

Effect of CaCl_2 on Char Reaction Kinetics

M. A. Serageldin and W. P. Pan

Department of Chemistry and Chemical Engineering
Michigan Technological University
Houghton, MI 49931

INTRODUCTION

This work describes the effect of CaCl_2 on coal char reactivity; it is the third part in a series of studies related to boiler application (1,2) involving this metal-based salt. The information obtained in this work should be useful in understanding the effect of similar materials on the oxidative behavior of coal-char. The char was combusted in a thermogravimetric analyzer, TGA, under different partial pressures of oxygen (0.16 - 70% by vol.) in nitrogen and at constant temperature. The furnace temperatures (isothermal) varied between 673 and 1223 K. The sample mass and volumetric flow rate were close to 2 mg and 5 ml/s, respectively. This temperature range should cover the regions where oxidation occurs mainly by diffusion and mainly by chemical control (3,4).

EXPERIMENTAL

Materials

Lignite coal from Velva Mine, North Dakota, was used in this work; its proximate and ultimate analysis is given in Table 1.

Char preparation

The coal was placed in a boat made of ceramic material and pyrolyzed in a Hoskin electric furnace (Hoskin Co.), which was regulated by an Omega 6000 temperature controller. The boat was made by splitting a length, l , of high purity alumina tube ($l = 75$ mm and I.D. = 10 mm); it was positioned in the center of the furnace. A shielded Chromel Alumel thermocouple ($d = 3$ mm) was placed approximately 5 mm above the boat to measure the sample temperature. The sample thermocouple reading (in the absence of a sample) was a few degrees lower than that of the furnace set temperature; for example, at the set temperature of 1248 K, the sample thermocouple (inside the furnace) recorded 1223 K.

Coal pyrolysis in a constant stream of nitrogen (0.425 ml/s at S.T.P.) was achieved over a number of steps (5). The sample was first purged at room temperature for 900 s (0.9 ks). The furnace was then switched on, setting the maximum temperature to 1248 K (which was reached in about 2.58 ks). It was left for one hour at the maximum temperature. The furnace was then turned off and left to cool in nitrogen for one hour, after which the remaining part of the coal sample, i.e. char, was emptied in a clean, dry container which was subsequently stored in a dessicator for later use.

Apparatus

The char was burned in a DuPont 951 thermogravimetric analyzer (TGA) coupled with a DuPont 990 recorder unit. Each sample (2 mg) was spread evenly on the platinum pan to avoid establishing a thermal gradient in the sample. O_2 and N_2 were mixed by different proportions. The total gas flow made by O_2 and N_2 was maintained at 5 ml/s. This provided a linear velocity of 18 mm/s. The percentage of O_2 in the O_2/N_2 mixture depended on the isothermal temperature: at the higher isothermal temperature (1223 K), the lower concentration (or partial pressure) of oxygen was used, i.e. 0.16% by volume, whereas a concentration of 70% O_2 was used when the isothermal temperature was set to the lowest value investigated, i.e. 683 K. Such combinations were necessary to maintain the value of the time to 50% decomposition, $t_{0.5}$, above 1200 s, thus ensuring that the effect of temperature gradient is negligible (4). Lastly, before pushing the sample into the furnace, the latter was heated to the desired isothermal temperature

and left to equilibrate for 300 s. This procedure helped to reduce the time-lag before the sample reached the desired temperature.

RESULTS

Information regarding the influence of CaCl_2 on char reactivity, reaction mode, and kinetic parameters is presented in this section.

Reactivity

The influence of oxygen concentrations and temperature on char reactivity is shown in Figure 1. A greater effect (on conversion) was produced as a result of increasing the temperature by a small percentage than by an equivalent increase in oxygen percentage in the gas. Treating the char with CaCl_2 also increased its level of conversion, Figure 2. Considering that conversion vs. time plots for chars under different atmospheres are similar in appearance, a more satisfactory representation, in terms of reactivity, can be achieved by replotting conversion against a dimensionless time, $t/t_{0.5}$ (6). Such a plot is given in Figure 3 and indicates that CaCl_2 produces an insignificant effect below a conversion of ~ 0.58 which would suggest that the mechanism of reaction is not altered within this zone. Between 0.58 conversion and up to ~ 0.68 the "master curve" separated into two curves, one for char and the other for char plus CaCl_2 . Above a conversion of 0.68 each of the above curves split into three curves, producing a total of six curves. Such a spread was not observed when char from demineralized coal was carbonized at around 1273 (6). However, evidence showing the effect of naturally occurring mineral matter in coal-char may be found (beyond a char conversion of 0.7) in Figure 1 of Tseng and Edgar's paper (4). It is, therefore, understandable that in the presence of additional mineral matter (i.e. CaCl_2), as in this study, a more pronounced effect occurs. This is clearly indicated (Figure 3) by a greater shift of the catalyzed reaction to the left, i.e. towards a pore diffusion mode of reaction (Figure 4). The spread in the curves may be attributed to the effect of particle temperature rise (7).

