaseous reactant to the micropores and the distribution and composition of mineral matter in the devolatilized fuel.

Results from recent studies (Solomon, 1986; Khan, 1987) suggest that char formation conditions that result in a higher H/C ratio (atomic) or hydrogen content favor reactivity. Low-temperature chars are significantly more reactive than high-temperature chars, at least in part, due to their greater hydrogen contents (Khan, 1987).

Burning profile

The term burning profile was first used (Wagoner and Duzy, 1967) twenty years ago to refer to a plot of the rate of weight loss versus temperature when a small amount of coal-derived fuel is heated (usually 15-20°C/min) in air. Derivative thermogravimetry (DTG) was used to obtain burning profiles. Characteristic temperatures from the burning profile corresponding to the onset of burning, peak burning rate and complete burn-out were taken as a measure of a fuel's reactivity, with lower characteristic temperatures indicating more easily burned fuels. The test was used with past experience and standard reference profiles to predict conditions, such as residence time or excess air, necessary for complete combustion of fuels in large furnaces. The burning profiles were found especially useful for evaluating combustion characteristics of unknown fuels when only small quantities of fuel were available.

In recent years, the concept of burning profiles has been used extensively in coal combustion studies to show the effect of variations in coal rank on reactivity (Morgan et al., 1986), to show the influence of maceral composition on combustion of pulverized coal (Morgan et al., 1986, 1987) and to determine the activation energy for combustion reactions (Cumming, 1984; Solomon et al., 1986; Khan 1987).

EXPERIMENTAL PROCEDURES

Char Production at the UCCRC

Samples of partially devolatilized coal were produced in the Mild Gasification Unit (MGU) at United Coal Company Research Corporation (UCCRC) in Bristol, Virginia. Six barrels of IBCSP-3 coal (2200 lbs) were delivered (by M. Rostam-Abadi and C. W. Kruse) to UCCRC on September 18, 1986. The treated samples were shipped to the ISGS on November 15, 1986. The details of char production at the UCCRC are given in Appendix 1.

Basically, the MGU was operated as follows: coal from volumetric loading hoppers was charged into 8-inch-diameter, 8-foot-long, tapered reactor tubes. The reactor tubes were located in a natural gas fired furnace which was kept at 760°C during the tests. Two reactor tubes, with 125 lbs of coal per tube, were used for each test. The coal was heated in the sealed reactor tubes under a slight vacuum to exclude air, for a predetermined length of time. Vapor from the devolatilization of the coal was pulled by a vacuum pump from the reactor tubes into the MGU's condensing system. At

the end of the test run, the char was discharged from the reactor tubes into the char discharge system by means of hydraulic plungers.

Three preliminary tests were conducted to determine the conditions necessary to produce the desired product chars. During these tests the char was discharged directly into the char quench chamber where it was cooled with a water spray. However, since this area of the MGU was not sealed from the atmosphere, the char discharge procedures were slightly modified for all production runs to prevent oxidation of the hot char by contact with air.

Three production tests were performed. The residence times were 1.70, 2.90 and 3.17 hours. After the reaction cycle was complete, the char was discharged from the reactor tubes and held on a gate in the char chute leading to the quench chamber. This section of the char chute was kept under a nitrogen blanket during the char discharge sequence. The char was partially quenched with water and allowed to cool on the gate to approximately 93°C. Char was discharged into the quench chamber and immediately transferred to a 55-gallon drum. The drum was then sealed and purged with nitrogen. The char was allowed to cool in the drum under a nitrogen blanket to ambient temperature. After reaching ambient temperatures, the char was crushed in a hammermill crusher without screen. After crushing the char, a total of 170-200 lbs was riffled to a sample size of 10-15 lbs. This sample was sent to United Coal Company's Wellmore Central Laboratory for moisture and volatile matter analysis. After sampling, the char was immediately transferred back to a 55-gallon drum. The drum was purged with nitrogen and then sealed under 2 psi of nitrogen.

Sample Preparation

The PD coals prepared during the three production tests at UCCRC and the original coal were crushed and riffled to prepare appropriate samples for distribution to ISGS, ANL and UI-UC. Figure 1 shows the flow chart followed to prepare representative samples. In accordance with ASTM standards, each sample was crushed using a roll crusher with rollers set progressively closer until 100% of the particles passed through a 3/8" mesh screen. A 40-50 pound sample was split out by successive riffling and set aside for UI-UC. The remaining sample was then crushed to -8 mesh. The sample was then riffled to a 70-80 pound size for ANL, and the remaining 40-70 lbs were kept for use at ISGS. The sample reserved for use at ISGS was further riffled to 300-500 grams for a sieve analysis as well as proximate and ultimate analyses. All samples were placed in plastic bags and transferred back to 55-gallon drums. The drums were purged with nitrogen and sealed under 2 psi of nitrogen.

As will be explained later, it became necessary to mix two of the chars produced under preliminary testing conditions to prepare a PD coal sample with a desired volatile matter content. A homogenized mixture was obtained by successive riffling of the two samples. Representative samples were prepared using the procedures outlined above.

Char production in the microbalance

A number of PD coals were prepared under controlled pyrolysis conditions in a thermobalance reactor (DuPont 951 or Cahn RG microbalance). In these

experiments, 500-600 mg of 8x14 mesh coal (IBCSP-3) were heated under nitrogen purge to a predetermined temperature. In some runs the sample was held at the final pyrolysis temperature for a sufficient time to achieve a desired level of devolatilization. Production conditions were: heating rates between 5 and 1200°C/min; pyrolysis temperatures between 400 and 950°C; soak times up to 4 hours. The samples were stored under nitrogen and were crushed and screened to -170 mesh before being tested for their combustion properties.

Physical and chemical analyses

The proximate analysis of each sample (-60 mesh) was obtained by an automatic LECO MAC 400 and the ultimate analysis was done using a LECO CHN 600 analyzer. A LECO SC32 analyzer was used to obtain total sulfur content. Forms of sulfur were determined according to the ASTM D2492 method.

Microproximate analyses and devolatilization behavior of some samples were obtained by nonisothermal thermogravimetry (TG) using a DuPont 951 TGA. A sample weighing 5-10 mg was placed on the platinum pan of the TGA. A nitrogen purge (dry, 99.999% pure) at a rate of 200 cc/min was used for a period of 20 minutes to remove any oxygen remaining in the system. During the purging period, a substantial portion of the sample moisture was removed. The sample was weighed and heated to 900°C at a constant heating rate of 20°C/min.

The specific surface areas of a number of samples were determined from nitrogen and carbon dioxide adsorption at -196 and -88°C, respectively, in conjunction with the Brunauer, Emmett, and Teller (BET) equation.

Reactivity measurements

A DuPont 951 model instrument coupled to an Omnitherm QC25 Programmer/Controller was used to obtain thermogravimetry (TG) and derivative thermogravimetry (DTG) combustion curves. The system was interfaced with an IBM-XT computer through a Keithley DAS series 500 data acquisition system to provide automated data collection and storage.

Reactivities of the fuels were determined by isothermal and nonisothermal TG methods. In a nonisothermal experiment, a sample mass of about 2 mg was loaded in a platinum pan and was heated at a constant heating rate of 20°C/min in air from ambient to temperatures up to 900°C. An air flow rate of 200 cc/min (STP) was used. When sample masses above 3 mg and air flow rates less than 100 cc/min were used, the temperature in the gas phase, measured by a thermocouple close to the sample pan, increased as much as 30°C. This was caused by sample ignition which resulted in uncontrolled heating. For some reactive fuels it was necessary to reduce the sample mass to less than 1 mg and reduce the heating rate to 5°C/min to eliminate the likelihood of sample ignition. Nonisothermal data were used to obtain burning profiles by plotting weight loss (TG thermal curve) and rate of weight loss (DTG thermal curve) versus temperature.

To determine reactivity under isothermal conditions, a sample mass of 1 to 2 mg was placed in the TGA pan and heated in the presence of nitrogen at

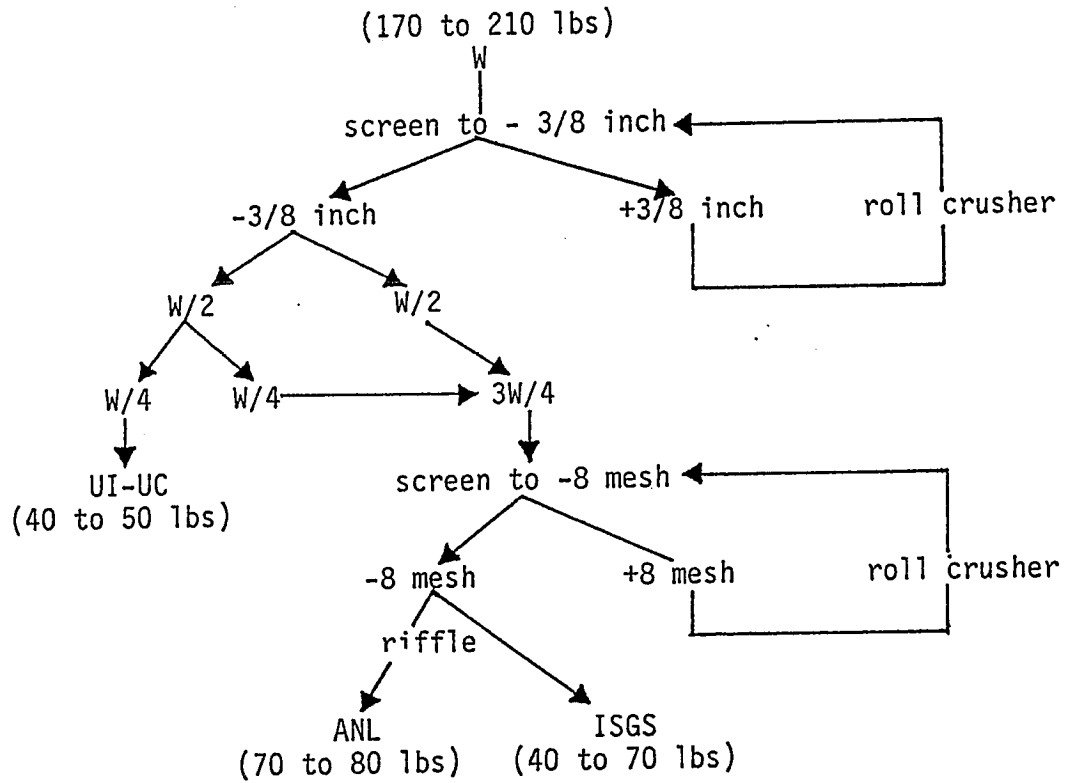


Figure 1. Crushing, screening and homogenizing procedure.

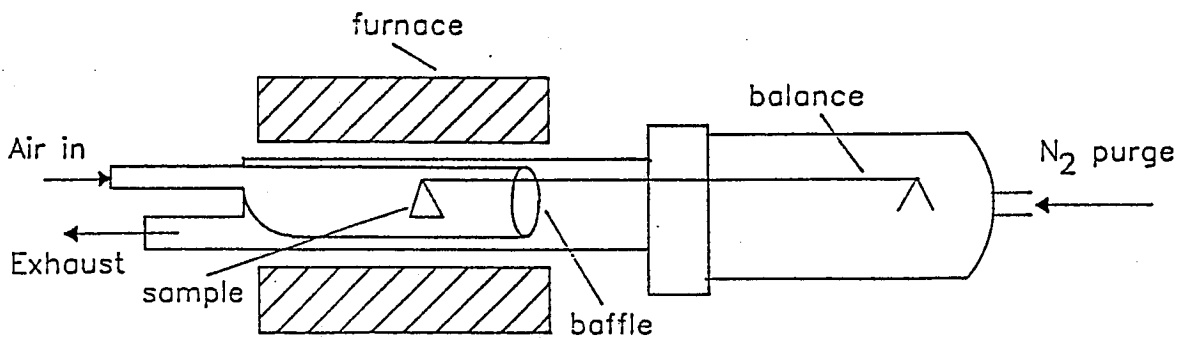


Figure 2. Modification of DuPont TGA quartz furnace tube for isothermal combustion tests.

50°C/min to the reaction temperature (between 425 and 575°C). After stabilization at this temperature (to insure sample temperature and weight remained constant), the flow of nitrogen was switched to dry air flowing at a rate of 100 cc/min. The percent weight of the unburned char and the rate of weight loss were monitored by the computer as a function of time.

For the isothermal experiments a modified TGA quartz furnace tube was constructed to obtain reliable rate data in the early stages of reaction. The objective was to achieve, as quickly as possible, uniform oxygen concentration (i.e. 21%) when air was first introduced to the furnace tube. In the modification, figure 2, air was introduced in the inner tube, passed over the sample, and exited through the annular space between the inner and outer tube through an opening near the end of the tube. A baffle at the end of the inner tube was used to prevent penetration of nitrogen, which continuously purged the balance housing, to the vicinity of the sample. Nitrogen purge rates through the balance housing as high as 800 cc/min were found to be satisfactory.

RESULTS AND DISCUSSION

Sample characterization

The particle size distribution of the feed coal, as determined by two dry sieve analyses of a twenty pound sample, are presented in table 1. Essentially all particles were 3/8" x 0. The size distribution of the devolatilized fuels were provided by the UCCRC and are given in table 2. The data are for a sample which was prepared during a preliminary test and crushed in a hammermill crusher without screen. The distribution given in table 2 is representative for all chars produced by UCCRC for this work.

Table 1. Sieve Analysis of IBCSP-3 Coal

Size, mesh	wt%	cumulative wt%
+8	67.2	67.2
8x14	16.4	83.6
14x28	7.0	90.6
28x48	4.1	94.7
48x100	2.3	97.0
100x200	1.4	98.4
-200	1.6	100.0
Total	100.0	

Table 2. Particle Size Distribution of the Crushed Char

Size, mesh	wt%	cumulative wt%
+4	50.4	50.4
4x16	26.4	76.8
16x30	8.2	85.0
30x60	7.5	92.5
60x0	7.5	100.0
Total	100.0	

The volatile matter content of the PD coals, as provided by UCCRC are presented in table 3. The analyses obtained at the ISGS, also shown in table 3, revealed that the differences in the volatile matter content between production run #1 and production run #3 was less than 0.5%. This difference was not satisfactory for the proposed research. These samples (169 lbs of #1 and 186 lbs of #3) were riffled several times to prepare a homogeneous mixture of the two PD coals. The resulting sample had a volatile matter content of 15.4% (dry basis). This fuel was designated as PD-2. The PD coal from production run #2 (VM=23.1%) was designated as PD-1. A third sample, designated as PD-3, was prepared by mixing PD coals from preliminary runs #5, 7a and 7b. The resulting sample had a volatile matter content of 11.4% (dry basis). It should be noted that during the preliminary tests, the hot char was exposed to air during discharge from the MGU reactor. It is possible that this sample was partially oxidized during the discharge sequence.

