

CHANGES IN ACTIVATION ENERGY WITH LEVEL OF BURN-OFF FOR BITUMINOUS COAL CHARs

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INTRODUCTION

The kinetics of oxidation of coal char has been extensively studied during the last decade (1-4). A common goal of these studies has been to evaluate reactivity of char under diffusion-free conditions and to identify physico-chemical properties of a char which influence its reactivity.

Thermogravimetric analysis has been widely used to obtain rate data for the reaction char oxidation (1-7). Isothermal studies have demonstrated that the oxidation rate changes with conversion and exhibits a maximum at a specific level of burn-off. Data have been analyzed to obtain the intrinsic reactivity and activation energy for char oxidation. In most of the previous studies, however, the activation energy has been calculated at a specific conversion, usually at 50% conversion or at a level corresponding to the maximum rate. Since the value of activation energy has a pronounced effect on the intrinsic reaction rate, it seems appropriate to investigate whether activation energy changes with conversion during oxidation of coal char.

In this paper the results of a study on the oxidation of three bituminous coal chars are presented. The focus is on the variation of activation energy with level of burn-off for the three chars.

EXPERIMENTAL

Char - Chars, also referred to as partially devolatilized (PD) coals, were made from two bituminous coal samples obtained from the Illinois Basin Coal Sample Program, samples IBCSP-3 and IBCSP-4(8). IBCSP-3 is mine-washed coal [a blend of Springfield (No. 5) and Herrin (No. 6)] and the IBCSP-4 is run-of-mine Herrin (No. 6) (see table 1 for analyses).

Two chars (char-1 and char-3) were made from two partially devolatilized (PD-1, PD-3) coals that were produced from IBCSP-3 in the United Coal Company's (UCC) Mild Gasification Pilot Unit (Bristol, Virginia). PD-1 and PD-3 had volatile matter contents of 25.6% and 13.0% (dry-ash-free basis). The details of PD coal production are given elsewhere (9). Chars were made by injecting PD coals into a 5-cm diameter batch fluidized-bed reactor which was preheated to 850°C under a purge of nitrogen. The samples were fluidized at 850°C for 5 minutes and then cooled to ambient conditions. The volatile matter content of char-1 and char-2 were 7.5% and 6.3%.

A third char, hydrodesulfurized (HDS) char, was prepared from IBCSP-4 which was first physically cleaned (14.8% ash and 6.2% S). The char was produced in the batch fluidized-bed reactor from a 74-589 micrometer-size fraction of the clean coal using the following processing steps: 1) preoxidation at 250°C in a 5% O₂ - 95% N₂ gas mixture for 30 minutes, 2) pyrolysis in nitrogen at 850°C for 15 minutes, and 3) desulfurization in hydrogen at 850°C for 90 minutes. The HDS char had 0.4% sulfur and 3% volatile matter.

Reactivity tests - The particle size of char samples was reduced to less than 90 micrometers prior to reactivity tests by crushing, and sieving and recrushing the oversize. Reactivity experiments were performed in an Omnitherm thermogravimetric analyzer (TGA) coupled to an Omnitherm QC25 programmer/controller. The TGA system was interfaced with an IBM XT computer through a Keithley DAS series 500 data acquisition system to provide automated data collection and storage.

In each experiment a sample mass of about 2 mg was placed in the TGA platinum pan and heated in nitrogen (200 cm³/min) at 50°C/min to the reaction temperature (between 425 and 575°C). The nitrogen was replaced by dry air flowing at a rate of 200 cm³/min. The percent weight of the unburned char, the rate of weight loss, and the gas temperature in the vicinity of the sample pan as a function of time were monitored by the computer. Data were collected at 5 to 40 second intervals depending on the reaction temperature.

RESULTS AND DISCUSSION

TGA data were used to calculate the apparent reaction rates, R, where

$$R = - \frac{1}{f} \frac{df}{dt} \quad 1)$$

and

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

f = fraction combustible remaining at time t, M = mass of sample at time t, M_o = initial sample mass, M_a = mass of sample at complete conversion, i.e. ash. Figures 1, 2, and 3 show plots of apparent rates versus fraction conversions for the chars at the indicated temperatures. As expected, apparent rates increased with increases in reaction temperature. Also, for each char, the shape of the reactivity curve did not change with temperature. However, there are clear differences among the reactivity curves of the three chars. For char-1, apparent rate increased initially, maximized at about 30% conversion and decreased slightly as the fractional burn-off increased. For char-3, the apparent rate maximized after 5 to 15% conversion, depending on the reaction temperature, and remained relatively constant after about 30% conversion. For HDS, the apparent rates did not show a maximum and increased with conversions up to 90% conversion in the studied temperature range. These results suggest that char formation conditions influence the shape of the reactivity curve.

