

THE REACTIVITY OF COAL CHARs WITH CO₂ AT 1100-1600°C

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INTRODUCTION

Knowledge of the coal char reactivity in the temperature range 1100-1600°C is of fundamental importance in understanding many coal gasification and direct combustion processes. However, due to the intricate interplay of the diffusional steps and the chemical or surface step in this temperature range, (1) studies in this area have been relatively rare compared to studies in the lower temperature range. Recently, a diffusion cell technique has been developed at Brookhaven for measuring the chemical rates in the diffusion/chemical reaction combined-controlled region and the technique has been applied to studies of the kinetics of the reactions between CO₂ and a nuclear graphite in the temperature range of 1200-1600°C (2) In this paper, we wish to report the initial results of the kinetics of the same reaction at a total pressure of 1 atm using coal chars of varying rank.

EXPERIMENTAL

Apparatus

The apparatus and the gas flow system are essentially the same as described previously, (2) except that the flow system was built on a Cahn-R100 null-type balance instead of a Mettler TA-1 balance. This reactor system is capable of 1700°C and 15 atm or higher pressures and is described elsewhere. (3) It would suffice in this report to note that the alumina diffusion cell had a dimension of 16 x 24 (diameter and length) and the gas flow was downward and at the same flow rate as in the previous work. (2)

Sample Materials and Preparation

The coal samples used were:

Pennsylvania Anthracite,
Illinois No. 6 Bituminous and
Montana (Rosebud) Lignite,

all kindly supplied by the Pittsburgh Energy Research Center. The samples were carbonized in N₂ at 1000°C for 16 hrs and subsequently ground and sieved to the size range of 590-840 microns which was the size used throughout this work. A demineralized Montana Lignite sample was also prepared by leaching the sample in a combined acid solution (6.2 M HCl and 7.4 MHF) at 50°C for 48 hrs. The leached sample was rinsed thoroughly and dried and was then carbonized and sized.

DATA TREATMENT

The chemical rates were calculated by using the following solution of the binary-diffusion equation for the diffusion cell:

$$R = \frac{CD k_1}{cD = k_1 \ell} \log (1 + P_{CO_2}) \quad (1)$$

where R is the overall rate or the mass flux which was measured gravimetrically; C the molar concentration of the diffusion gases; D the approximate binary-diffusion coefficient; ℓ the path length and P_{CO_2} the partial pressure of CO_2 in the bulk stream. k_1 is the rate constant in the Langmuir-Hinshelwood rate expression and is defined by:

$$R = k_1 P_{CO_2} \text{ at the surface (or } \ell = 0) \quad (2)$$

Detailed discussion of these equations and the calculation of D in the temperature range being studied can be found in reference (2). The value of k_1 calculated with equation (1) is in general 2-4% higher than that calculated by using the solutions of the exact multi-component diffusion equations.⁽²⁾ Also, k_1 is based on per unit area of the cross section of the diffusion cell. Discussion of the usage of this unit and the depth of the reaction zone in the particles can also be found in references (2) and (8).

RESULTS AND DISCUSSION

The rate constant k_1 calculated from equation (1) represents the intrinsic chemical reactivity of the carbon surface. To obtain k_1 , a series of measurements of R at varying P_{CO_2} were first made, a linear plot of R vs $\log (1 + P_{CO_2})$ was then obtained and k_1 was calculated from this plot according to equation (1). The value of k_1 varied with the percentage carbon burn-off and in this work, the value of k_1 was taken in the burn-off range of 20-40%.

In Figure 1, the first kinetic data are summarized for the three coal samples and the leached lignite at selected temperatures. The most prominent feature in this figure is the peaking (or plateauing) of the rate constant at varying temperatures. Except for the anthracite, the peak temperatures are too low to be related to the well-known peaking phenomenon of the reactivity of graphite.⁽²⁻⁶⁾ However, an excellent match can be obtained between the peak temperature and the temperature range for melting of the ash. The three coal samples present a wide range of the ash melting temperatures. The ash softening temperatures (supplied by the Pittsburgh Energy Research Center) and the ash content in the chars (average value of at least three samples) are shown in Table 1. The k_1 measured for the leached Montana lignite showed that the peaking (or plateauing) does not

occur around 1200°C. This result indicates that the match between the peak temperature and the ash melting temperature is not coincidental.

Below the peaking temperatures, the reactivity of the char obeyed the general rule; lignite > bituminous > anthracite. This aspect has been discussed by Walker and Hippo. (7) At higher temperatures, this rule can no longer be applied, as shown in Figure 1. For example, the reactivity of the Illinois No. 6 bituminous coal char is about twice as that of the lignite at 1400°C and the reactivity of the anthracite can also exceed that of the lignite at about 1500°C. Peaking of the reactivity of the anthracite char may be attributable to the peaking phenomenon due to carbon alone. (2-6) The slight plateauing of the rate of the leached sample at above 1300°C was probably due to the residual ash in char.