The proximate and ultimate analyses of the coal and chars are shown in table 4. It is interesting to note that while the total sulfur and pyritic sulfur decreased with decreasing volatile matter content, the organic sulfur increased. Note also that the nitrogen concentration was lowest for the char with highest volatile matter content, i.e., PD-1.

The UI-UC samples were pulverized by an outside firm to particle sizes suitable for combustion testing in the EDFF. The particle size distributions of the pulverized samples were obtained by a wet screen method and are presented in table 5. Over seventy percent (by weight) of the particles were -200 mesh (except for PD-3 which was 61.8%). The proximate and ultimate analyses of these samples are shown in table 4. The pulverized samples had volatile matter contents comparable to those obtained for the -60 mesh particles. However, the coal, PD-2 and PD-3 showed increases in their oxygen content. For PD-3 the oxygen content increased by 228%. This could be attributed to oxygen uptake by samples during pulverization.

Table 3. Volatile matter content of coal and chars

UCCRC Run No.	Residence time, hrs	Volatile matter, dry wt %	
		UCCRC ^a	ISGS
<u>Preliminary Runs</u>			
4	2.00	17.7	---
5	4.58	10.1	---
6	1.00	28.9	
7a, 7b	3.58, 4.08	10.9, 10.5	12.3 ^b
8	2.00	23.6	
<u>Production Runs</u>			
1	3.17	12.4	14.9
2	1.70	25.0	23.1
3	2.90	17.1	15.3

^a determined by ASTM method at UCCRC.

^b mixture of 7a and 7b

Table 4. Proximate and ultimate analyses for coal and chars (dry basis)

	Coal ^a		PD-1		PD-2 ^b		PD-3 ^c	
	60x0	pulv.	60x0	pulv.	60x0	pulv.	60x0	pulv.
Moisture, wt %	5.3	5.0	10.1	8.8	6.3	4.7	3.5	3.6
<u>Proximate, wt %</u>								
volatile matter	35.7	35.4	23.0	23.1	15.4	15.8	11.4	11.4
fixed carbon	55.9	56.1	66.8	66.8	73.1	73.0	76.2	76.4
H-T ash	8.5	8.4	10.1	10.2	11.4	11.1	12.4	12.2
<u>Ultimate, wt %</u>								
hydrogen	5.53	4.87	3.83	3.41	2.89	2.58	2.18	1.98
carbon	77.57	76.28	78.11	79.62	79.91	79.74	80.89	79.38
nitrogen	2.01	1.78	1.79	1.84	1.86	1.84	1.93	1.83
oxygen	4.16	6.38	4.16	2.96	2.06	2.82	.85	2.79
Sulfatic sulfur	.04		0		0		0	
Pyritic sulfur	1.06		.60		.38		.29	
Organic sulfur	1.15		1.40		1.45		1.50	
Total sulfur	2.25		2.00		1.83		1.79	
Total Chlorine	---		---		.139		.104	
BTU/lb	13470		13296		13174		12844	

^a IBCSP-3

^b Mixture of chars from UCCRC production runs 1 & 3

^c Mixture of chars from UCCRC preliminary runs 5 & 7

Table 5. Wet sieve analysis of pulverized coal and chars.

Size, mesh	Coal	PD-1	PD-2	PD-3
+200	20.9	29.7	21.6	38.2
200x270	16.8	15.1	13.1	14.0
270x325	6.2	6.0	5.5	6.0
325x400	5.9	5.3	5.0	4.0
-400	50.2	43.9	54.8	37.8
Total	100.0	100.0	100.0	100.0

Devolatilization behavior of coal and PD coals

Volatile release data for the coal and the PD coals prepared at the UCCRC are shown in figure 3. A major portion of the weight loss occurred between 350°C and 550°C with the maximum rate of weight loss at 460°C. This is the temperature range where the major portion of liquid and gaseous hydrocarbons are released from coal during carbonization. Inspection of the data indicates that weight loss between 350 and 600°C was 30% for the raw coal, 15% for PD-1, 7.5% for PD-2, and 6% for PD-3. Note that reduced volatility

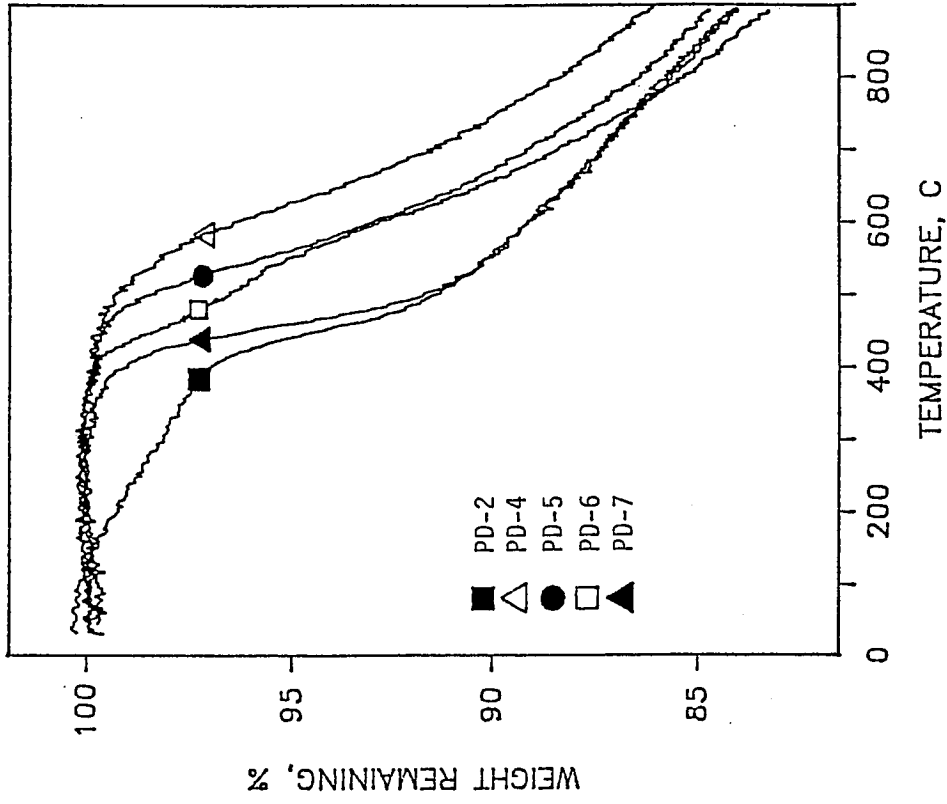


Figure 4. Devolatilization data for 15% volatile matter chars produced under various conditions.

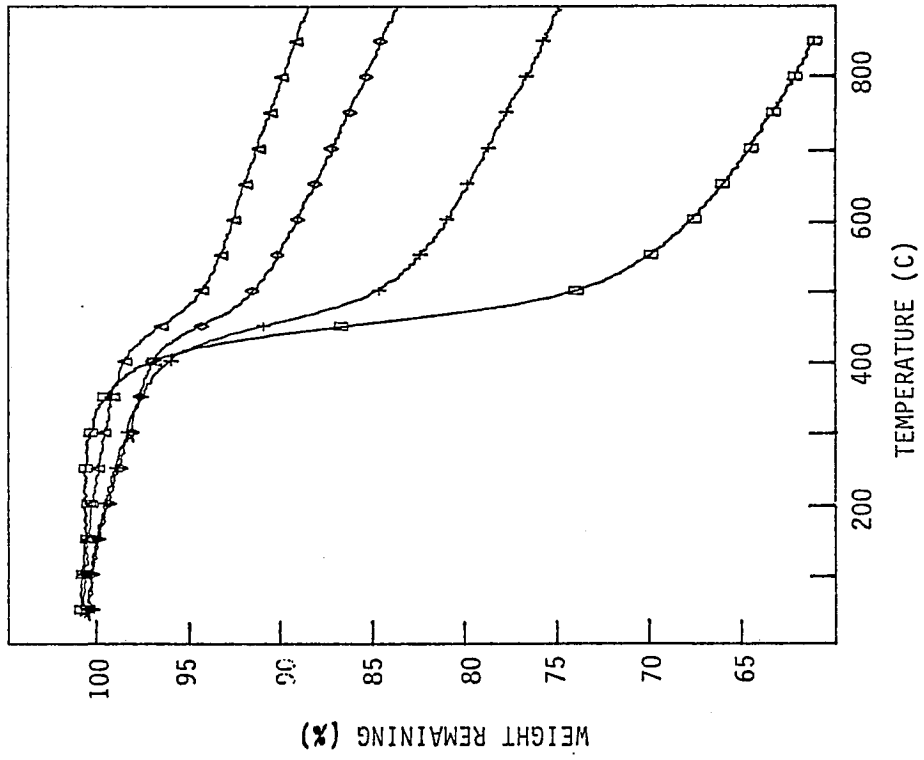


Figure 3. Devolatilization of coal and PD fuels; \square coal; \diamond PD-1; \triangle PD-2.

did not influence the temperature at the maximum rate of weight loss. The average weight loss for the PD coals between 550 and 900°C was 6%, a value comparable to 7.5% observed for the raw coal. This indicates that differences in volatile matter content were due to hydrocarbon materials that are essential to ignition and flame stability properties. Weight losses at 900°C were 35% for the coal, 25% for PD-1, 15.5% for PD-2 and 12% for PD-3. These values are in good agreement with the volatile matter contents reported for the samples in table 4.

Devolatilization data for PD coals prepared in the microbalance reactor under different pyrolysis conditions are shown in figure 4. PD-4 and PD-5 were produced by heating the coal at 5°C/min to 525°C and 425°C, respectively. The latter char was held at 425°C for two hours. PD-6 was a mixture of the raw coal and PD-4. PD-7 was a mixture of raw coal and a sample prepared at 800°C. As seen in figure 4, these fuels had volatile matter contents of about 15%. However, the type of volatile matter present in these samples was not the same. In the temperature range between 350 and 550°C, the weight losses were about 2% for PD-4 and PD-5, 4% for PD-6, and 10% for PD-7. These data indicate that even at temperatures as low as 425°C, a major fraction of hydrocarbons were released when PD coals were prepared in the microbalance reactor system.

Figure 4 also illustrates weight loss data for PD-2 coal produced at UCCRC. This sample had a volatile matter content comparable to those prepared in the microbalance reactor. It is clearly seen that between 350-550°C, the general shapes of the weight loss curves of the coal-blend samples are similar to that of PD-2. This observation indicates that the PD coals produced in the MGU at UCCRC were mixtures of different types of fuels. The MGU was essentially a fixed-bed reactor with an external source of heating. Therefore, it is expected that coal particles close to the reactor wall were subjected to higher temperatures for a longer period than particles in the center of the reactor. This could have resulted in production of particles with different volatile matter content.

Combustibility of coal and PD coals

Typical weight loss and rate of weight loss data obtained in air for PD-2 are shown in figure 5. As described earlier, the weight loss below 150°C corresponds to the release of moisture. The noticeable gain in sample weight, as indicated by the DTG thermal curve between 290 and 300°C was due to oxygen adsorption, i.e., preignition oxidation. A major weight loss began at 315°C (T_I). This temperature was taken at the point where the rate of weight loss was 1%/min. PD-2 exhibited a double-burn profile. The first burn peaked at 490°C (T_H) and the second 540°C (T_L). Sample oxidation was essentially complete at 630°C (T_B). This burn-out temperature was taken at the point where the rate of weight loss was 1%/min. The weight remaining at 650°C was the ash content of the sample which was approximately 12%. This value is comparable to that shown in table 4.

The burning profiles obtained at a heating rate of 20°C/min for the raw coal and the PD coals are shown in figure 6. The curves are offset to avoid overlap. Also shown in figure 6 are the burn-off data (carbon loss data on dry-ash free basis). There are clear differences among the burning profiles. Raw coal exhibited a single-burn profile. However, double-burn

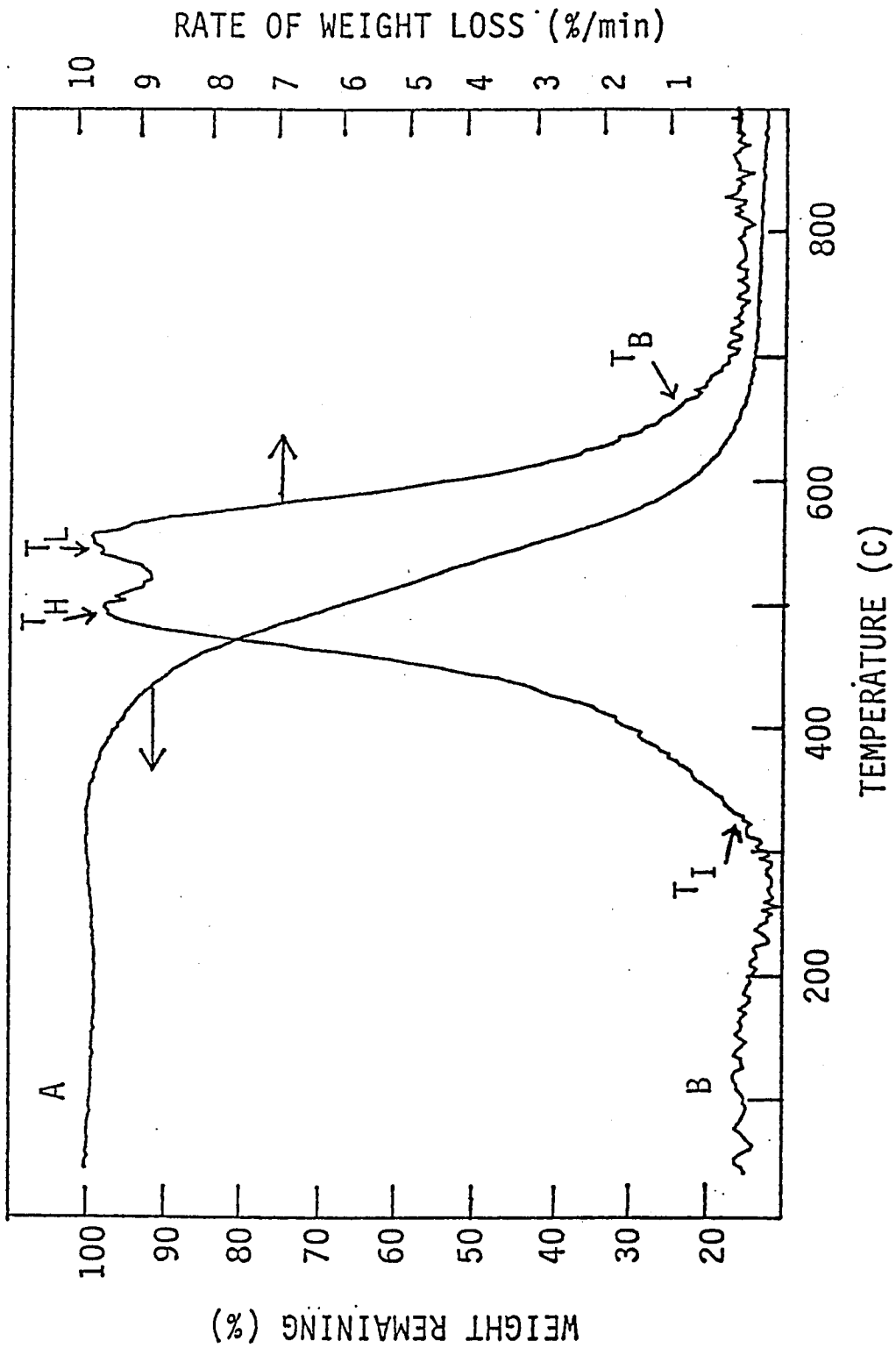


Figure 5. Typical burning profile curve for PD-2 (heating rate = 20°C/min) A, TG; B, DTG