The differences observed in the reactivity curves could be partially due to the variations that occur in internal pore surface area during char oxidation. In order to gain information with respect to relative available pore surface area, the oxidation rate of char was expressed as:

$$- \frac{df}{dt} = SkP_{O_2}^n f \quad 3)$$

where k = reaction rate constant, g/m².atm.min; P_{O₂} = oxygen partial pressure, atm; S = available pore surface area, m²/g; n = reaction order with respect to oxygen pressure.

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

$$- \left(\frac{df}{dt} \right)_i = S_o k P_{O_2}^n \quad 4)$$

where S_o is the initial pore surface area. Dividing equation 3) by 4) and solving for S/S_o gives

$$\frac{S}{S_o} = \frac{1}{(-df/dt)_i} \frac{(-df/dt)}{f} \quad 5)$$

According to equation 5), a plot of $(-df/dt/f)/(-df/dt)$, versus conversion should represent changes in available surface area with conversion. Figure 4 shows how the relative available pore surface area of the samples changed with conversion. In these figures, the values of $(df/dt/f)$ were normalized by the corresponding values at the 10% conversion because at the lower conversion levels TGA data could not be obtained accurately. For each char a single curve could adequately represent the data in the studied temperature range. A similar observation has been reported by previous investigators (1,2). This indicates that the rate data were obtained under diffusion-free conditions and surface area development was independent of reaction temperature. Each fuel demonstrates a unique pore area development. HDS which had the lowest initial internal surface area among the fuels tested (because it was subjected to most severe heat treatment condition) exhibited the largest change.

The rate data shown in figures 1, 2, and 3 were used to determine activation energies for the oxidation of the chars. The rate constant was assumed to have Arrhenius form:

$$k = k_0 e^{-E/RT} \quad 6)$$

where k_0 is the pre-experimental factor and E is the activation energy (kJ/mole). Substituting equation 6) into equation 4), solving for $(-df/dt/f)$, and taking logarithm of both sides yields equation 7)

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

According to equation 7) a plot of $\ln(-df/dt/f)$ versus $1/T$ gives activation energy from the slope at a given conversion if the values of S are independent of reaction temperature.

The values of $\ln(-df/dt/f)$ evaluated at 10%, 20%, 30%, 50%, and 70% burn-off were plotted against $1/T$, and are shown in figures 5, 6, and 7. The observed changes in the slopes of the plots demonstrated variations in activation energies with conversion. This is clearly seen in figure 8 where the values of activation energies are plotted against conversion. According to this figure, activation energies may increase, or may show a maximum or minimum as reaction proceeds, depending on the fuel tested. The most often reported value for the activation energy of char combustion at temperatures $<600^\circ\text{C}$ is 130 KJ/mole (Radovic, 1983; Khan, 1987). The results obtained in this study indicate values ranging from 107 to 145 KJ/mole, depending on the fuel and the level of burn-off. Results of a recent kinetic study conducted with a sucrose char also indicated that activation energy for the oxidation of the char increased from 136 to 147 kJ/mole as conversion increased from 20 to 90% (10).

The variation in activation energy with the level of burn-off could be partly due to the presence of a distribution or type of active sites in the char with each type having its own characteristic reactivity. Past studies (11) have indicated that two types of surface oxides, stable and fleeting, are formed when oxygen chemisorbs on carbon active sites. Oxidation char is represented by several reactions including formation and desorption of surface oxides as well as direct burn-off of the carbon. These reactions may have different activation energies. Also, the contribution of each reaction to the progress of char oxidation may be significant at different levels of burn-off. This could result in variation of activation energy with conversion as observed in this study.

The results obtained in this study suggest that to more fully describe burning characteristics of a char, reactivity data should be examined at different conversions. This observation was also reported in a recent study in which an average reactivity

the whole char burn-off was used to describe char reactivity rather than one determined at a specific level of burn-off (12).

