PROPERTIES OF MILD GASIFICATION CHARS: A COMPARISON OF PILOT PLANT- AND LABORATORY-PREPARED SAMPLES

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INTRODUCTION

Mild gasification (MG) of high volatile bituminous coal to produce high quality liquid, solid and gaseous products has been a major coal research activity at the Illinois State Geological Survey (ISGS) since 1986. Three major foci of the program have been to 1) evaluate conditions for producing the highest quality liquids; 2) characterize the char; and 3) develop a market for char. The feasibility of using MG chars, alone or as a coal-char blend, in typical industrial pulverized-coal boilers has been examined as one avenue for char use. In the ISGS studies, MG chars of various volatile matter (VM) content have been prepared both in laboratory and pilot plant facilities. In this paper, the effect of char preparation conditions on the physical and chemical properties of MG chars is discussed.

EXPERIMENTAL

Pilot plant-prepared samples - Chars were prepared from sample number 3 of the Illinois Basin Coal Sample Program (I8C-103) (1). This sample is a mine-washed coal (rank HvBb) and consists of a blend of 80% Herrin (No. 6) and 20% Springfield (No. 5) coals. The chars were produced in the Mild Gasification Unit at The United Company (formerly United Coal Company Research Corporation) in Bristol, Virginia (2). The chars were prepared by heating the coal (<2000 μm) under a slight vacuum in an 8-inch i.d., 8-foot fixed-bed reactor. The reactor was located inside a natural gas-fired furnace maintained at 760°C during the production runs. Three partially devolatilized (PD) samples (herein referred to as PD chars) designated as PD-1, PD-2 and PD-3 were prepared using residence times of 1.70, 2.90 and 3.17 hours. For each sample, 38-53, 53-75, 75-105, 105-150 and 150-212 μm particle size fractions were prepared. Further details of sample preparation are given elsewhere (3). All samples were stored under nitrogen prior to use.

Laboratory-prepared samples - Chars were derived from sample number 1 of the Illinois Basin Coal Sample Program (I8C-101). This sample was obtained from the Herrin (Illinois No. 6, HvCb) seam and was a mine-washed coal. Three PD coals (herein referred to as PD-89 chars) were prepared from 150-600 μm IBC-101 coal in a 2-inch i.d. batch fluidized-bed reactor system. A multi-step heating procedure was used to minimize agglomeration of coal particles in the reactor. The final temperature and final soak time were adjusted to produce the desired level of VM in the char. Final temperatures and soak times for laboratory chars were 475°C, 10 mins for the high-volatile char (PD-1-89); 505°C, 30 mins for the medium-volatile char (PD-2-89); and 600°C, 60 mins for the low volatile char (PD-3-89). All samples were ground and sieved in a step wise manner to prepare 38-53, 53-75 and 105-150 μm size fractions. Other details of sample preparation are given elsewhere (4).

Devolatilization behaviors of the coal and chars were determined using a thermogravimetric analyzer (TGA). Each sample was heated in flowing nitrogen (200 cc/min) to 900°C at a constant heating rate of 20°C/min. The weight of sample remaining, the rate of weight loss and the gas temperature in the vicinity of the sample were monitored by a computer as a function of time. The proximate and ultimate analyses and total sulfur contents of the samples were measured using LECO MAC 400, CHN 600, and SC32 analyzers. Internal surface areas of the samples were obtained from nitrogen and carbon dioxide absorption at -196° and -77°C, respectively. Ash

composition and ash fusion temperatures of the samples were determined according to method ASTM D1857.

Reactivities of chars were measured in air using the TGA system. A sample mass of 2-4 mg was heated at 50°C/min under nitrogen flow (200 cc/min) to between 400 and 480°C for these experiments. A modified TGA quartz furnace tube was used to allow the reactant gas (200 cc/min) to enter the quartz reactor tube directly (3). The objective was to achieve, as quickly as possible, a uniform concentration when the reactant gas was introduced into the furnace tube to obtain reliable rate data in the initial stage of reaction. The percent weight of the char remaining, the rate of weight loss and gas temperature in the vicinity of the sample were monitored.