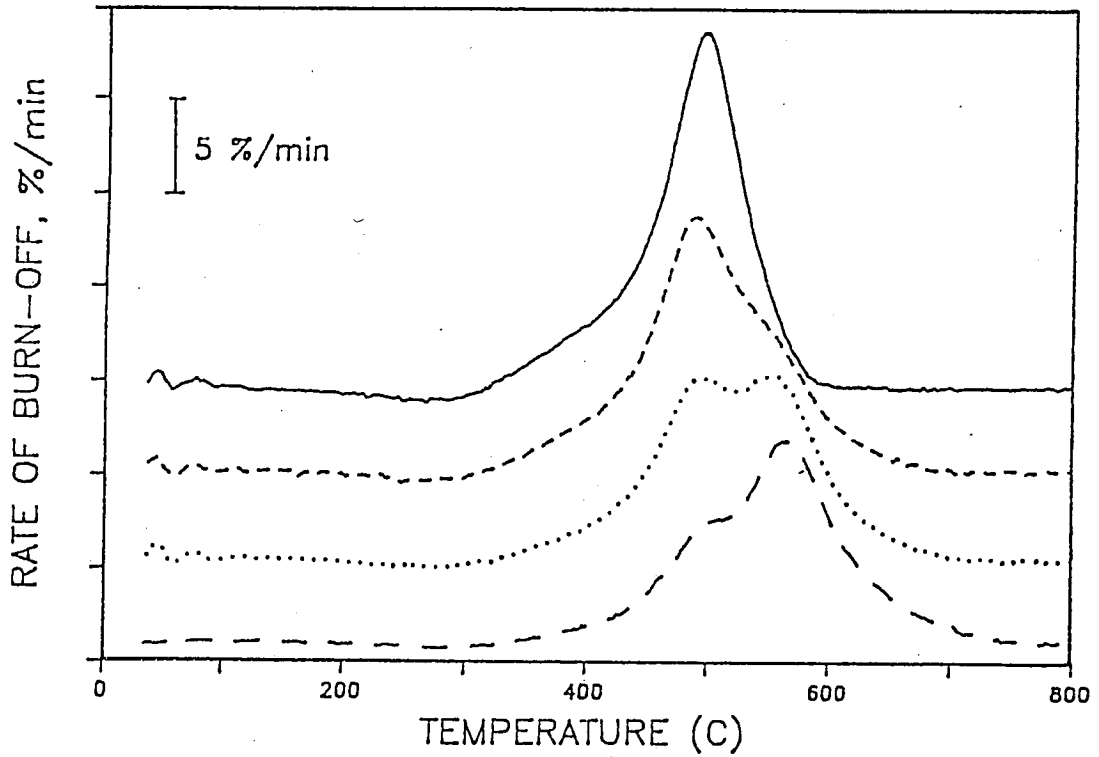
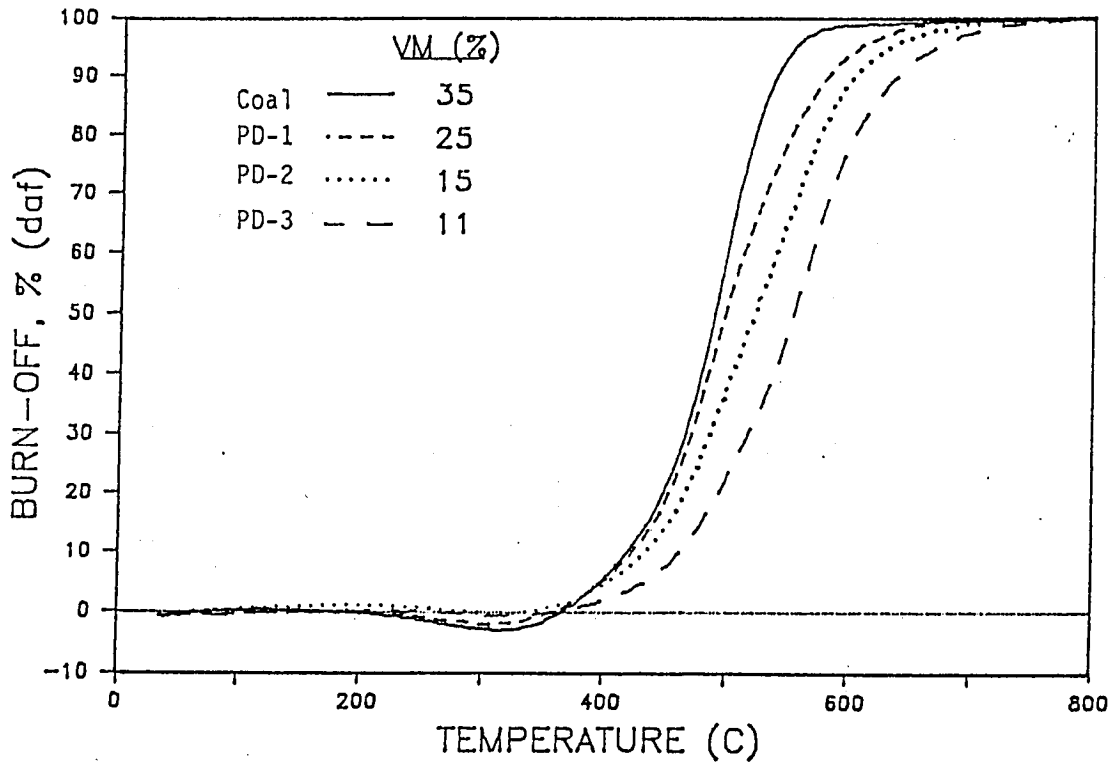


Figure 6. Burn-off and rate of burn-off curves for the parent coal (IBCSP-3) and three PD fuels.

profiles were observed for PD-1, PD-2 and PD-3. The second burn appeared as a shoulder peak for PD-1 (VM=23%) and became more pronounced for PD-2 (VM=15%) and PD-3 (VM=11.4%).

The double-burn behavior observed for the PD coals suggested the presence of at least two types of combustibles in the fuels. The two portions of combustibles burned in two distinct stages with peak burn rates at approximately 500°C and 550°C. The higher reactivity materials had combustion properties similar to that of the raw coal and were present in larger concentrations in PD-1. These data support observations reported for devolatilization behavior of the PD coals.

The burn-off curves indicated that the onset of oxidation was at about 375°C for samples tested. However, fuels with higher volatile matter content burned more rapidly. For example at 500°C, the amount of material burned was 20% for PD-3, 40% for PD-2, 55% for PD-1 and 70% for the raw coal. Characteristic temperatures, given in table 6, show that the most pronounced impact of the volatile matter was on burn-out temperatures which varied by about 110°C. The results indicate that under the conditions used, raw coal was the most readily combusted fuel, followed by PD-1, PD-2 and finally PD-3.

Table 6. Burning characteristics of coal and chars.

Heating rate °C/min	$T_I, ^\circ\text{C}$		$T_H, ^\circ\text{C}$		$T_L, ^\circ\text{C}$		$T_B, ^\circ\text{C}$	
	20	50	20	50	20	50	20	50
Coal	315	325	490	510	---	---	580	630
Char #1	315	335	490	515	540	570	630	715
Char #2	325	340	495	525	550	580	660	750
Char #3	335	350	500	535	560	600	690	800

Burning profiles obtained at a heating rate of 50°C/min are shown in figure 7. Although the nature of the profiles, i.e., single or double-burn, did not change, characteristic temperatures (T_I , T_H , T_L and T_B) increased with increased heating rate (see table 6). At a heating rate of 50°C/min, burnout temperatures were 50°C (for coal) to 110°C (for PD-3) higher than those for runs at a heating rate of 20°C/min. These results indicate that when fuel samples are subjected to a high rate of heating such as those encountered in boilers, higher operating temperatures may be required for the complete burning of fuels.

Burn-off curves of fuels shown in figure 4 are given in figure 8. As mentioned earlier, these samples were prepared in the microbalance reactor and had about 15% volatile matter. There are distinct differences among the burning characteristics of these fuels. These fuels exhibited single burn behavior during combustion in air in contrast with PD-2 (also a 15% volatile matter char) which exhibited a double-burn behavior. Burn-off data indicate that low temperature chars, alone (PD-4 and PD-5) or when mixed with the raw coal (PD-6), exhibited the low temperature peak and were

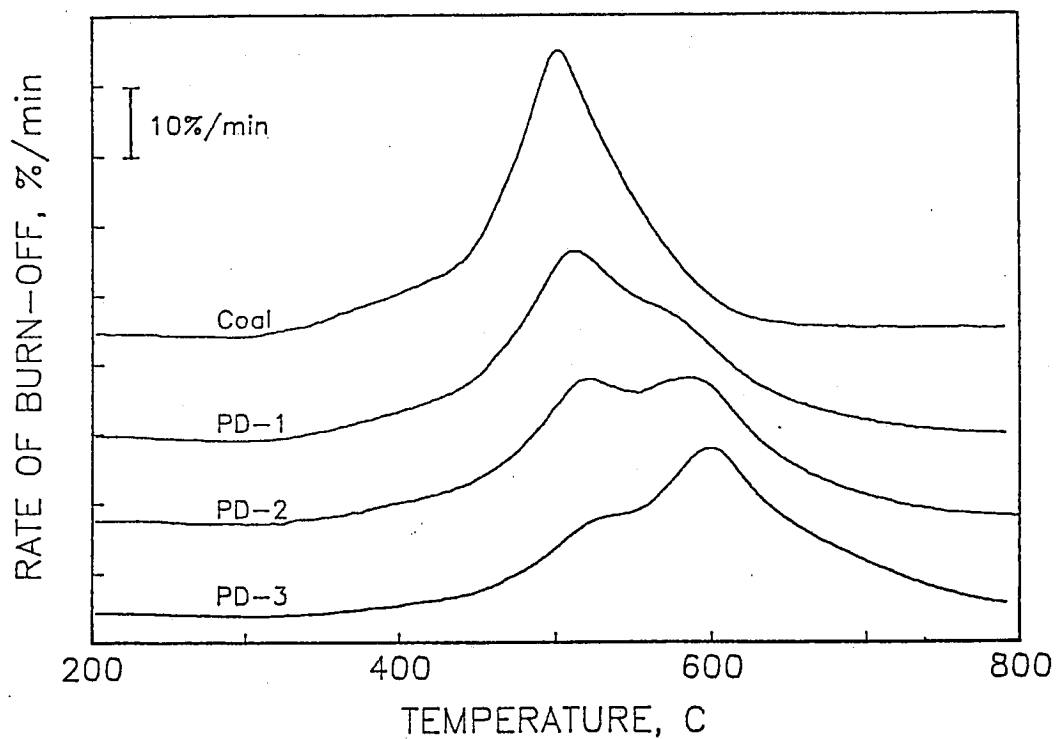


Figure 7. Burning profiles of coal and chars at a programmed heating rate of 50°C/min.

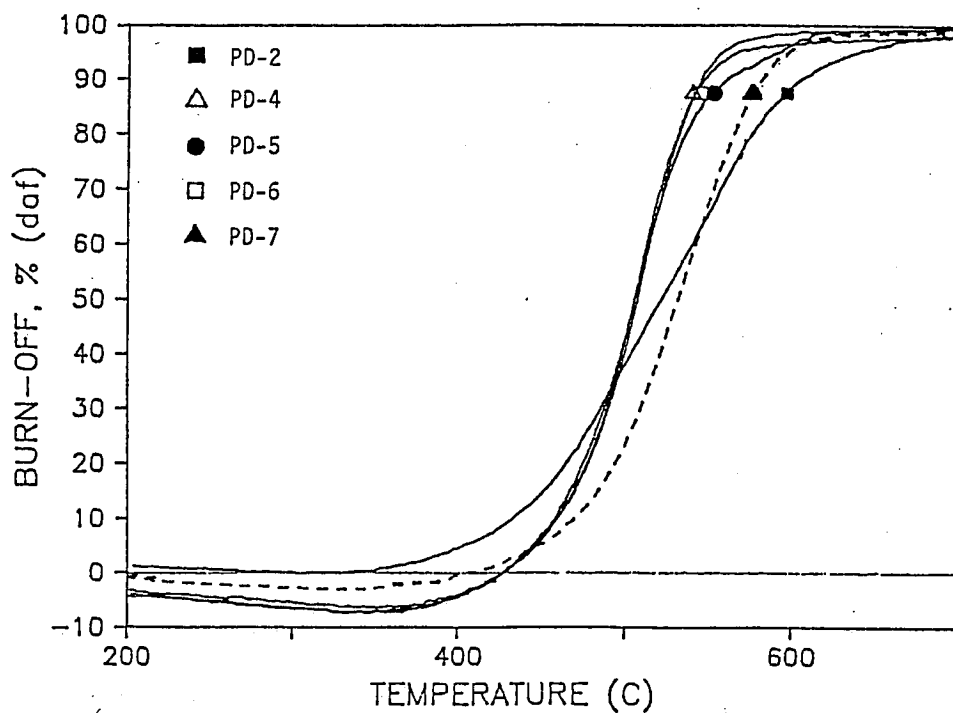


Figure 8. Burn-off curves for chars prepared in the TGA and coal blend fuels.

more reactive than the higher temperature char (PD-8) and its coal-blend fuel (PD-7). The latter samples exhibited the high temperature burning peak. These data suggest that volatile matter alone cannot be used as an index of reactivity. It also shows that the addition of the raw coal to a relatively low reactive char (PD-8) can improve combustion reactivity of the resultant mixture. However, a fuel with comparable volatile matter content prepared by a low temperature carbonization process would be more reactive. Char preparation conditions appear to be important as they dictate the properties and type of fuels produced.