ACKNOWLEDGEMENTS

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Table 1. Chemical characterization of coal samples
wt% (moisture-free basis)

Coals	IBCSP-3	IBCSP-4
Seam	No. 5 ¹	No. 6
Rank	HVBB	HVCB
Moisture	5.4	10.2
Volatile matter	39.2	30.6
Fixed carbon	52.4	31.3
Ash	8.4	38.1
Carbon	73.8	46.0
Hydrogen	4.9	3.5
Nitrogen	1.7	0.80
Oxygen	8.7	7.4
Sulfur	2.3	4.2
Chlorine	0.2	0.05
Heating value (Btu/lb)	13,437	8,492

¹ Predominantly Springfield (No. 5). Approximately 20% Herrin (No. 6) blended at washing plant.

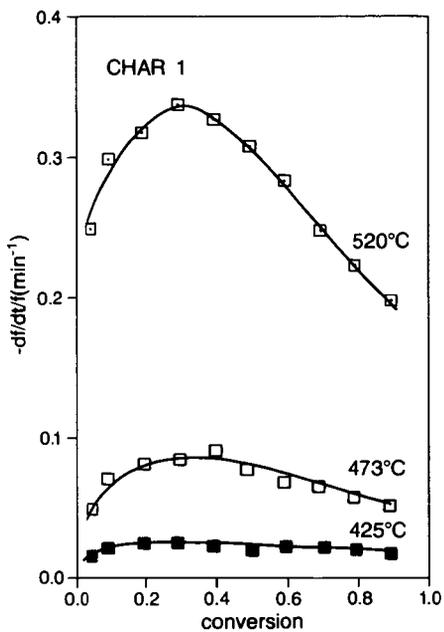


Figure 1. Apparent rate vs. conversion for oxidation of Char 1 in air.

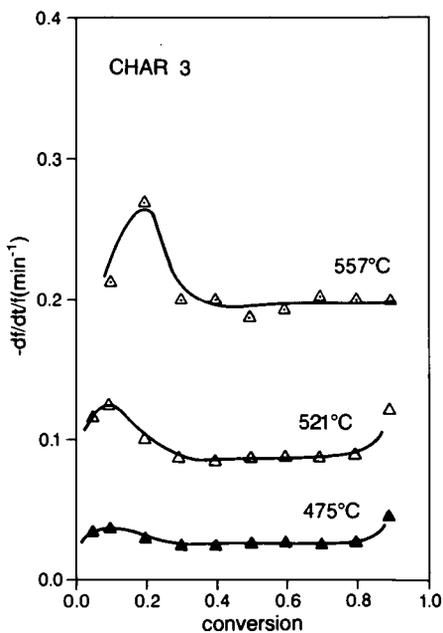


Figure 2. Apparent rate vs. conversion for oxidation of Char 3 in air.

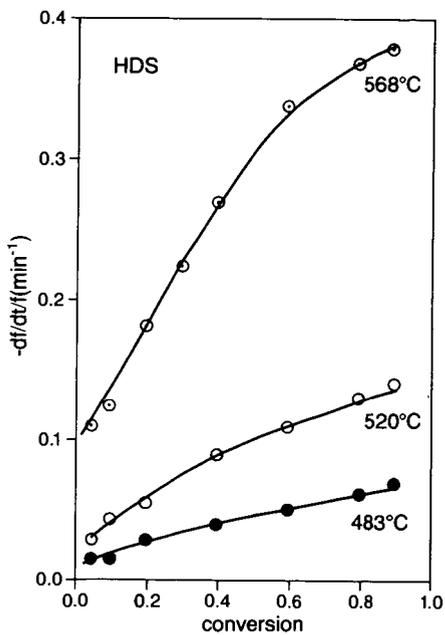


Figure 3. Apparent rate vs. conversion for oxidation of HDS char in air.