RESULTS AND DISCUSSION

The results of the proximate and ultimate analyses for 105-150 μm IBC-101, IBC-103, PD chars and PD-89 chars are given in table 1. The VM contents (dry basis) of pilot plant chars were 22.1% (PD-1), 14.1% (PD-2) and 10.3% (PD-3). The laboratory chars had VM contents (dry basis) of 18.5% (PD-1-89), 15.4% (PD-2-89) and 9.8% (PD-3-89). Coal IBC-101 has a higher VM and sulfur content, and lower carbon content, than IBC-103. The laboratory chars had projected SO_2 emissions 27% less than IBC-101 while pilot plant chars had projected SO_2 emissions 14% less than IBC-103 coal. The differences in projected emissions could be that only half the sulfur present in IBC-103 is organic sulfur, while nearly 75% of the sulfur in IBC-101 is present in the organic form. It has been shown that at pyrolysis temperatures below 600°C, organic sulfur is more easily removed than pyritic sulfur (5).

The TGA devolatilization profiles of 105-150μm IBC-103 and pilot plant chars are shown in figure 1. The devolatilization process for coal can be divided into three stages: stage I, below 380°C, the loss of "free" moisture and the release of trapped gases and low molecular weight materials; stage II, 380°C to 550°C, the release of major amounts of tar and gas; and stage III, the thermal decomposition and/or reactions of pyrite impurities in the coal and secondary pyrolysis of the char (6).

Devolatilization profiles obtained for pilot plant chars (figure 1) exhibit weight loss in the three stages described for the coal. The weight loss (about 2.2%) in stage I could have been due to oil and tars that were trapped within the particles during preparation of these chars. TGA analysis to determine boiling point curves for coal oil and tars have indicated that these materials devolatilize below 400°C (7). Weight losses for stage II were about 14% for PD-1, 7.5% for PD-2, and 5% for PD-3. This stage of reaction should be absent for chars that have already been processed at temperatures above 550°C. The weight loss for IBC-103 coal was about 25% between 380 and 550°C. The fact that pilot plant chars lose weight in stage II indicates varying amounts of "coal-like" material remaining in these chars. Devolatilization data for a 15% VM coal-char blend prepared by mixing a char made in a microbalance reactor at 800°C with IBC-103 are shown in figure 1. It is seen that between 350-550°C, the shape of the weight loss curve for the coal-char blend is similar to that of PD-2; confirming the notion that the pilot plant chars contain coal-like material.

Because the pilot plant reactor was heated externally, it is expected that, due to heat transfer limitations, coal particles in the center of the 8-inch reactor were subjected to temperatures lower than those near the wall of the reactor. Unsteady-state one-dimensional heat transfer calculations revealed that the temperature near the center of the reactor was less than 400°C, temperatures at which the rate of pyrolysis is appreciable, even after 3 hours. This implies that there was a radial temperature profile at least within a portion of the reactor. As a result, coal particles were subjected to various thermal histories producing mixtures of highly devolatilized coal and "raw" coal.

The weight percent of coal-like material in each char was calculated using the relationship given below.

$$p = \frac{W_{PD}/(W_{PD} + FC_{PD})}{W_c/(W_c + FC_c)} \times 100\%$$

where: W_c = percent weight loss in stage II for coal; W_{PD} = percent weight loss in stage II for chars; FC_c = percent fixed carbon (dry-ash-free basis) in coal; and FC_{PD} = percent fixed carbon (dry-ash-free basis) in chars. The values of FC_c and FC_{PD} were obtained from table 1. A value of 25.6% was used for W_c (see figure 1). These calculations show that for 105-150 μm chars, the amount of coal-like material present in PD-1, PD-2 and PD-3 was 49%, 24% and 14%, respectively.