A series of experiments was conducted to further examine the relationship between the extent of devolatilization of coal during mild pyrolysis and the combustibility of the resultant fuel. The study was designed to obtain information on the burning characteristics of PD coals prepared by pyrolysis in nitrogen under varying conditions of heating rate (5 to 1200°C/min), heat treatment temperatures (400 to 950°C), and soak time at the heat treatment temperature (1 min to 4 hrs). The fuel samples were produced in the microbalance reactor.

Figure 9 shows a plot of characteristic temperatures, obtained by heating the samples in air at 20°C/min, versus a fuel's volatile matter content. Volatile matter contents were determined by TG micro-proximate analyses. Higher pyrolysis temperatures resulted in lower volatile matter content. Inspection of the results show that there were only slight differences in T_I , T_H and T_B for fuels with volatile matter contents above 10%. However, with further decrease in volatile matter, burn-out temperatures increased markedly. These observations are in agreement with results reported in a previous study on the reactivity of PD coals derived from an Illinois hvB coal (Jenkins et al, 1973). The values of T_B for PD coals prepared at UCCRC are also shown in figure 9. It is clearly seen that these samples had higher burn-out temperatures than those prepared in the microbalance reactor under controlled pyrolysis conditions. This again indicates that temperature-time history of the fuel particles during pyrolysis and the type of reactor in which the coal is processed greatly influences the reactivity of the resultant char.

Characteristic temperatures were also plotted against heat treatment temperatures. Figure 10 shows that peak-burn temperatures and burn-out temperatures were particularly sensitive to preparation temperatures above 600°C. Furthermore, results indicate that fuels prepared at the fastest heating rate, i.e. 1200°C/min, and shorter soak times at heat treatment temperatures were more reactive.

It is known that a combination of pore structure and chemical nature (e.g. involving hydrogen) of the fuel influence burning characteristics (Jenkins et al., 1973). The porosity of a coal char usually increases as heat-treatment temperature is increased up to about 600 to 700°C. Further heating results in a progressive decrease in reactivity due to development of a more graphitic structure and loss of hydrogen (Solomon, 1984).

Figure 11 shows results of the surface area determinations. The nitrogen surface area (feeder pores) is moderately developed to a maximum of 13 m²/g at about 700°C-800°C and then declines with increased heat-treatment temperature. The carbon dioxide surface area, which represents micro-

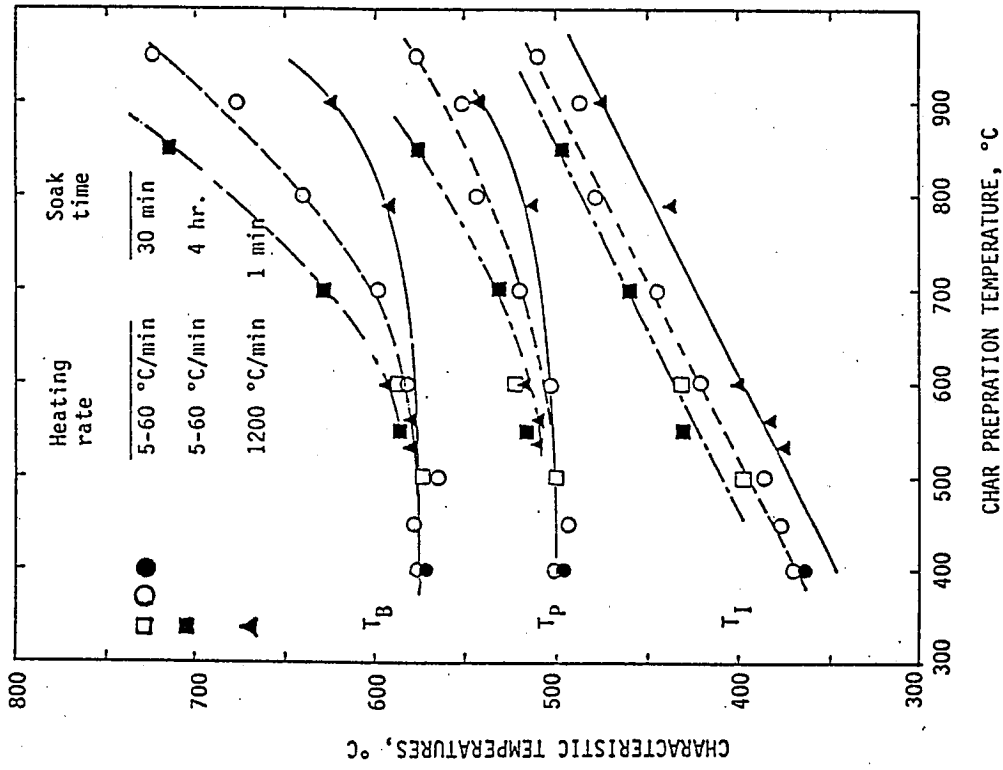


Figure 10. Effect of heat-treatment temperature on characteristic temperatures.

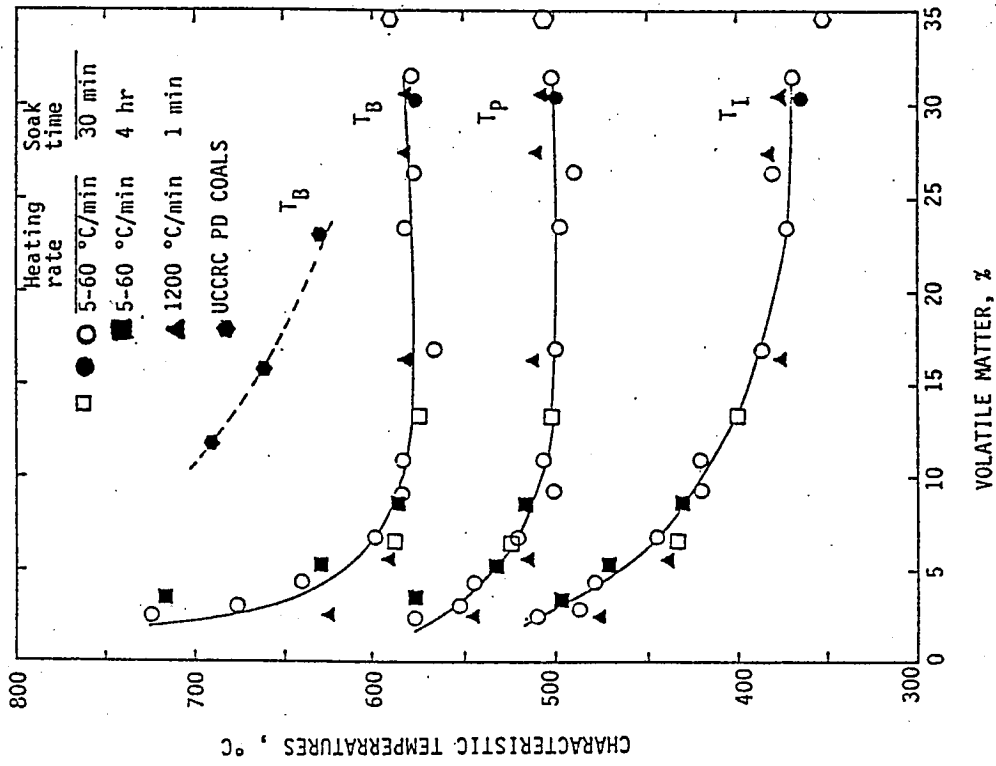


Figure 9. Effect of volatile matter on characteristic temperatures.

pores, is markedly developed to a value of 300 m²/g at about 600 to 700°C, followed by a decrease to 65 m²/g at 950°C.

It should be noted that both nitrogen and carbon dioxide surface areas vary with conversion during char combustion and that values shown in figure 11 represent the physical nature of the fuels prior to studying their burning characteristics. A different type of surface area referred to as active surface area (ASA) has been used to explain char reactivity (Radovic et al., 1983; Khan, 1987). The ASA is determined from the amount of oxygen chemisorbed by the char at temperatures low enough (usually 200°C) that carbon burn-off does not occur appreciably. The values of ASA for the chars was not determined in this study.

Isothermal reactivity tests

Reactivities were determined under isothermal conditions to gain some information on changes taking place in pore structure during combustion and to obtain activation energies for the char oxidation reaction. Reaction temperatures below 570°C were selected to insure that reaction rates were not limited by mass transfer resistance.

Figure 12 demonstrates combustion data of -170 mesh PD-1 taken at temperatures of 428°C, 475°C and 523°C. As expected the combustion rate increased sharply with increasing temperature. Figure 13 shows combustion data as a function of dimensionless time, τ . The reference time is chosen such that $\tau = t/t_{0.5} = 1$ at a fractional burn-off of 0.5. The time to reach 50% burn-off increased from 3.2 min to 29.3 min as the temperature was decreased from 523 to 428°C. It is obvious from figure 13 that the normalized combustion data could be correlated well with a single burn-off characteristic curve (conversion vs τ) which is independent of temperature.

Figure 14 demonstrates burn-off characteristic curves expressed in the form of the rate of burn-off on an ash-free basis (-df/dt) versus fraction conversion. It is clearly seen that the rate of combustion initially increases, goes through a maximum at about 10% conversion and slowly decreases as the fractional burn-off approaches one. It has been suggested that development of porosity and surface area in micropores chars as they undergo oxidation is responsible for the observed maximum in burn-off rates (Mahajan et al., 1978; Dutta and Wen, 1977). Initially, the chars contained closed porosity. As the reaction proceeds, the total number of pores and therefore total surface area is increased which results in increasing the rate of carbon burn-off. The rate reaches the maximum value when the rate of surface area growth is off-set by the loss in sample weight due to carbon burn-out. As the reaction proceeds, neighboring pores collapse, which causes the total surface area to decrease. This in addition to loss of combustibles causes the rate of reaction to decrease.

Figure 15 shows rate versus conversion curves at 525°C for six different fuels derived from the same parent coal (IBCSP-3), but under different processing conditions. The 600 char and 950 char were prepared in the microbalance reactor by heating the coal at 20°C/min to 600 and 950°C, respectively. PD-1-FBR and PD-3-FBR were obtained by injecting the PD-1 and PD-3 coals into a 2-inch ID batch fluidized-bed reactor at 850°C.

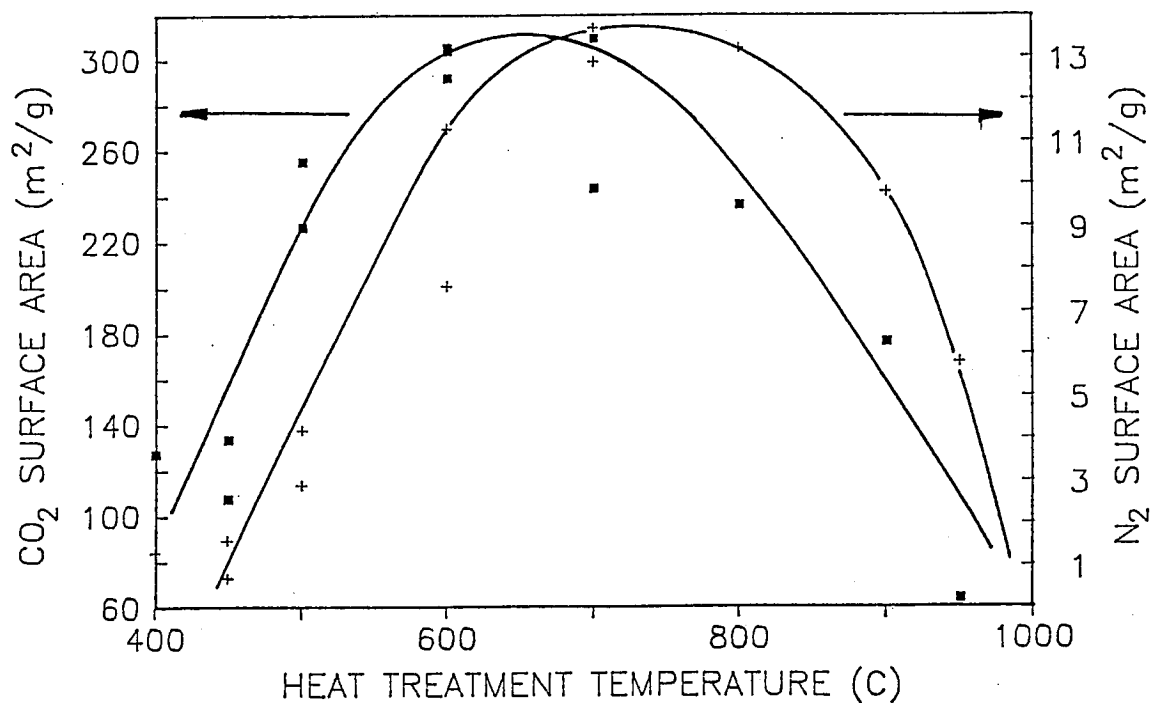


Figure 11. Effect of heat-treatment temperature on N₂ and CO₂ surface areas.

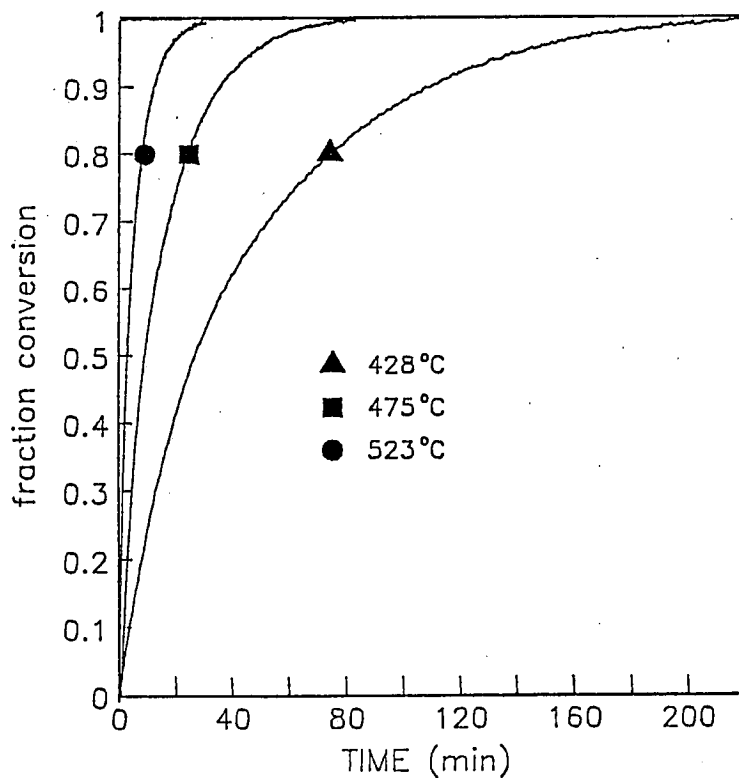


Figure 12. Isothermal burn-off curves (daf) in air for PD-1 coal.