Reaction Mode of Control

To determine the mechanism controlling the reaction the data used to plot Figures 3 and 4 was replotted in terms of specific rate, dC/dt , and $t_{0.5}$, the time to 50 percent conversion. Values of dC/dt were obtained using the cubic spline interpolation technique (8) and the cubic spline smoothed technique. Figure 5 illustrates the extent of scatter when the cubic spline smoothed technique was not applied (white circles) to the data from Figure 3. This method was previously used by Tseng and Edgar (4) to compare the reactivities of different chars in the absence of catalysts. Figure 6 shows a number of curves obtained using this procedure for char combusted at several of the low temperatures investigated and different oxygen levels. A maximum occurred in all cases at around 0.25 conversion, which indicates that the control mechanism is chemical (3,4). Beyond 0.58 the curves delineating the different experimental conditions separated and were therefore clearly identifiable. From this presentation one can see that the maximum specific rate at a given temperature was somewhat increased by treatment with CaCl_2 . It should be stated that when the conversion was less than 0.5, Figure 6 provided more detail than Figure 3.

Figure 4 was obtained by treating the data corresponding to the runs at high temperature (>1123 K). The data for the six experiments followed very closely the film diffusion theoretical curve (dotted line). The theoretical lines in Figure 4 were calculated using the equations provided in reference 4.

Kinetic Parameters

The order of reaction in the kinetic control regime was determined by plotting $t_{0.5}$ against oxygen partial pressure (0.16 - 70 KPa) on log-log paper (4) and measuring the slope. Figure 8 shows such plots obtained at different temperatures for untreated char. The slope of the different lines was practically the same, suggesting that the average value of n for the char was 0.84. This figure is somewhat higher than 0.70 reported by a number of workers for lignite coal (see ref. 4). The value of n for char treated with CaCl_2 was 0.73. Both values of n are valid for a limited temperature range, i.e. 683 - 723 K. In the diffusion control regime n equals

one (9). The activation energy was obtained by plotting $t_{0.5}^*$, against $1/T$ on semi-log paper as is illustrated in Figure 9. The former value is defined as follows (4):

$$t_{0.5}^* = (P_{O_2}/P^*_{O_2})^n \cdot t_{0.5} \quad 1)$$

where $t_{0.5}$ corresponds to the value at a base of reference partial pressure of oxygen, P_{O_2} . This was chosen to be 0.005 MPa in the present study. On the other hand, the values marked with an asterisk correspond to char reacted at the same temperature under other partial pressures of oxygen. n is the reaction order. Figure 9 illustrates results for both the high temperature runs (lower left of figure) and the low temperature runs (upper right of figure). Each circle shown in Figure 9 represents the average of four runs at different P_{O_2} , i.e. the points at a given temperature fall within the bounds of such circles. However, for calculating the activation energy, all the points were used. For example, all the runs shown in Figure 8 were used to calculate the activation energy, E , in the kinetic regime. This was equal to 154 KJ/mol for char and was reduced to 141 KJ/mol when the char was treated with $CaCl_2$. However, for the higher temperature runs where the mode of control was diffusional, the value of E for the untreated char was 29.5 ± 0.5 and for the treated char was 28.0 ± 0.5 KJ/mol. The fact that the difference is insignificant suggests that char combustion under such a regime is independent of the nature of the catalyst, a point made before by others (3,10). The activation energy in the chemical control regime may also be obtained using the following equation:

$$\log_e (P_{O_2}^n \cdot t_{0.5}^*) = \log_e A' + E/RT \quad 2)$$

where A' is a measure of the char reactivity (4) and can be expressed as :

$$A' = (1/AS_0) \int_0^{0.5} (S_0/S) dC \quad 3)$$

A in Equation 3 is the Arrhenius pre-exponential factor; S_0 is the specific surface area at time zero and dC is the fraction converted. Values of A' and E obtained using Equation 2 are shown in Table 2 and indicate that the reactivity of the treated char was significantly increased as a result of adding $CaCl_2$. The higher reactivity can also be deduced from Figure 10.

