

REACTIVITIES OF HEAT-TREATED COALS IN HYDROGEN

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INTRODUCTION

In previous papers, we reported reactivities of various American coal chars in air (1) and in carbon dioxide (2). It was found that reactivities of chars are predominantly determined by the rank of the parent coal and mineral matter composition. The main aim of this paper is to compare the reactivities in hydrogen with those obtained earlier.

The reaction of coal chars with hydrogen is an important part of the over-all process for the production of substitute natural gas; consequently it has received considerable attention (3-8). The reaction of low temperature chars with hydrogen proceeds in two stages: a very rapid first stage reaction and a slow second stage reaction, involving the gasification of a remaining char which has a graphitic-like (trigonally-bonded) structure. Most workers have studied the reactivity of the chars which have been pretreated at some fixed maximum temperature. Because the maximum temperature was usually reasonably low, the chars had, however, a certain amount of volatile matter remaining. In order to study the slow, second stage hydrogasification reaction, it would be better to work with a char prepared at a higher temperature. Throughout this study chars prepared at 1000°C are used. The variables chosen for investigation were the rank of parent coals, mineral matter content, particle size, reaction temperature and pressure.

EXPERIMENTAL

Char Preparation Eighteen U.S. coals, of widely varying rank, were carbonized in nitrogen at 1000°C for 2 hr. This procedure was sufficient to devolatilize these coals. The preparative method of 'acid-washed' char, demineralized char, and chars with different particle sizes were essentially the same as described earlier (2).

Procedure A high-pressure, electronic balance was used to record continuously small weight changes during hydrogasification. The balance assembly, a DuPont 951 TGA, was mounted in an autoclave. Generally, char powders of 40x100 U.S. mesh were charged to a sample holder in 10 mg quantities. The autoclave was evacuated and then pressurized with nitrogen to 400 psi. Helium was introduced into the quartz tube reactor, which was attached to the balance housing and also was surrounded by a tube furnace. The furnace was activated to raise the reactor temperature to 980°C. The pressure was kept constant by bleeding off excess gas. Helium was kept flowing at reaction temperature for 15 min to ensure thermal stability; and then a stream of hydrogen was admitted to the reactor at a flow rate of 1200 cc/min (STP). The weight of the sample was then continuously recorded.

Reactivity Measurement The conversion vs time curve usually had a slow induction period, followed by a rate increase as was reported for the reaction with air (1), carbon dioxide (2), hydrogen (7), and steam (7). Jenkins et al (1), found that the rectilinear portion, after an induction period, extended over a range in which about 40% of the char was gasified. They calculated the reactivity parameter by the following equation:

$$R_0 = \frac{1}{W_0} \frac{dw}{dt}$$

where W_0 is the initial weight of char on a dry ash free basis (mg) and dw/dt is the maximum^o rectilinear weight loss rate (mg hr^{-1}). In the present study, the rectilinear region was considerably shorter than reported previously (1,2). On the other hand, the rate calculated on the basis of unreacted char remained constant for a longer period. This reactivity parameter R is expressed as

$$R = \frac{1}{W} \frac{dw}{dt}$$

where W is the weight of char at time t . Two parameters R_1 and R_c were determined by this equation. R_1 represents the initial rate at $t = 0$, and R_c represents the constant rate in the region where kinetics follows a first order rate expression with respect to unreacted char.

RESULTS AND DISCUSSION

Reactivity versus rank of parent coal Table 1 summarizes the analyses of coals and chars together with the reactivity parameters. It can be seen that there is some relation between R_1 values and the rank of the parent coal. The lower rank coal chars have larger R_1 values. However, R_c values have no definite correlation with rank. For example, the reactivity of the Pennsylvania anthracite char (PSOC 81) is larger than most chars of lower rank. This fact is in marked contrast with those reported for the reactivity of the same series of chars with air and carbon dioxide. In these cases, a plot of reactivity R_0 vs carbon content shows a fairly well defined band. Even if the parameter R_0 is used for the hydrogasification reactivity, no correlation with rank of parent coal is found. Feldkirchner et al (4) found a similarity in hydrogasification rates of the residual portion of three coal chars with greatly different initial properties.