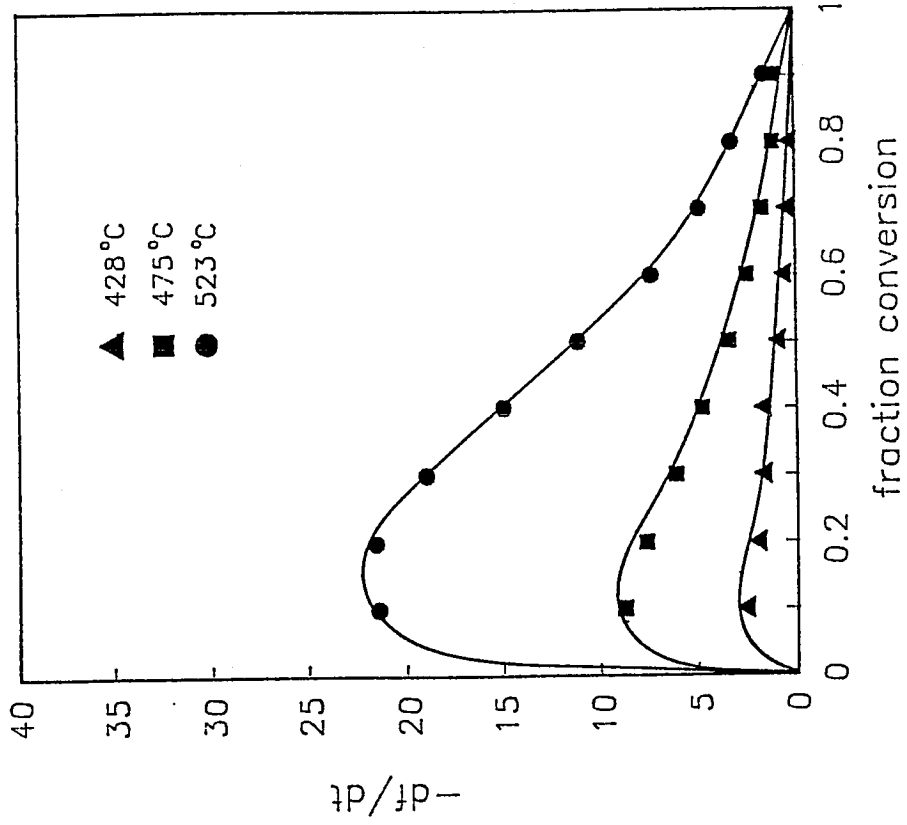


Figure 13. Characteristic burn-off curves for PD-1.

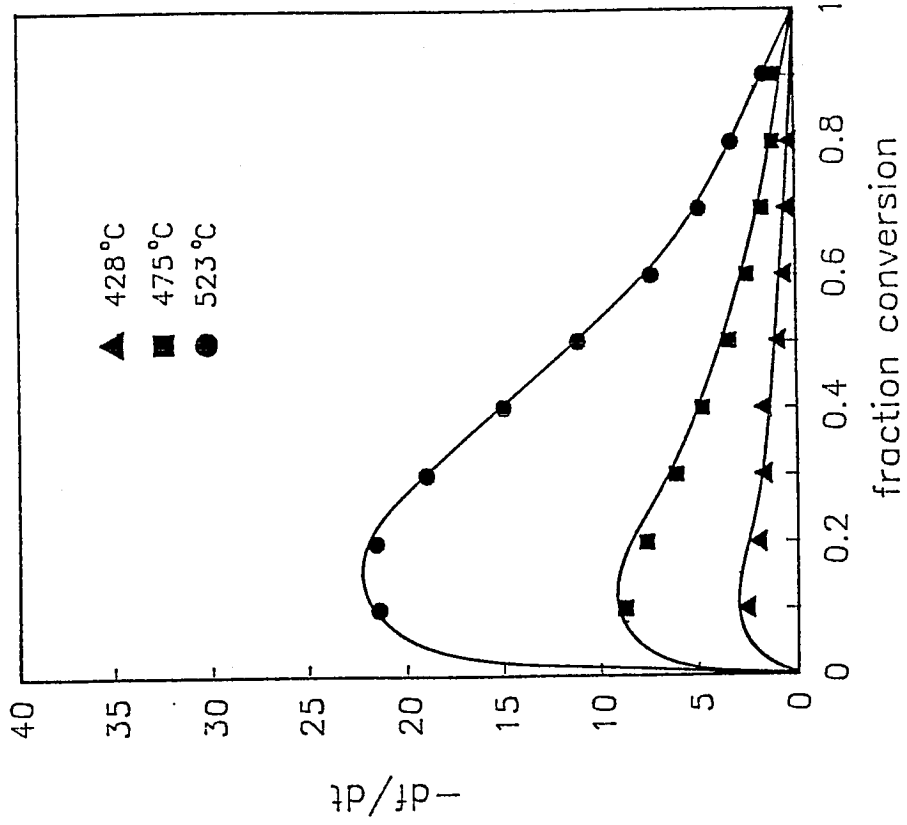


Figure 14. Rate vs. conversion curves for PD-1 coal.

These chars were prepared in this manner to simulate the initial rapid heating that coal particles experience in fluidized-bed combustors (see the following section). The HDS was a low sulfur char (0.4% sulfur) and was prepared at 850°C by reacting with hydrogen for 90 minutes. Combustion data are for -170 mesh particles.

As shown in figure 15, the combustion behavior of the fuels are different possibly, at least in part, because of differences in the micropore structure development during combustion and their heat-treatment conditions. It is also clearly seen that fuels exhibit their maximum combustion rates at different conversion levels.

The variety of rate-conversion curves is due to the fact that changes in pore structure with conversion vary greatly from one sample to another. In order to gain some information with respect to the relative available pore surface area at any stage of conversion the rate data was presented in the following form;

$$-\left(\frac{df}{dt}\right) = SkP_{O_2} f \quad (1)$$

and

$$f = (M - M_a) / (M_0 - M_a) \quad (2)$$

where;

- f = fraction combustible remaining at time t
- M = mass of sample at time t
- M₀ = initial sample mass
- M_a = mass of the sample at complete conversion, i.e. ash
- k = reaction rate constant
- P_{O₂} = oxygen partial pressure
- S = available pore surface area

The initial available rate of the reaction at t=0 (or f=1) is:

$$\left(\frac{-df}{dt}\right)_i = S_0 k P_{O_2} \quad (3)$$

where S₀ is the initial pore surface area.

At any stage of conversion at time t, the rate is given by expression (1). Dividing (1) by (3) and solving for S/S₀ gives

$$\frac{S}{S_0} = \frac{1}{\left(\frac{-df}{dt}\right)_i} \frac{(-df/dt)}{f} \quad (4)$$

Since the rate observed at zero conversion, i.e., $\left(\frac{-df}{dt}\right)_i$ is constant for a given fuel and at a given temperature, a plot of $(-df/dt)/f$ versus conversion represents changes in available surface area with conversion during the combustion reaction. Figure 16 shows how the relative available

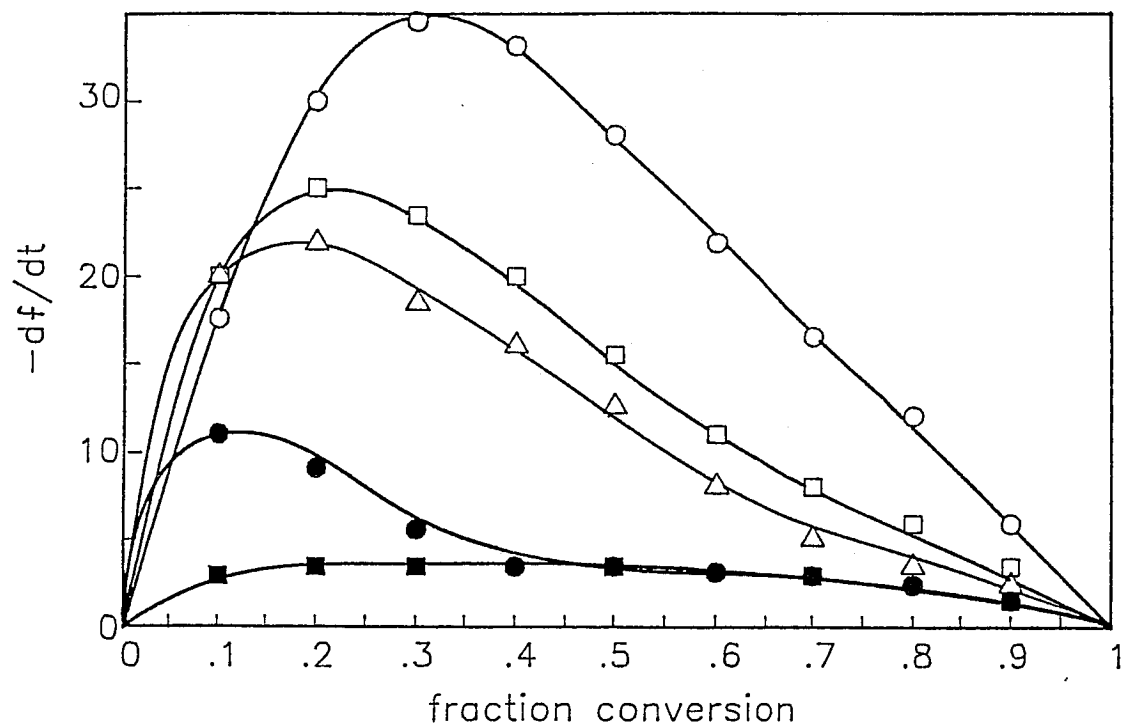


Figure 15. Rate vs. conversion curves at 525°C in air: ○ 600 char; □ PD-1-FBR; △ PD-1; ● PD-3-FBR; ■ HDS, 950 char.

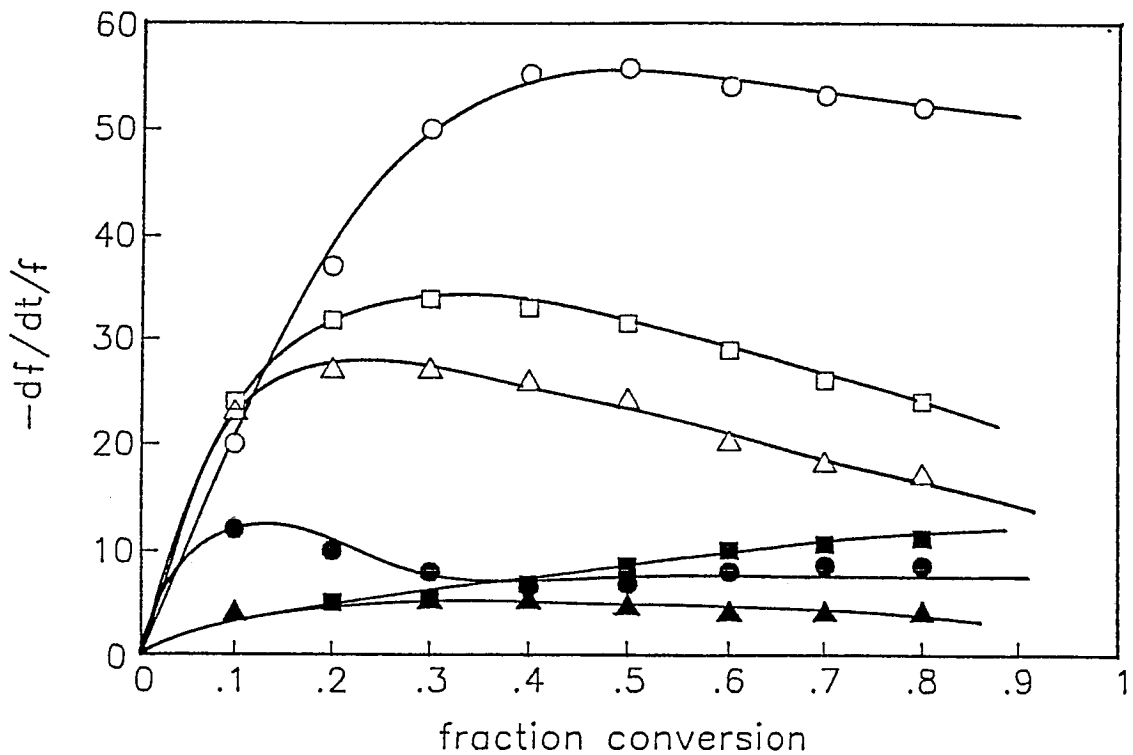


Figure 16. Relative available pore surface area ($df/dt/f$) vs. conversion. ○ 600 char; □ PD-1-FBR; △ PD-1; ● PD-3-FBR; ■ HDS; ▲ 950 char.

pore surface areas of the six samples change with conversion. It is clearly seen that surface area development follows the order of char reactivity noted earlier for these samples. The 600 char showed the largest increase in surface area and the 950 char the lowest. It appears that high temperature treatment inhibits pore surface area development when char is burned under the chemically controlled reaction region.

Isothermal combustion data were also used to obtain activation energies for combustion of selected chars. Assuming Arrhenius-type temperature dependence for the rate constant k ,

$$k = k_0 e^{-E/RT} \quad (5)$$

equation (1) becomes

$$(-df/dt)/f = Sk_0 e^{-E/RT} P_{O_2} \quad (6)$$

At a given conversion level a plot of $\ln(-df/dt/f)$ versus $1/T$ gives the value of activation energy according to the following equation:

$$\ln(-df/dt/f) = \ln(k_0 P_{O_2}) + \ln S - \frac{E}{RT} \quad (7)$$

The above equation assumes that the values of S are independent of temperature. This, however, may not be true for some solid fuels.

In figure 17, the values of $\ln(-df/dt/f)$ evaluated at 20% conversion are plotted against $1/T$. This figure shows that the higher the heat-treatment temperature of the coal, the lower the reactivity of the resultant fuel. For example, the 600 char is three times more reactive than the 950 char. The average values of activation energy calculated from the slopes of the plots shown in figure 17 was about 31 kcal/mole. This value is comparable to those reported in literature (Radovic et al., 1984; Khan 1987) for the combustion of lignite, subbituminous and bituminous derived chars in the temperature range in which the fuels in this work were studied.

Combustion characteristics of EDFF residues

As described earlier, 25 pounds of the IBCSP-3 coal and each of the PD coals prepared at the UCCRC were delivered to the Coal Combustion Laboratory located in the Mechanical Engineering Department at the University of Illinois, Champaign-Urbana. Faculty members Herman Krier, Richard O. Bukius, and James E. Peters and their graduate students carried out research on the flammability characteristics of the samples. A relatively large scale pulverized coal burner which operated with a downward flowing coal/air flame was utilized. The combustor is commonly referred to as an Entrained Dust Flow Facility (EDFF).