An attempt was also made to elucidate the relationship between the reactivity and the melting of the minerals by measuring the surface areas of the samples heat-treated at above and below the ash melting temperature. The results are shown in Table 1. Unfortunately, the surface area measured is a total surface area of the carbon and the minerals. Thus, the results of the surface area measurements do not contribute to the proposition that the molten minerals could flow in the micro-structure; covering the surface sites as well as blocking the accessible pores. Nevertheless, this phenomenon is being further investigated in our laboratory.

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Table 1. Ash content and softening temperature

<u>Char</u>	<u>Ash Content, % of Char</u>	<u>Softening Temp., °C</u>
Pa. Anthracite	5	> 1600
Ill. No. 6 Bitum.	17	1350
Montana Lignite	21	1200
Leached Lignite	2.4	--

Table 2. BET N₂ surface area of Montana lignite chars

<u>Treatment</u>	<u>Surface Area, m²/g</u>
carbonized at 1000°C	11.9
leached and carbonized at 1000°C	20.2
carbonized at 1400°C	38.4
leached and carbonized at 1400°C	28.5

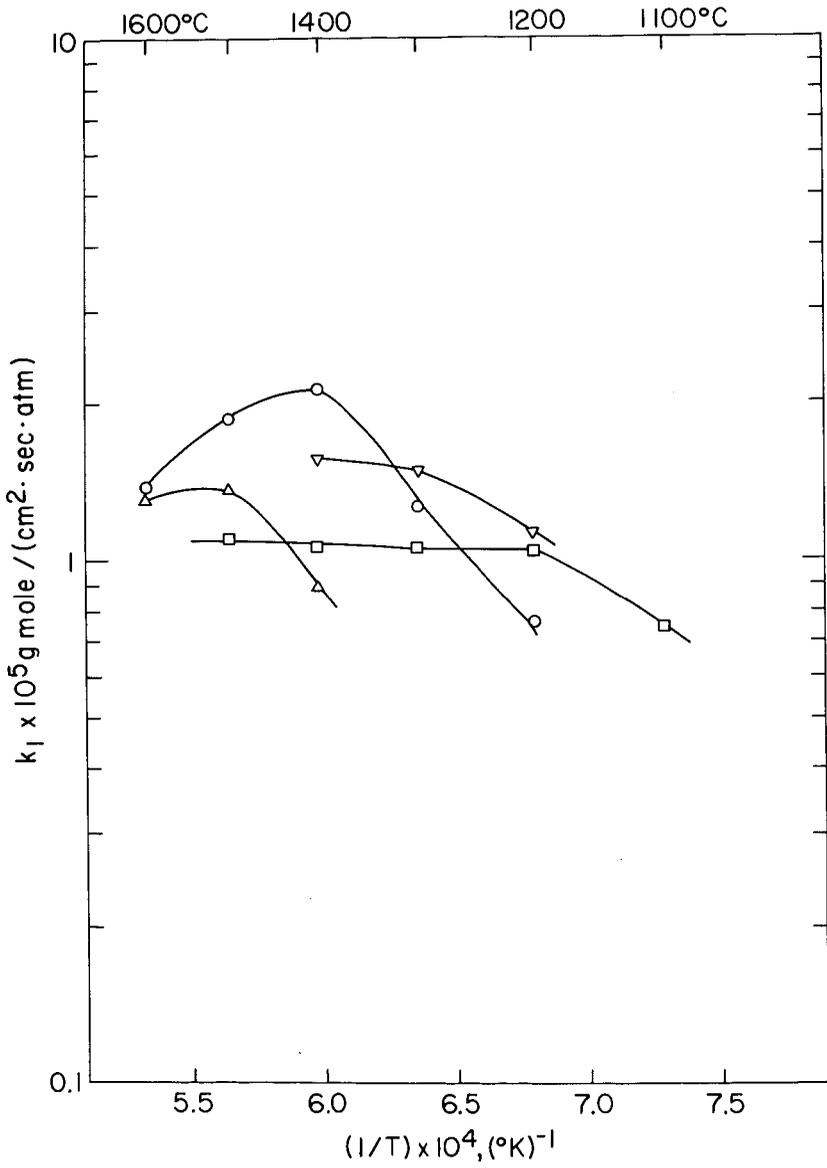


Figure 1. Rate constant vs temperature for the following chars: Pa. Anthracite (Δ), Illinois No. 6 Bituminous (O), Montana Lignite (\square), and leached Montana Lignite (∇).