The devolatilization profiles of 105-150 μm IBC-101 coal and laboratory chars are shown in figure 2. Coal IBC-101 exhibits a volatile release profile similar to that of IBC-103. The weight loss below 150°C amounted to 6.5% for IBC-101, and less than 1.0% for the laboratory chars. The weight loss between 150 and 380°C was about 2% for the coal, and less than 1% for the laboratory chars. For these chars a noticeable weight loss begins about 460°C for PD-1-89, 520°C for PD-2-89 and 615°C for PD-3-89. These temperatures are consistent with the maximum heat treatment temperatures used during laboratory char preparation. This indicates that laboratory chars were homogeneous and not mixtures of highly devolatilized coal and raw coal.

Internal surface areas for 53-75 μm samples are presented in table 2. The two coals have comparable CO_2 surface areas, but IBC-101 had a substantially higher N_2 surface area than IBC-103. The CO_2 surface areas for the coals ranged from 216 to 239 m^2/g and were typical of HvC bituminous coals. Chars had lower N_2-BET surface areas than their parent coal, indicating perhaps that the incomplete removal of volatile matter resulted in partial plugging of a large fraction of the pores in the coal that were previously accessible to N_2 at -196°C. The extent of devolatilization had little influence on development of CO_2 surface area. The pilot plant chars had lower CO_2 surface areas than IBC-103, whereas the laboratory chars had higher CO_2 surface areas than IBC-101. The laboratory chars (PD-3-89) had about twice the surface area of the pilot plant chars (PD-3). It has been found previously that chars prepared from IBC-101 and IBC-103 under identical conditions in laboratory-scale reactors had identical surface areas (5). This suggests that different char preparation conditions, not different parent coals, are responsible for differences in surface areas of the chars. During laboratory char preparation, special precautions were taken to minimize agglomeration of IBC-101, while no such precautions were used for pilot plant char production using IBC-103. This could explain the differences in the surface areas of the chars, but without further study, no definite conclusions can be inferred.

Apparent rates [R = (1/m)·dm/dt; m = mass (ash-free) of sample] from TGA reactivity tests, calculated at 50% burn-off, indicate virtually no dependence on particle size in the temperature range used for oxidation studies (400-480°C) (2,3). This suggests that oxidation rates were sufficiently low such that pore diffusion had no rate-limiting effect and the reaction proceeded under kinetically controlled conditions.

Arrhenius plots (apparent rates vs 1/T) for PD-3 and PD-3-89 chars are presented in figure 3. The activation energies calculated are approximately 33 kcal/mol for both chars. Laboratory chars are about an order of magnitude more reactive than pilot plant chars. A comparison of reactivities of these chars, with those reported previously for chars prepared from Illinois No. 6 coal (3,8,9), is also shown in figure 3. The reactivity of PD-3-89 (laboratory-prepared char) is comparable with those of chars prepared in similar laboratory-scale reactors (3,8). A 15% VM char prepared in the TGA from IBC-103 (the same coal used to prepare PD-3) exhibited similar reactivity to that of PD-3-89. PD-3 has reactivity comparable to the reactivity which has been reported

for a pilot-scale char (9). These results confirm that char preparation conditions and reactor size and type influence the reactivity of the resultant char.

Ash composition and ash fusion temperature data were used to calculate a number of empirical parameters (10). The results of these tests and other ash characterization data for IBC-101, IBC-103, PD-3 and PD-3-89 are compiled in table 3. The two coals exhibit differences in ash composition which can affect the empirical parameters derived. Coal IBC-101 has a higher concentration of CaO, Na_2O and SO_3, and a lower concentration of Al_2O_3 than IBC-103. The higher Na_2O content translates into a significantly higher fouling index for IBC-101 (high fouling type) than IBC-103 (low fouling type) (10). The slagging index (10) for IBC-101 is significantly higher than that of IBC-103 due to the higher sulfur content of IBC-101. Both coals, however, fall in the range consistent with medium-slagging coals.

A direct comparison of the ash properties of PD-3 and PD-3-89 is not appropriate since the ash properties of the parent coals are different. However, the ash composition and ash characteristic values for PD-3 and PD-3-89 are nearly identical to those of their parent coals. MG processes did not significantly alter the composition of the ash, and there is no evidence that chars have different slagging of fouling indices than those of their parent coals.