Of the four samples tested only the raw coal and the PD-1 coal could be burned in the EDFF. PD-2 and PD-3 coals could not be ignited, showing a lower limit on the volatile matter for fuels to be used in the EDFF.

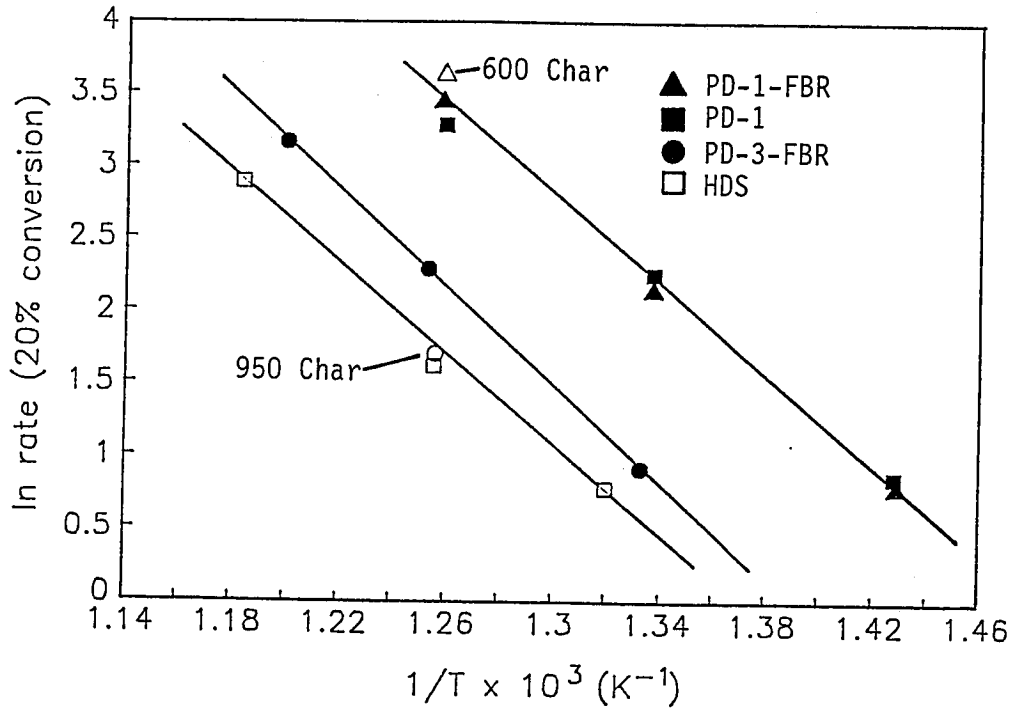


Figure 17. Arrhenius plots for the combustion of various coal-derived fuels.

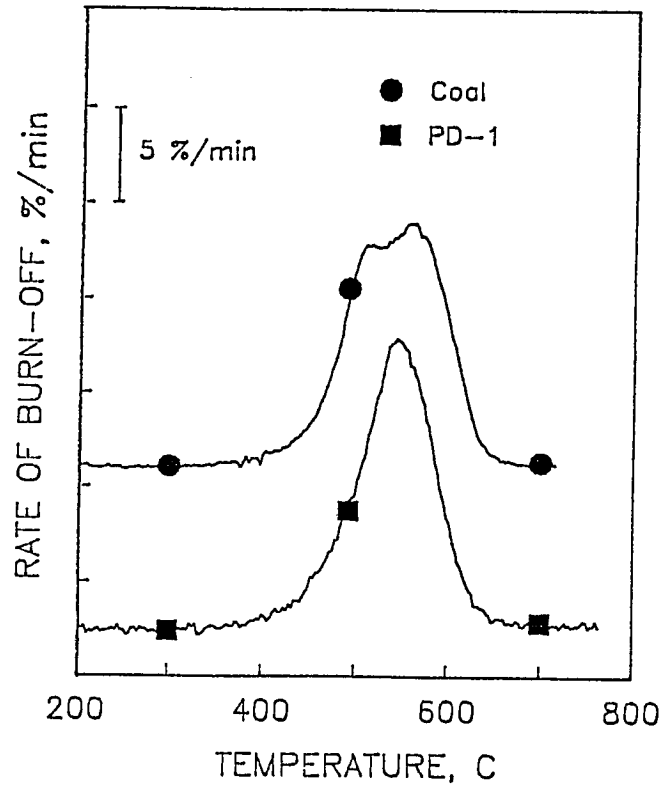


Figure 18. Burning profile comparison for EDFF residues.

The bottom ash (residues) collected from the combustion of coal and PD-1 were examined by nonisothermal TG-combustion method. The burning profiles are shown in figure 18. The weight loss curves illustrated that the EDFF bottom ashes from the coal and PD-1 contained 80% and 87% combustible materials. Elemental analyses revealed 81.5% and 82.9% carbon and 0.95% and 0.97% hydrogen in the samples. The residue from coal exhibited a double-burn profile similar to that shown in figure 5 for the PD-2 coal. A single burn was noted for the residue from PD-1. The above results indicate the fuel particles were partially burned and that only a portion of volatile matter was removed from the fuel particles during combustion. The incomplete combustion may be attributed to the short residence time of particles in the combustion zone of the EDFF, or to the low reactor temperature (temperatures varied from 550°C at the reactor wall to 1000°C at the center).

Combustion characteristics of fluidized-bed cyclone ashes

In Part B of this work, combustion characteristics of the raw coal and three PD fuels prepared at UCCRC were investigated in fluidized-bed combustion tests at Argonne National Laboratory (ANL). The primary objective of the fluid-bed experiments was to obtain data on combustion efficiency that can be correlated with the thermogravimetric measurement of combustion reactivity made at the ISGS. In the combustion tests, the bed temperature was varied over the range of 750 to 900°C and excess air was varied over the range of 10 to 30% (table 7). Data on combustion efficiency and sulfur retention for each of the fuels tested were obtained and correlated with the volatile content of the fuels, bed temperature and excess air. The details are given in a separate report submitted by Dr. William Swift.

Table 7 Nominal Operating Conditions for Fluidized-Bed Combustion Tests

Test Condition	Bed Temperature (°C)	Excess Air (%)	Dry Flue Gas O ₂ (%)	Air Flow Rate (M ³ /h)	Air Flow Rate (Kg/h)	Pressure kPa	Superficial Fluidizing Velocity (m/s)
1	750	30	5	24.1	2.2	43	0.91
2	750	10	2	20.4	2.2	21	0.91
3	825	10	2	20.4	2.2	30	0.91
4	900	10	2	20.4	2.2	39	0.91

Nonisothermal TG-combustion results for the pulverized cyclone ashes received from ANL are shown in figure 19. Samples were burned in air at a programmed heating rate of 20°C/min. The cyclone ashes were obtained under the nominal FBC test conditions given in table 8. The differences among the combustion properties of the cyclone ashes are clear. Examination of the data revealed that there were two zones of weight losses. A major weight loss (30 to 55%) occurred between 450°C and 625°C due to the presence of the combustible materials remaining in the cyclone ashes. The second weight loss, usually less than 5%, was between 625 and 750°C. This was attributed to the calcination of the limestone which was present in the

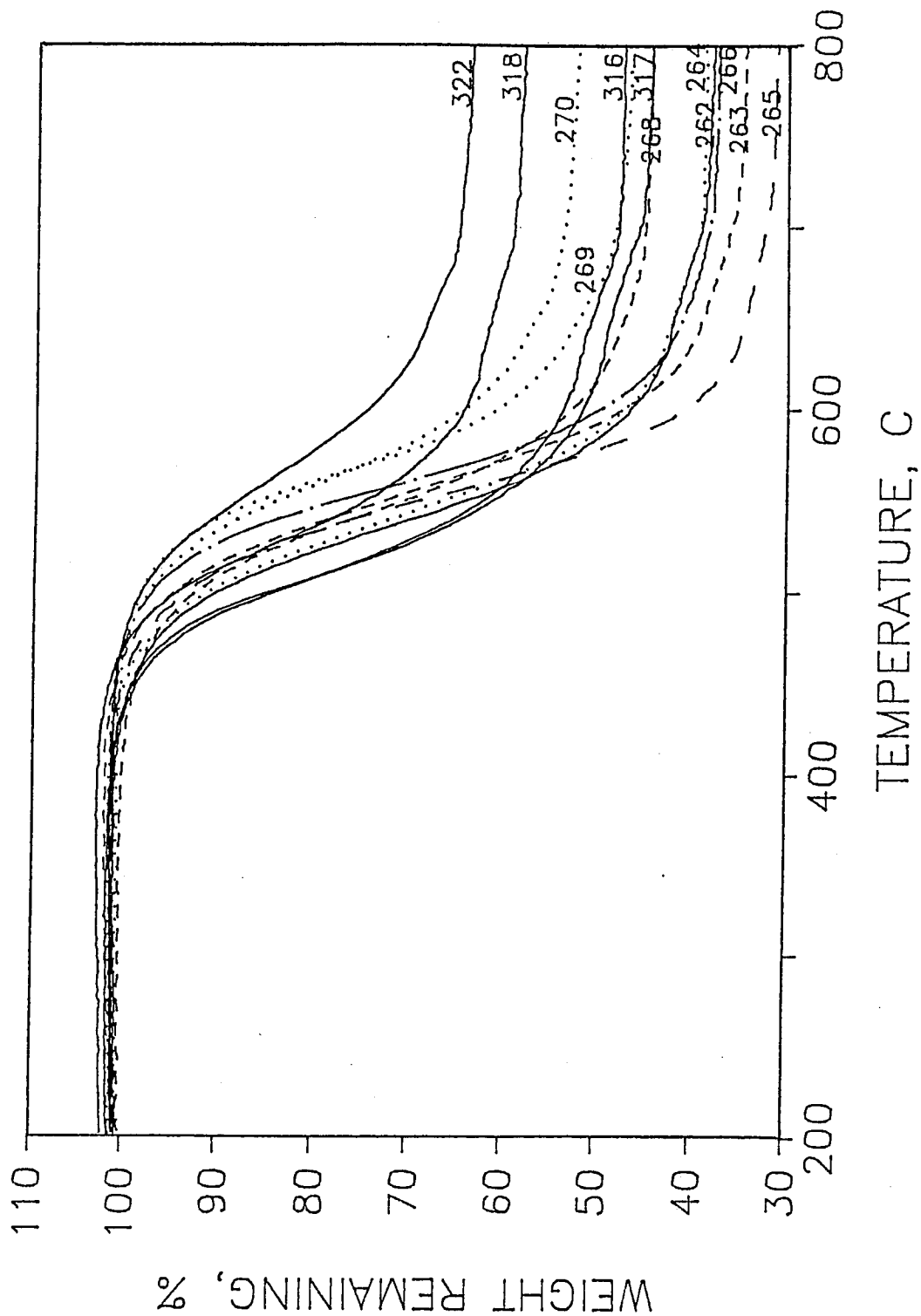


Figure 19. TG-combustion curves for FBC cyclone ashes.

cyclone ash. Further examination of the results indicate that the amount of combustibles in the cyclone ashes varied with test conditions and type of fuel. This is clearly shown in figure 20 where the percent of combustibles remaining in the cyclone ashes presented in table 8 (values obtained at 625°C) are plotted against bed temperatures.

Table 8. Nominal FBC test conditions

Test Material	Sample Number		Test Condition	Combustibles in Cyclone Ash (%) ^a
	ANL	ISGS		
Coal	183-139-3	TG316	1	48
	183-139-5	TG317	2	50
	183-139-7	TG318	3	37
	183-139-9	TG322	4	31
PD-1	183-147-2	TG262	1	55
	183-147-4	TG264	2	55
	183-147-6	TG268	3	51
	183-147-8	TG270	4	40
PD-2	183-145-2	TG263	1	58
	183-145-4	TG265	2	63
	183-145-6	TG266	3	55
	183-145-8	TG269	4	45

^adetermined from TG-combustion data shown in figure 19

Figure 20 shows that the coal had the highest level of carbon burn-out followed by PD-1 and PD-2. It is also clear that bed temperature had a pronounced effect on the carbon burn-out. An increase in percent excess air had a minor influence on the performances.

Combustion efficiencies reported for the coal and PD coals in part B of this work are shown in figure 21. These data are in agreement with results presented above and indicate the coal was easiest to burn followed by PD-1 and PD-2. This order of reactivity was concluded from examination of the fuels by the TG method and was described earlier in the report (see figure 6).

Combustion properties of desulfurized fuels

Burning characteristics of a number of partially desulfurized fuels were determined by TG-combustion method. The fuels were provided by the project managers of three ICDB funded projects and included a physically deep-cleaned coal, five hydrodesulfurized chars and a steam desulfurized char. The deep-cleaned coal was prepared from IBCSP-4 coal utilizing the ISGS Aggregate Flotation process. It was provided by Dr. Richard Read. The hydrodesulfurized chars were prepared in a 2-inch ID batch fluidized bed reactor of the ISGS and were provided by Mr. Michael Stephenson. The steam desulfurized char was prepared in a 4-inch ID fluidized bed in the Mechanical Engineering Department at the University of Illinois, Champaign-Urbana and was provided by Professor Soo.

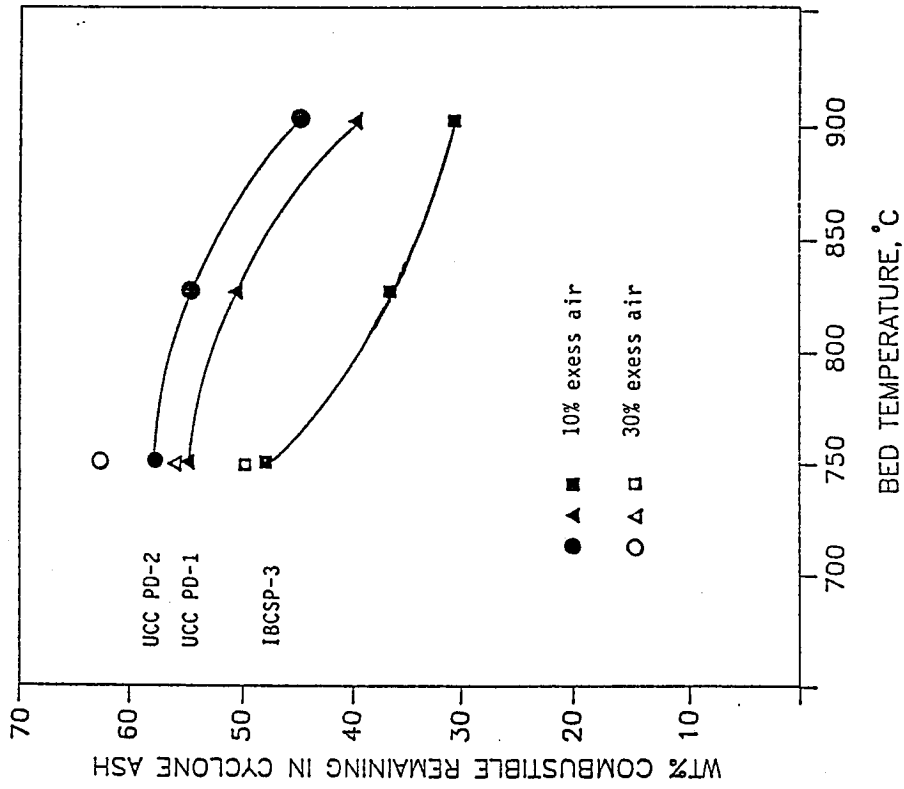


Figure 20. Effect of FBC bed temperature on carbon burn-off.