Mineral matter removal Jenkins et al (1) found that the reactivity of lignite and anthracite chars in air decreased upon demineralization, whereas reactivity of a LV bituminous char increased. The same effect of demineralization was observed in this study for PSOC 138, 101, 127 and 81. However, the removal of mineral matter from lignite char PSOC 87 resulted in a remarkable increase of R_c value, although the R_1 value decreased considerably.

Bed weight and particle size In order to determine the possible effect of diffusional resistance, reactivity measurements were made for PSOC 91, 87, 87 Dem, 127 and 127 Dem at different bed weights and particle sizes. For starting weights below 10 mg, reactivity is constant for most chars. There is some effect of particle size, but the rate increase due to the reduction of size is rather small compared with that reported for the reactivity study in CO_2 (2). Reduction in particle size of PSOC 127 char from 40x100 to 200x325 mesh results in a reactivity increase of only 1.6-fold in hydrogen, whereas a similar particle size reduction of the same char resulted in a reactivity increase of 35-fold towards carbon dioxide (2). This fact can be attributed to the smaller kinetic diameter of hydrogen (2.9A) compared to carbon dioxide (3.3A).

Pressure The dependence of rate on hydrogen pressure in the range between 100 and 400 psi was determined for PSOC 91 char. The rate was proportional to hydrogen pressure as reported in the literature (4-7).

Temperature Zielke et al (3) reported that the pseudo-activation energy changed from 17 to 49 kcal/mole as a function of conversion. Gardner et al (8) also found an increase of activation enthalpy with conversion of char to methane. Although the chars used in this study had a different thermal treatment than those used by

Gardner et al (8), we also observed a similar trend. The pseudo-activation energy for PSOC 91, 87 Dem, and 127 Dem chars were 31, 29, and 14 kcal/mole at the initial slow stage, while at a steady state rate they were 48, 44, and 44 kcal/mole, respectively. This fact suggests that the reaction during the induction period is diffusion-controlled, and further that the later stage is a chemically-controlled step. During the induction period, the char undergoes activation, and thus the diffusion rate of hydrogen or methane into the interior of the char particles becomes more rapid.

PSOC 217 char has an unusually low reactivity among all chars. The pseudo-activation energy was determined for this char up to a conversion of 20%, and it was found to be nearly constant at 16 kcal/mole. This low activation energy (and, thus extensive diffusion control of the gasification rate) is expected because of the small percentage of feeder pores in the parent LV bituminous coal (9).

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TABLE 1
CHAR REACTIVITY IN HYDROGEN

PSOC Sample No.	Parent Coal			Char Ash, %	Reactivity, mg hr ⁻¹ mg ⁻¹	
	ASTM Rank	State	C(daf), %		R _i	R _c
89	Lignite	N.D.	63.3	22	0.73 ^a	1.0
91	Lignite	Mont.	70.7	11	1.0 ^a	1.2
87	Lignite	N.D.	71.2	13	2.1 ^a	2.1 ^b
140	Lignite	Tex.	71.7	12	0.55	1.7
138	Lignite	Tex.	74.3	16	0.62	1.5
98	Sbb. A	Wyo.	74.3	12	0.34	1.0
101	Sbb. C	Wyo.	74.8	8	1.2 ^a	1.2 ^b
26	HVB	Ill.	77.3	20	0.37	0.99
22	HVC	Ill.	78.8	23	0.38	2.0
24	HVB	Ill.	80.1	14	0.50	2.3
67	HVB	Utah	80.4	5	0.30	1.9
171	HVA	W.Va.	82.3	11	0.08	0.64
4	HVA	Ky.	83.8	2	0.13	1.7
137	MV	Ala.	87.0	19	0.23	0.24 ^b
114	LV	Pa.	88.2	12	0.22	0.39 ^b
127	LV	Pa.	89.6	7	0.05	0.09
81	Anthracite	Pa.	91.9	6	0.13	2.0
177	Anthracite	Pa.	93.5	5	0.06	0.73

a No or very short induction period.

b Constant rate region is less than 50% of complete burn-off.