REACTIVITIES OF HEAT-TREATED COALS IN STEAM

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INTRODUCTION

We have previously reported reactivities of various American coal chars in air (1), CO_2 (2) and H_2 (3). In this paper, we are presenting reactivities of the same set of chars in steam. Reactivities have been measured at 910°C in one atmosphere of N_2-H_2O mixture containing water vapor at a partial pressure of 17.5 torr. The variables chosen for investigation were rank of parent coals, mineral matter content, particle size, reaction temperature and pressure. Effect of addition of H_2 to steam on char reactivity has also been studied.

EXPERIMENTAL

Char Preparation Seventeen U.S. coals (40x100 mesh) varying in rank from anthracite to lignite were used for the preparation of chars. The coals were heated to 1000°C in a N_2 atmosphere at a rate of 10°C/min. Soak time at 1000°C was 2 hr. In order to study the effect of mineral matter removal on char reactivity, selected coals, prior to carbonization, or raw chars, were acid-washed (AW) with 10 volume % HCl or demineralized with a 1:1 HCl-HF mixture.

Procedure A Fisher TGA unit, Model 442, was used for reactivity measurements. About 3 mg of char contained in a platinum pan were heated in N_2 (300 cc/min) up to 1000°C at a rate of 20°C/min. Heating at 1000°C was continued until the char weight became constant. The sample was then cooled to the reaction temperature (910°C) and held at this temperature for 20 min for temperature stabilization. After this, N_2 was replaced by the appropriate reacting mixture. Water vapor pressure was generated by bubbling prepurified N_2 through deaerated distilled water at 20°C. Following introduction of the reacting mixture, the weight of the sample was recorded continuously as a function of time.

Reactivity Measurement Burn-off curves usually had a slow induction period followed by a rate increase. Following the suggestion of Jenkins et al. (1), the reactivity parameter was calculated by the following equation:

$$R = \frac{1}{w_o} \cdot \frac{dw}{dt}$$

where w_o is the starting weight of the char on a dry-ash-free (daf) basis and dw/dt is the maximum rectilinear weight loss rate (mg hr^{-1}).

RESULTS AND DISCUSSION

Reactivity Versus Rank of Parent Coal Reactivity parameters for various chars along with relevant analyses of coals and chars are listed in Table 1. It is seen that char reactivity decreases, in general, with increase in rank of the parent coal. There is a considerable spread in reactivities of chars produced from coals of different rank. The LV bituminous char, PSOC-127, is the least reactive, whereas the lignite char, PSOC-91, is the most reactive, its reactivity being about 250 times that of the PSOC-127 char.

Mineral Matter Removal Removal of mineral matter decreases, in general, subsequent char reactivity. However, in the case of chars derived from higher rank coals mineral matter removal enhances reactivity. Removal of mineral matter from coals prior to their carbonization brings about profound changes in surface area and porosity. The decrease in char reactivity and changes in surface area are much less pronounced when the chars rather than the coal precursors are acid-washed or demineralized.

Particle Size For a lignite char, PSOC-87, the reactivity parameter is essentially the same for 40x100, 100x150 and 200x325 mesh fractions. However, the reactivity of a LV bituminous char, PSOC-127, increases 4-fold when particle size is reduced from 40x100 to 200x325 mesh, indicating that the reaction is partly diffusion controlled. Upon demineralization, the reactivity parameter for the lignite char decreases for all the three size fractions, whereas the reactivity of the PSOC-127 char increases about 10-fold for each size fraction.

Pressure The dependence of rate on steam partial pressure in the range between 6.5 and 17.5 torr was determined for PSOC-91 char. The reactivity was found to be proportional to steam pressure raised to the 0.60 power.

Temperature Reactivity of a lignite char, PSOC-91, was studied in the temperature range 750-930°C. Below 890°C, the reaction is chemically controlled with an apparent activation energy of 42 kcal/mole. Above 890°C, the reaction is diffusion controlled and has an activation energy of 18 kcal/mole.

Addition of H_2 In order to study the effect of H_2 addition to steam on char reactivity, a mixture of N_2 and H_2 containing 20% H_2 was bubbled through water at 20°C; the partial pressure of water vapor in the mixture was 17.5 torr. Reactivities of a few selected chars in steam, as well as in the steam-H_2 mixture, are given in Table 2. Reactivities of the two lignite chars, PSOC-91 and 87, decrease sharply in the presence of H_2 indicating its strong inhibitive effect. Addition of H_2 has little or no effect on the reactivities of chars derived from PSOC-26, 22 and 24 coals. Reactivity of the LV bituminous char, PSOC-127, increases by 20-fold in the presence of H_2. It is noteworthy that the addition of H_2 to steam increases slightly the reactivity of the raw lignite char, PSOC-138, but has an inhibiting effect on the reactivity of the acid-washed char. These results suggest that in the case of the PSOC-127 and 138 raw chars, H_2 reacts with some catalytically inert inorganic impurity initially present in the char converting it to a catalytically active chemical form and that the inhibitive effect on char reactivity due to H_2 is more than offset by the catalytic effect of the 'regenerated' impurity.

In the steam partial pressure range 6.5 to 17.5 torr, the reactivity of PSOC-91 char in steam-H_2 mixtures is proportional to the steam pressure raised to the 0.93 power.

Reactivity of PSOC-91 char in the steam-H_2 mixture, unlike that in steam, is chemically controlled over the 750-930°C temperature range; the apparent activation energy for the reaction is 84 kcal/mole compared to 42 kcal/mole for the reaction in steam. The higher activation energy in the steam-H_2 mixture is indicative of the strong inhibiting effect of H_2 on the char-steam reaction for PSOC-91.

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REFERENCES

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TABLE 1

CHAR REACTIVITY IN STEAM

PSOC Sample No.	Parent Coal ASTM Rank	State	C(daf), %	Char Ash, %	Reactivity, mg hr^{-1} mg^{-1}
91	Lignite	Mon.	70.7	11	2.9
87	Lignite	N.D.	71.2	13	2.8
140	Lignite	Tex.	71.7	12	1.5
138	Lignite	Tex.	74.3	16	1.2
98	Sbb-A	Wyo.	74.3	12	1.0
101	Sbb-C	Wyo.	74.8	8	2.5
26	HVB	Ill.	77.3	20	0.25
22	HVC	Ill.	78.8	23	0.45
24	HVB	Ill.	80.1	14	0.52
67	HVB	Ut.	80.4	5	0.22
171	HVA	W.Va.	82.3	11	0.15
4	HVA	Ky.	83.8	2	0.30
137	MV	Ala.	87.0	19	0.10
114	LV	Pa.	88.2	12	0.07
127	LV	Pa.	89.6	7	0.011
81	Anthracite	Pa.	91.9	6	0.13
177	Anthracite	Pa.	93.5	5	0.11

TABLE 2

EFFECT OF HYDROGEN ADDITION TO STEAM ON CHAR REACTIVITY

PSOC Sample No.	Reactivity, mg hr^{-1} mg^{-1} Steam	Steam-H_2
91	2.9	0.63
91 AW	1.8	0.51
87	2.8	1.0
138	1.2	1.3
138 AW	0.88	0.63
26	0.25	0.24
22	0.45	0.40
24	0.52	0.59
127	0.011	0.20