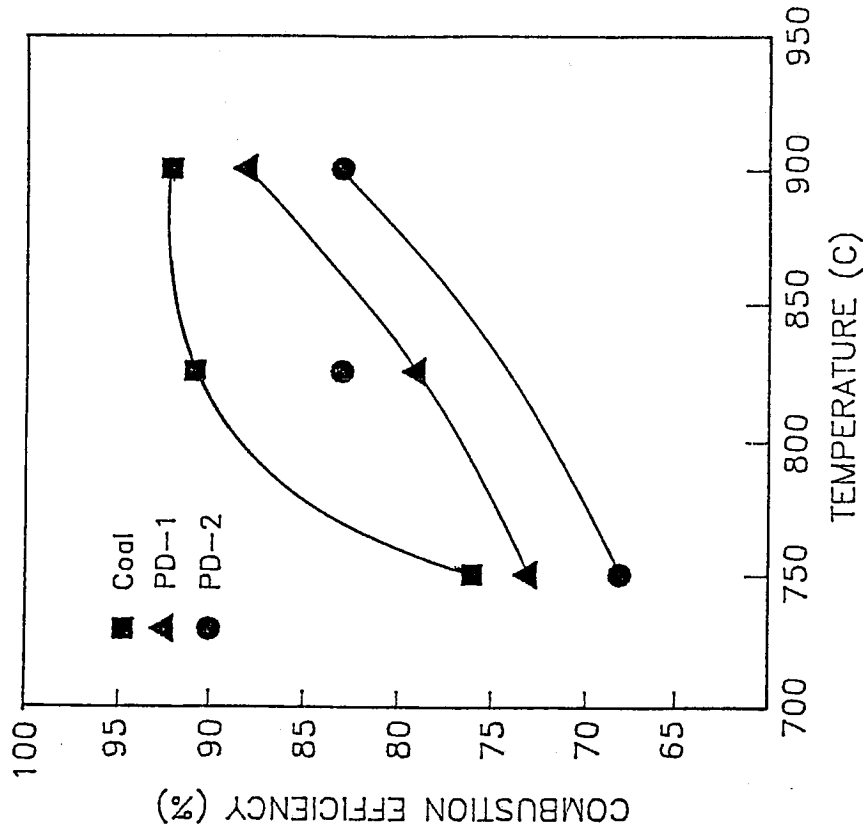


Figure 21. Combustion efficiencies vs. FBC bed temperature - values obtained from Part B of this work.

Burn-off curves for the representative samples of desulfurized fuels are shown in figure 22. Burning characteristics of the deep-cleaned coal were identical to those of the coal. This was expected since the sample was not subjected to any thermal or chemical cleaning methods which could remove organic components of the coal. Results shown in figure 22 also indicate that the steam desulfurized fuel which was prepared at 700°C was less reactive than the raw coal, but more reactive than the hydrodesulfurized chars. The low reactivities observed for the hydrodesulfurized chars are attributed to the more severe heat-treatment conditions to which they were subjected. It is clearly seen that char hydrodesulfurized at 750°C was easier to burn than char prepared at 850°C. These observations are in agreement with results described earlier on reactivities of PD fuels prepared in the microbalance reactor (see figure 10).

It has been suggested that low reactive fuels can be burned successfully when mixed with a high volatile coal. A fuel with about 17% volatile matter was prepared by blending the hydrodesulfurized char and IBCSP-3 coal. Data obtained for the mixture are shown in figures 23 and 24. A double-burn characteristic similar to those obtained for UCCRC chars was observed for the sample. The burn-off data indicate that the mixture was less reactive than a fuel with a comparable volatile matter content prepared in the microbalance reactor. The data also suggest that the two fractions of the fuel (i.e. coal and the char) burned independently. This is illustrated in figure 24 where the burning profile is compared with a curve made by graphically adding the burning profiles for the raw coal and hydrodesulfurized char. The predicted profile reflects the same ratio of coal to char that was present in the mixture. The two profiles are the same. This indicates that under the test conditions employed the addition of coal did not affect the burning behavior of the char. The results suggest that fuels with inherent volatile matter are more reactive than fuels with similar volatile matter prepared by blending low volatile chars and raw coal.

SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

Three partially devolatilized (PD) coals with volatile matter content (dry basis) of 23%, 15.4% and 11.4% were produced from IBCSP-3 coal (35.7% volatile matter) in the Mild Gasification Unit at the United Coal Company Research Corporation (UCCRC) in Bristol, Virginia. Representative sub-samples were prepared from the coal and three PD coals at the ISGS for thermogravimetry combustion studies (Part A), fluidized-bed combustion testing (Part B), and flame stability characterization at UI-UC (a separate study funded by ICDB).

Burning profiles (a plot of rate of carbon burn-off against temperature as the sample is heated in air at 20°C/min) were obtained to determine relative combustion characteristics of the fuels. Two types of combustibles of higher and lower reactivity were present in the PD coals. The two portions of combustibles burned in two distinct stages with peak burn rates at about 500 and 550°C. The burning characteristic of the higher-reactivity portion, which was present in a larger percentage in the high volatile PD coal; was similar to that of the raw coal. The results suggested that the coal was the easiest fuel to burn followed by the high, medium and low volatile PD coals.

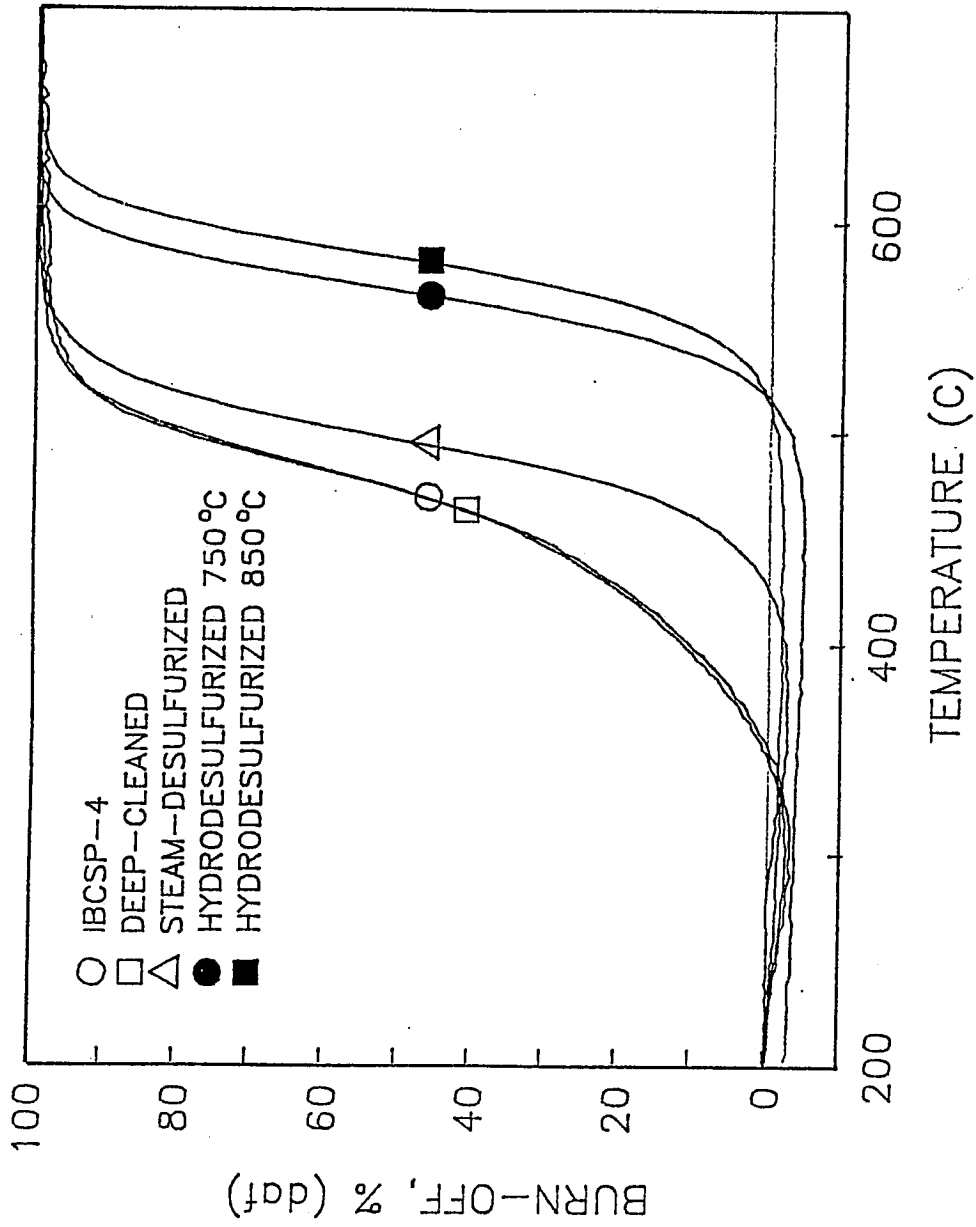


Figure 22. Burn-off curves for coal and partially desulfurized fuels.

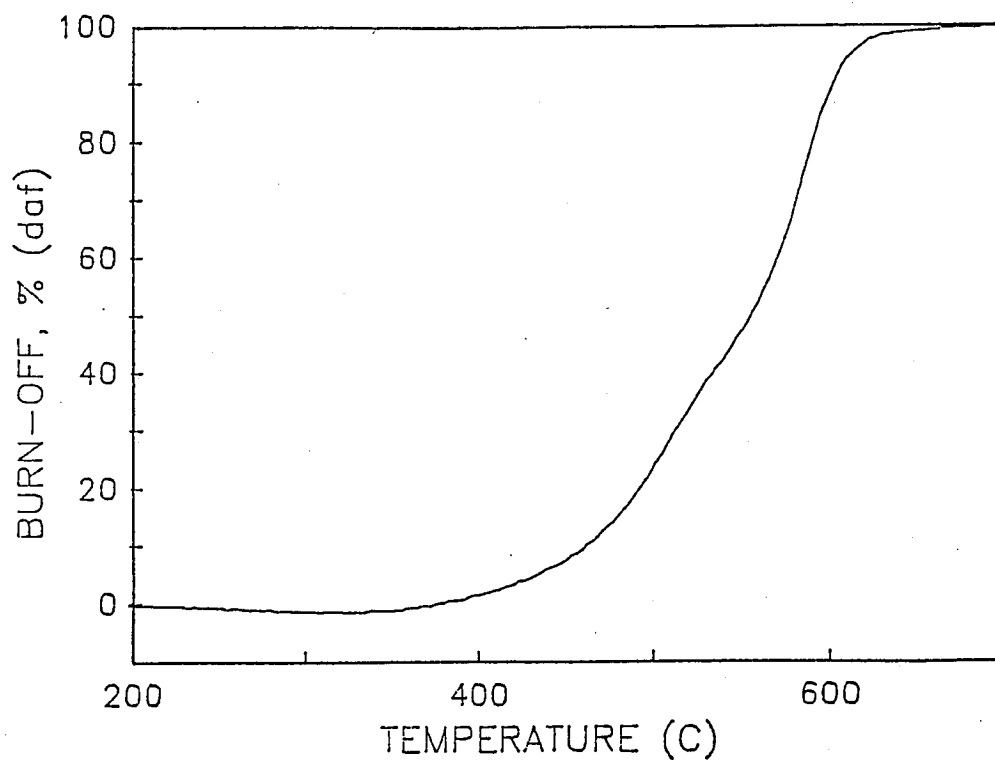


Figure 23. Burn-off curve for a mixture of hydrodesulfurized char and coal.

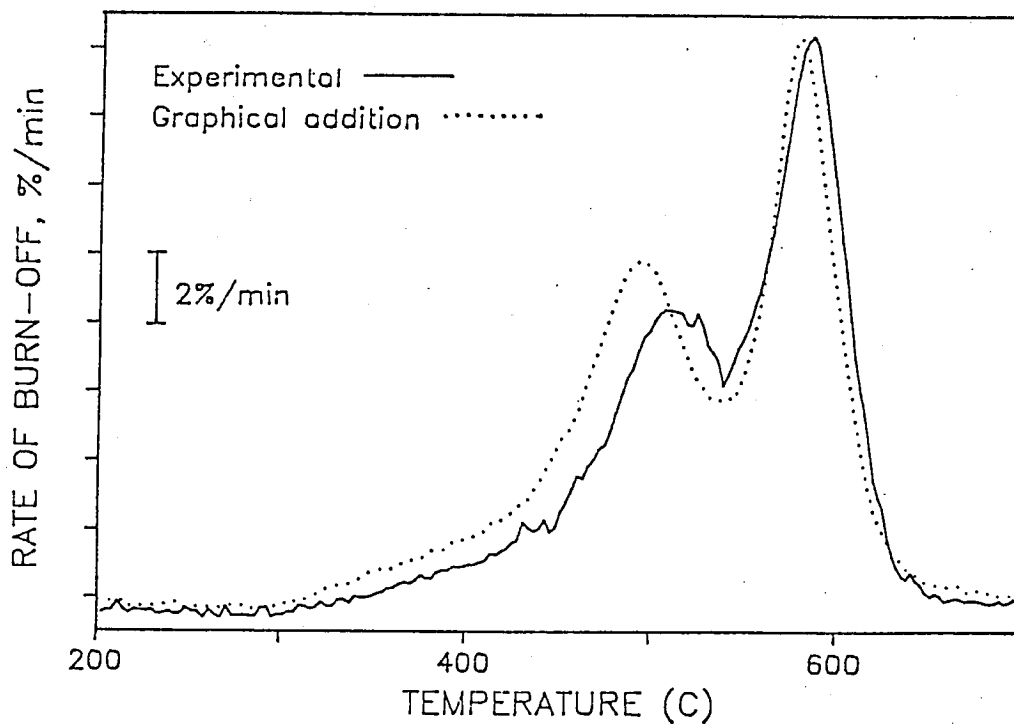


Figure 24. Experimental and predicted burning profiles for hydrodesulfurized char.