To evaluate the mass transfer resistance the Sherwood number of the char samples were calculated (Appendix 1) (4) for the data in the film diffusion controlled regime and summarized in Table 3. These values are significantly increased in the presence of $CaCl_2$ and by temperature; however, they have a value less than 2 which refers to a spherical particle suspended in stagnant air. The occurrence of a lower Sherwood number was attributed by Tseng and Edgar (4) to a reduction in mass transfer efficiency by the sample pan (4). They also concluded that the mass transfer resistance around a single large particle would be lower than that around smaller particles on a pan. In the latter case the particle packing is also important.

DISCUSSION

This work shows that $CaCl_2$ promotes the overall decomposition of coal-char, i.e. it occurs during a shorter time, at constant temperature. This is in agreement with previous results but under temperature programming (non-isothermal) conditions (11). In this case the same level of conversion occurred at a lower temperature which indicates agreement between isothermal and non-isothermal studies.

Since changes in porosity and density prior to oxidation can influence reactivity, these were measured for char prepared from coal and that for coal mixed with $CaCl_2$ (12). From Table 4 we can deduce that there is no significant change in density, total pore volume and porosity prior to combustion. Therefore the effectiveness of the additive in promoting char-oxygen reaction may be explained in terms of the following carbon-oxygen reactions (13,14):



In the above model the catalyst promotes the dissociation of the oxygen molecule adsorbed making it thus more reactive. In other words, dissociative adsorption is promoted (14). Such a

mechanism could account for the observed decrease in activation energy in the chemical control regime.

In the diffusion control regime E did not vary significantly, which would suggest that the above explanation is not applicable in this case. However, the fact that E was -28 KJ/mol, i.e. higher than the usually accepted range of $8 - 12$ KJ/mol (9), would suggest that it is possible that the regime is not totally film diffusion controlled, but that pore diffusion may also be important during the initial decomposition stage, Figures 7 and 9. (E for pore diffusion is around half of the intrinsic activation energy.) This reasoning could account for the observed shorter char decomposition time, which is indicated by lower values of $t_{0.5}$. The significance of the Sherwood numbers in Table 3 is now questionable. The results indicate that CaCl_2 increases this number significantly and, therefore, under these conditions, mass transfer resistance was reduced. However, we can see that the values of the constant b for the film diffusion controlled regime was not significantly altered by CaCl_2 . The theoretical value of b is 0.55 (4). The use of this form of the Sherwood number may be misleading considering that we do not have single spherical particles as assumed in the derivation by the authors (4) and considering that we have reason to believe that pore diffusion may also be involved.

CONCLUSIONS

1. CaCl_2 decreased the activation energy and increased the reactivity of coal char in the chemical control regime. It did not, however, have an important effect the diffusion control regime.
2. In the kinetic control regime the mechanism was not altered below a conversion of 0.58. However, at higher conversion the reaction was moved towards the pore diffusion regime.
3. At the higher temperatures pore diffusion may also play a role during decomposition, which explains why the activation energies obtained were higher than that for a totally film diffusion controlled regime.

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Appendix 1: Sherwood Number

$$Sh = \frac{(1-X_a)\rho_p r_0^2 RT}{D_b \omega P_{O_2} t_{0.5}} \left(1 - \sqrt[3]{1/4}\right) \quad 1)$$

where X_a is the ash yield; ρ_p , particle density; r_0 , initial particle radius; D_b , bulk diffusivity; R , the gas constant; T , the absolute temperature; P_{O_2} , partial pressure of oxygen; $t_{0.5}$, time to 50% decomposition and $\omega = 12$, assuming all $C \rightarrow CO_2$.