SUMMARY AND CONCLUSIONS

Chars with about 10, 15 and 20 percent VM were prepared from Illinois coals under mild gasification conditions both in pilot- and laboratory-scale reactors. The method of char preparation influenced the physical and chemical properties of the chars. Pilot-scale chars were mixtures of highly devolatilized coal and relatively unreacted coal, and had devolatilization characteristics similar to a blend prepared by mixing the parent coal and char. Pilot-scale chars were an order of magnitude less reactive than laboratory-scale chars. Measured CO_2 surface areas of laboratory-scale chars were about two times greater than those of pilot-scale chars. MG processes did not significantly alter the composition of the ash, and there was no evidence that chars have different slagging of fouling indices than their parent coals.

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REFERENCES

1. Harvey, R. D. and C. W. Kruse, 1988. J. Coal Qual., 7(4), pp. 109-112.
2. Rostam-Abadi, M., J. A. DeBarr, C. W. Kruse. D. L. Moran, R. D. Harvey and R. R. Frost, 1987. Final Technical Report, CRSC, Champaign, IL.
3. Rostam-Abadi, M., J. A. DeBarr and W. T. Chen, 1988. "Combustion Characteristics of Coal-derived Solid Fuels". Final Technical Report, CRSC, Champaign, IL.
4. Rostam-Abadi, M., J. A. DeBarr, R. D. Harvey, S. A. Benson, D. P. McCollor, 1989. "Reactivity and Combustion Properties of Coal-derived Solid Fuels". Final Technical Report, CRSC, Champaign, IL.
5. Hackley, K. C., R. R. Frost, C-L. Liu, S.J. Hawk and D. D. Coleman, 1990. Illinois State Geol. Survey Circ. #545.
6. Rostam-Abadi, M. and C. W. Kruse, 1983. Proc. of the 12th Annual North Amer. Thermal Analysis Society Conf., paper #175.
7. Kruse, C. W., A. D. Williams and F. D. Guffey, 1989. Final Technical Report, CRSC, Champaign, IL.
8. Khan, M. R., 1987. Fuel, 66(12), pp. 1626-1634.
9. Dutta. S. and C. Y. Wen, 1977. Ind. Eng. Chem. Process Des. Dev., 16(1), pp.31-37
10. Attig, R. C. and A. F. Duzy, 1969. Proc. Amer. Power Conf., 31, pg. 290-300.

Table 1. Proximate and ultimate analyses for 105-150 μm fuels (dry basis).

	IBC-101	PD-1-89	PD-2-89	PD-3-89	IBC-103	PD-1	PD-2	PD-3
Moisture	6.6	1.3	1.3	0.6	2.0	2.1	1.9	1.8
Proximate								
Volatile Matter	42.0	18.5	15.4	9.8	36.7	22.1	14.1	10.3
Fixed Carbon	48.4	68.4	71.8	76.6	54.3	67.5	74.2	78.0
Ultimate								
Hydrogen	5.04	3.47	3.08	2.16	5.13	3.47	2.39	1.64
Carbon	69.68	72.55	75.66	77.99	75.06	77.85	79.71	80.58
Nitrogen	1.44	1.70	1.82	1.87	1.67	1.95	1.92	1.78
Oxygen	9.96	5.83	3.74	1.48	6.89	4.43	2.46	2.46
Sulfur	4.28	3.35	2.96	2.93	2.24	1.95	1.81	1.79
Ash	9.6	13.1	12.7	13.6	9.01	10.34	11.71	11.74
Btu/lb	12790	12504	12716	12706	13490	13245	13010	12828
lbs SO_2/MM Btu	6.7	5.4	4.7	4.6	3.3	2.9	2.8	2.8

Table 2. Surface areas for 53-75 μm fuels.

	IBC-101	PD-1-89	PD-2-89	PD-3-89	IBC-103	PD-1	PD-2	PD-3
BET(CO_2)	239	249	305	354	216	194	175	165
BET(N_2)	61.3	2.0	3.8	9.5	3.8	1.2	1.0	0.8

Table 3. Ash characterization of coals and chars.