PD coals were also produced in a microbalance reactor under the following pyrolysis conditions: heating rates between 5 and 1200°C/min; heat-treatment temperatures between 400 and 950°C; soak times up to 4 hours. The resultant PD coals had volatile matter content between 2 and 30%. These fuels had different burning characteristics, but exhibited a single burn profile during combustion. Lower heat-treatment temperatures, rapid heating rate and shorter soak times at peak pyrolysis temperature increased reactivity. Fuels with volatile matter contents above 10% had similar burning behavior. However, burn temperatures increased markedly with further decreases in volatile matter content. PD coals prepared in the microbalance reactor were more reactive than their UCCRC counterparts. Fuels prepared by blending low volatile chars and raw coal were less reactive than a PD coal with comparable volatile matter content.

Reactivities of a number of fuels were determined under isothermal conditions to gain some information on changes taking place in pore structure during combustion and to obtain activation energies for the char oxidation reaction. Reaction temperatures below 570°C were selected to insure that reaction rates were not limited by mass transfer resistance. The results showed that the relative available pore surface area changed with conversion during combustion and that the extent of surface area development was higher for fuels prepared at lower temperatures. The reactivities of fuels were closely related to surface area development during combustion. Arrhenius-type plots were made to determine activation energies for a selected number of fuels. The activation energy was 31 kcal/mole in all cases. However, a PD coal prepared at 600°C was three times more reactive than a char produced at 950°C.

Burning characteristics of a number of partially desulfurized fuels were also determined by non-isothermal TG-combustion methods. A physically cleaned coal burned similar to its parent coal. A steam desulfurized fuel prepared at 700°C burned at lower temperatures than did a hydrodesulfurized fuel prepared at 850°C. Again, heat-treatment temperature was the major factor dictating burning characteristics.

In Part B of this work, combustion characteristics of the raw coal and three PD fuels prepared at UCCRC were investigated in fluidized-bed combustion tests at Argonne National Laboratory (ANL). Results of fluid-bed experiments were in agreement with thermogravimetric measurements of combustion reactivity made at the ISGS.

The major conclusions of this work are 1) volatile matter alone may not be a valid index of reactivity; 2) PD coal reactivity highly depends on the process through which it was produced (i.e. temperature, heating rate, soak time and reactor type); and 3) TG is a rapid and cost effective method to obtain relative burning characteristics of fuels tested under specified conditions.

Future research efforts should be directed to determine the interrelationships between volatile matter and particle size and their effects on combustion characteristics. It would be desirable to obtain carbon loss data in a drop tube furnace type reactor under conditions representative of a coal-fired boiler. Finally, it is highly recommended that a process scheme for producing PD coals be identified prior to combustion tests.

ACKNOWLEDGEMENTS

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APPENDIX 1

*United Coal Company*

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November 11, 1986

Dr. Massoud Rostam-Abadi
Minerals Engineering Section
Illinois State Geological Survey
Natural Resources Building
615 East Peabody Dr.
Champaign, Ill. 61820

Re: Purchase Order No. RQ82337DR
UCC Research Corporation
Devolatilized Coal Samples

Dear Dr. Rostam-Abadi:

As promised, please find enclosed a final report on production of char (partially devolatilized coal) from IBCSP #3 coal, using the Mild Gasification Unit @ UCC Research Corporation.

I am sorry to hear from your colleague, Dr. Carl W. Kruse and Dr. Joseph Debarr, on last Friday that some of the containers for the char and unused coal among the shipment we sent you on October 31, 1986 were damaged during the shipping. I hope it does not cause too much effect on the properties of the material. By the way, as I told you over the telephone earlier, there are two barrels of unused coal. However, with your permission, we have sent you just one of them and retained the other barrel here for our future testing purpose.

It has been a great pleasure working with you and your organization. I want to thank you for all the help you rendered us. Please convey, on my behalf, our thanks also to Dr. Carl W. Kruse, Dr. Bill L. Wells, and Dr. Joseph Debarr.

If you have any questions about either the report or the material we shipped to you, please do not hesitate to give me a buzz.

With best regards,

Charles I.C. Chu

Charles I.C. Chu
Manager, Coal Conversion/
Process Development
UCC Research Corporation

CICC/lgl

CC: Dick Wolfe
Chang Im
Keith Pearson
Barry Gillespie
Bob Wright

PRODUCTION OF CHAR (PARTIALLY DEVOLATILIZED COAL)
From IBCSP #3 COAL USING THE MILD GASIFICATION
UNIT @ UCC RESEARCH CORPORATION

FINAL REPORT

By

Charles I.C. Chu
Barry L. Gillespie

November, 1986

Work Performed Under Purchase Order No. RQ82337DR

For

Illinois State Geological Survey
Applied Research Lab
Oak and Gregory
Champaign, Illinois 61820

By

UCC RESEARCH CORPORATION
P.O. Box 1280/Glenway Avenue
Bristol, Virginia 24203
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Three types of char (partially devolatilized coal) each with a different volatile matter content, were produced from Illinois coal, IBCSP #3, in the Mild Gasification Unit (MGU) @ UCC Research Corporation (UCCRC). The target levels for volatile matter were $10 \pm 2\%$, $15 \pm 2\%$, and $25 \pm 3\%$ with no two chars having volatile matter contents closer than $\sim 5\%$. The actual chars produced had volatile matter levels of 12.40%, 17.15%, and 25.08% respectively.

Per Illinois State Geological Survey, the proximate and ultimate analyses as well as the particle size distribution (essentially $3/8$ " x 0) of the feedstock, IBCSP #3, are shown in Tables I & II.

Basically, the MGU operates as follows: coal from volumetric loading hoppers is charged into 8 inch diameter, 8 feet long, tapered reactor tubes. The reactor tubes are located in a natural gas fired furnace which is kept at 1400°F during the tests. The coal is heated in the reactor tubes, under a slight vacuum, sealed to exclude air, for a predetermined length of time. Vapor from the devolatilization of the coal is pulled by a vacuum pump from the reactor tubes into the MGU's condensing system. At the end of the test run, the char is discharged from the reactor tubes into the char discharge system by means of hydraulic plungers. During normal operation the char is discharged directly into the char quench chamber where it is cooled with a water spray. However, since this area of the MGU is not sealed from the atmosphere, the char discharge procedures were slightly modified for all production runs to prevent oxidation of the hot char by contact with air. The exact discharge procedures are discussed in the following as they were applied for each run.

Three preliminary tests, using six different residence times were performed. The purpose of the preliminary tests was to pinpoint the conditions necessary to produce the desired product chars. The residence times during the preliminary tests were varied from 1 hour to 4.5 hours. Test conditions which were constant for each test were a furnace temperature of 1400°F and 125 lbs. of coal per reactor tube. Two reactor tubes, each subject to identical conditions, were used for each test. The results of the char analyses from the preliminary tests are shown in Table III. Due to the need to quickly find out volatile matter content of the char after each run in order to plan for the next run, only the content of volatile matter and moisture in the chars were analyzed throughout this work. Thus, no other compositions and properties of either proximate or ultimate analysis for chars are reported herein.

It should be noted that during the preliminary tests, hot char was exposed to air during char discharge, crushing, and sampling. The method employed for the preliminary tests was chosen in order to greatly increase the speed and convenience of char handling and to insure completion of the work in the specified time period. The char discharge and cooling sequence for the preliminary tests was as follows: At the completion of the reaction cycle, the char was discharged into the char chamber where it was immediately water quenched to a temperature of $300\text{--}350^{\circ}\text{F}$. After the water quench, the char was transferred to a 55-gallon drum and allowed to air-cool for one hour. The char was then crushed in a hammermill crusher without screen. The size distribution of the crushed char is given in Table

IV. The distribution given in Table IV is representative particle size distribution for all the chars produced during this work. After crushing, the char, a total of 170-200 lbs, was riffled down to get a sample size of 10-15 lbs. This sample was sent to United Coal Company's Wellmore Central Laboratory for moisture and volatile matter analysis.

For the coal liquids collected during this work, only the liquid sample obtained from Preliminary Test #1 can be analyzed in time for inclusion in this report. The results of this analysis are shown in Tables V and VI.

Using the results of the preliminary test runs as the guide in selecting coal residence times, three final production runs were then carried out. The purpose of the final production runs was to produce the product chars with the desired volatile matter content. The residence times used for the three production runs were 3.17 hours, 2.90 hours, and 1.70 hours respectively. The results of the char analysis from these runs are shown in Table VII.

For the 3.17 hour production run the char discharge and quench sequence was slightly modified to prevent the hot char from contacting the atmosphere. After the reaction cycle was complete, the char was discharged from the reactor tubes and held on a gate in the char chute leading to the quench chamber. This section of the char chute is airtight and kept under a nitrogen blanket during the char discharge sequence. The char was partially quenched with water and allowed to cool on the gate for one hour. When the char had cooled to approximately 200°F, it was discharged into the quench chamber and immediately transferred to a 55-gallon drum. The drum was then sealed and purged with nitrogen. The char was allowed to cool in the drum under a nitrogen blanket to ambient temperature. After reaching ambient temperatures, the char was crushed and sampled using the same sampling procedure used in the preliminary tests. After sampling the char was immediately transferred back to a 55-gallon drum. The drum was purged with nitrogen and then sealed under 2 p.s.i. of nitrogen.

For the remaining two production runs, with 2.90 hours and 1.70 hours residence time, the char discharge sequence more closely resembled the sequence used during the preliminary test runs except the addition of nitrogen blanketting. Due to an inability to achieve an even quench of the hot char while it rested on the char gate, hot spots remained in the char. During cooling, the hot spots continued devolatilizing giving unpredictable results as far as volatile matter content was concerned. This was evidenced by the production run at 3.17 hours residence time discussed above. The volatile matter content of the char had been estimated, before the run, to be approximately 15% (through interpolation of preliminary test run data). Instead, it turned out to be only 12.40%. In order to prevent the continued devolatilization of char after discharge from the reactor tubes, the char was partially quenched on the char gate (but without the 1-hour delay on the gate as of first production run) before allowing it to go into the quench chamber. This served two major purposes. The first purpose was that it cooled a large portion of the char while still in an airtight section of the system. The second purpose was that it generated sufficient steam pressure to prevent the ingress of air while the char was being dropped into the open-air chamber for the final

quench. Upon cooling to $\sim 300^{\circ}\text{F}$, the char was quickly transferred, within 3-4 minutes, to a 55-gallon drum. The drum was purged with nitrogen and sealed. The char was allowed to cool to ambient temperature in the nitrogen atmosphere of the drum. After cooling to ambient temperature the char was handled in the same manner described above for the first production run. With the revision in the char discharge and quenching sequence, the predictions of char volatile matter content, before hand, for these two production runs were able to match the sample analysis results, after the run, almost right on the money.

Table I. Proximate and Ultimate Analyses of IBCSP sample #3
Coal (moisture free basis)¹

Analysis	C22443 July 83	C22740 July 84	C23923 Sept 85	Av C24440-1 March 86	C24892 July 86
Moisture	5.0	5.4	5.7	5.4	5.3
V/M	39.1	40.5	37.8	39.2	39.4
FC	52.6	51.2	53.8	52.6	52.2
H-T ASH	8.3	8.4	8.4	8.3	8.4
Carbon	72.72	73.51	72.78	74.98	75.12
Hydrogen	4.87	4.93	4.91	4.89	5.09
Nitrogen	1.62	1.54	1.72	1.71	1.79
Oxygen	10.24	9.37	10.02	7.84	7.28
Sulfatic Sulfur	0.12	0.14	0.14	0.04	0.0
Pyritic Sulfur	1.03	1.00	1.04	1.01	1.08
Organic Sulfur	1.08	1.14	1.03	1.27	1.26
Total Sulfur	2.23	2.28	2.21	2.32	2.33
Total Chlorine		0.18	0.16	0.15	0.21
BTU/lb	13387	13423	13422	13504	13449
FSI	4.5	4.5	5.0	6.25	5.5

¹Mixture of 80% Springfield (No.5) coal with 20% Herrin (No.6) coal from southern Illinois slope and strip mines, respectively, blended in the washing plant, collected July 15, 1983.

Table II. Sieve Analysis of IBCSP #3 Coal

Size, mesh	<u>Analysis A</u>		<u>Analysis B</u>	
	Wt.%	Cumulative Wt.%	Wt.%	Cumulative Wt.%
+8	67.2	67.2	67.7	67.7
8 x 14	16.4	83.6	16.1	83.8
14 x 28	7.0	90.6	7.0	90.8
28 x 48	4.1	94.7	4.0	94.8
48 x 100	2.3	97.0	2.2	97.0
100 x200	1.4	98.4	1.4	98.4
-200	1.6	100.0	1.6	100.0
Total	100.0		100.0	

Table III. Results from Preliminary Testing

<u>Residence Time, Hrs.</u>	<u>Volatile Matter, Dry Wt.%</u>	<u>Moisture, Wt.%</u>	<u>Test #</u>
1.00	28.86	5.25	3
2.00	23.65	4.14	3
3.00	17.77	0.68	2
3.58	10.95	2.14	1
4.08	10.52	4.97	1
4.58	10.14	2.78	2

Table IV. Particle Size Distribution of the Crushed Char

<u>Size, mesh</u>	<u>Wt.%</u>	<u>Cumulative Wt.%</u>
+4	50.4	50.4
4 x 16	26.4	76.8
16 x 30	8.2	85.0
30 x 60	7.5	92.5
60 x 0	7.5	100.0

Table V. Elemental & Average Molecular Weight Analyses For Coal Liquid Sample From Preliminary Test #1 (IGS-1-L)

<u>Elemental Analysis</u>	<u>As Received, Wt.%</u>	<u>Dry Basis, Wt.%</u>
Carbon	90.07	91.06
Hydrogen	4.86	4.79
Nitrogen	1.24	1.25
Sulfur	1.36	1.38
Oxygen	2.43	1.48
Moisture	1.09	-
Average Molecular Weight	361	-

Table VI. Boiling Point Distribution For Coal Liquid
Sample From Preliminary Test #1 (IGS-1-L)

<u>Boiling Point</u> <u>Distribution, ° F</u>	<u>Boiling Point</u> <u>Distribution, Wt. %</u>
301-400	-
401-500	8.4
501-600	15.1
601-700	13.8
701-800	9.5
801-900	7.3
901-1000	3.8
Residuum	42.1

Table VII. Char Analysis for Production Runs

<u>Run #</u>	<u>Residence</u> <u>Time, Hrs.</u>	<u>Volatile Matter</u> <u>Dry, Wt. %</u>	<u>Moisture</u> <u>Wt. %</u>
1	3.17	12.40	4.40
2	1.70	25.08	7.43
3	2.90	17.15	10.20