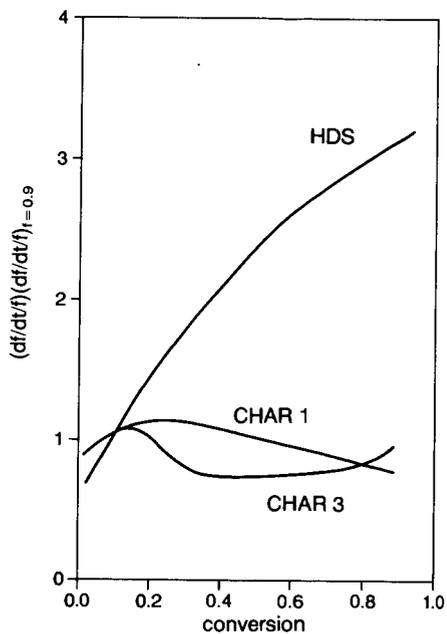


Figure 4. Surface area development vs. conversion for various chars.

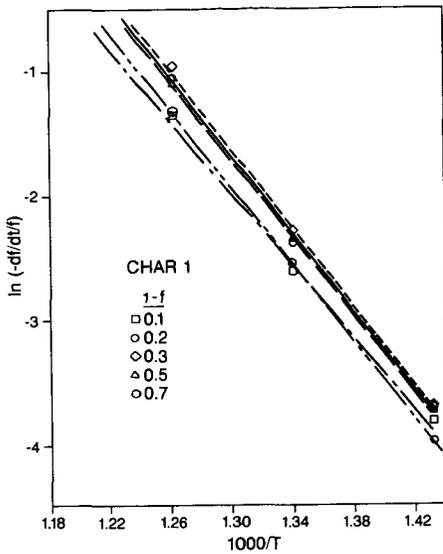


Figure 5. Arrhenius plot with rates observed at various conversions for oxidation of Char 1 in air.

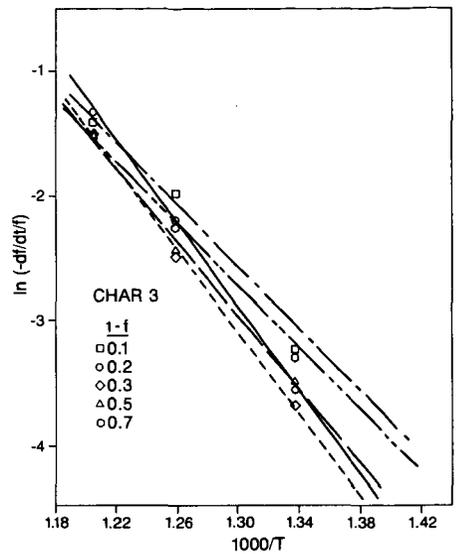


Figure 6. Arrhenius plot with rates observed at various conversions for oxidation of Char 3 in air.

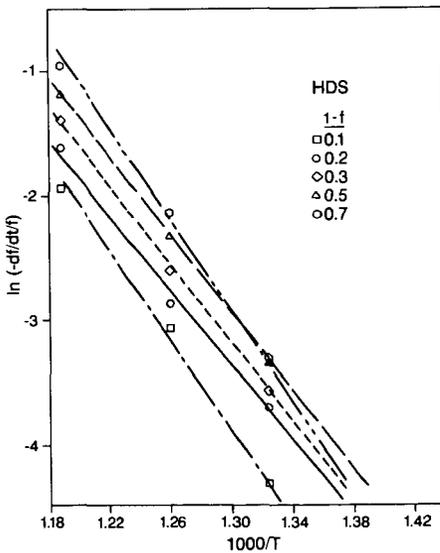


Figure 7. Arrhenius plot with rates observed at various conversions for oxidation of HDS char in air.

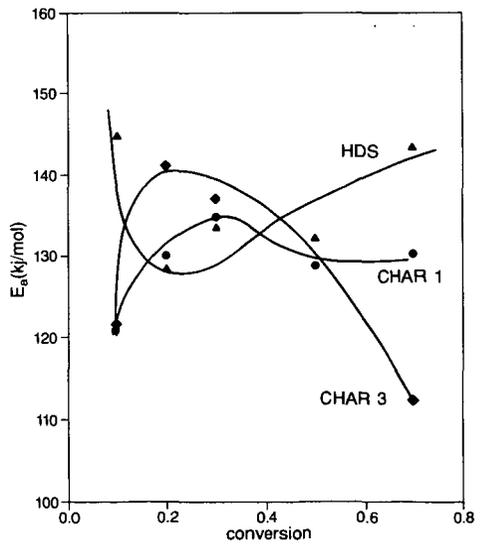


Figure 8. Variation of activation energy with conversions for oxidation of various chars.