Character	IBC-101	PD-3-89	IBC-103	PD-3
Ash analyses (% of ash)				
SiO_2	48.60	48.20	49.63	47.77
Al_2O_3	17.49	17.36	22.13	21.82
Fe_2O_3	18.22	18.08	18.16	21.82
CaO	4.89	4.76	1.59	1.58
MgO	0.99	0.98	0.92	0.90
K_2O	2.22	2.22	2.44	2.35
Na_2O	1.47	1.50	0.33	0.30
TiO_2	0.89	0.90	1.30	1.20
P_2O_5	0.27	0.26	0.33	0.37
MnO	0.05	0.06	0.02	0.03
SrO	0.04	0.04	0.06	0.03
BaO	0.04	0.04	0.06	0.05
SO_3	4.19	4.29	1.43	1.22
Silica ratio	68.85	66.93	70.6	69.0
Base/acid	0.41	0.41	0.32	0.34
Ash fusion temp., °F, reducing				
Initial deformation	2055	2115	2000	2050
Softening	2140	2185	2160	2220
Hemispheric	2225	2260	2310	2335
Fluid	2310	2330	2465	2460
Empirical ash properties				
T_{250}, °F	2425	2460	2490	2510
T_{cv}, °F	2584	2584	2305	2310
Slag viscosity (poise @2600°F)	105	106	175	140
Slagging				
index	1.75	1.20	0.71	0.61
type	medium	medium	medium	medium
Fouling				
index	0.60	0.62	0.11	0.11
type	high	high	low	low

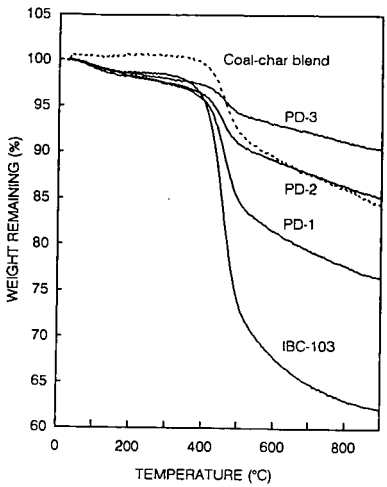

Figure 1. TGA devolatilization profiles for IBC-103, PD chars and a coal-char blend.

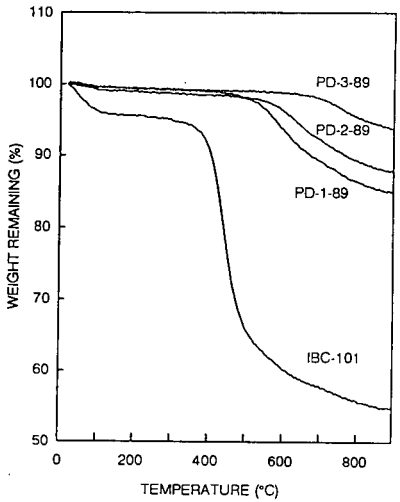

Figure 2. TGA devolatilization profiles for IBC-101 and PD-89 chars.

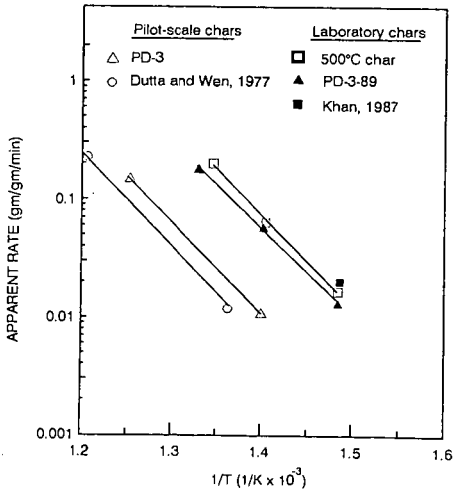

Figure 3. Arrhenius plot for fuels in 1 atm air