Table 1: Analysis of lignite coal (-100, +270) mesh

	<u>Proximate analysis</u>		<u>Ultimate Analysis</u>	
	<u>As received</u>		<u>Moisture-Ash free</u>	
Moisture (wt%)	34.00	Carbon	64.55	
Fixed Carbon	27.46	Hydrogen	4.72	
Volatiles	32.86	Nitrogen	1.02	
Ash	5.68	Sulfur	0.33	
		Oxygen*	29.38	

*by difference

Table 2: Values of A' and activation energy

<u>Sample</u>	<u>A'</u>	<u>Activation energy (KJ/mol)</u>
untreated char	9.3×10^{-10}	154 ± 1
CaCl ₂ treated char	68.4×10^{-10}	141 ± 4

Table 3: Sherwood number and film diffusion constant (b) of char samples

<u>Temperature (K)</u>	<u>Sherwood number</u>		<u>$dC/d\tau = b(1-C)^{1/3}$</u>	
	<u>Untreated char</u>	<u>CaCl₂ treated Char</u>	<u>untreated char</u>	<u>CaCl₂ treated char</u>
1123	0.76	1.11	0.59 ± 0.03	0.56 ± 0.02
1173	0.91	1.23	0.59 ± 0.02	0.57 ± 0.02
1223	1.26	1.52	0.57 ± 0.03	0.57 ± 0.02

Table 4: Density, total pore volume and porosity (12)

<u>Sample</u>	<u>Density (g/cm³)</u>		<u>Total pore volume (cm³/g)</u>	<u>Porosity (%)</u>
	<u>Helium</u>	<u>Mercury</u>		
untreated char	2.12	1.30	0.298	38.7
CaCl ₂ treated char	2.14	1.32	0.29	38.5

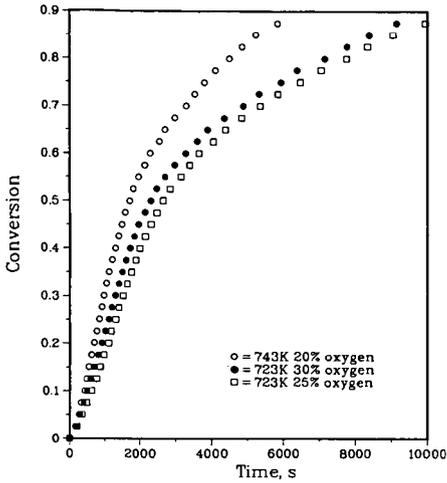


Figure 1: Influence of oxygen concentration and temperature on reactivity of char.

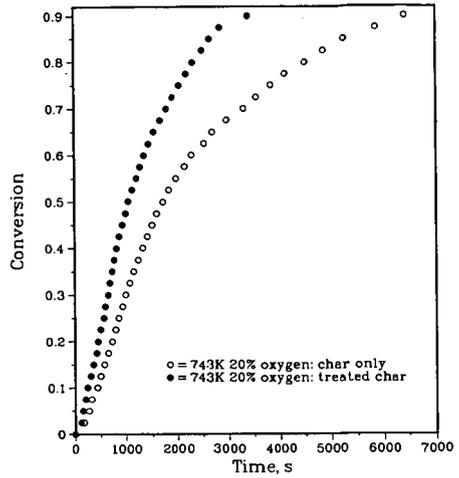


Figure 2: Effect of CaCl_2 on the reactivity of char.

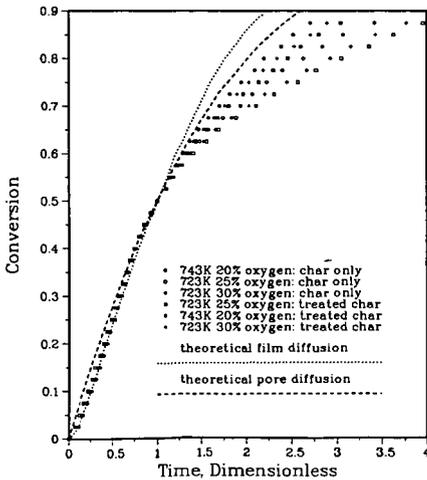


Figure 3: Effect of CaCl_2 on the normalized plot of char at different temperatures and oxygen concentrations.

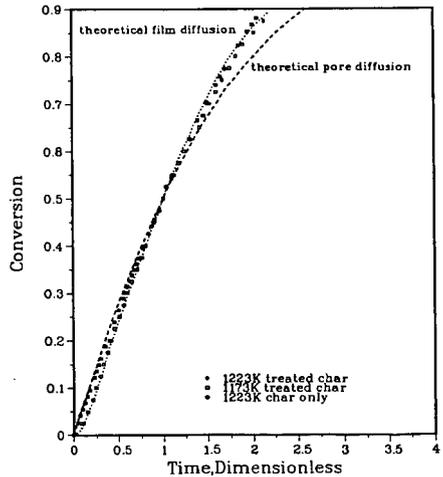


Figure 4: Effect of CaCl_2 on the normalized plot of char under diffusional control.

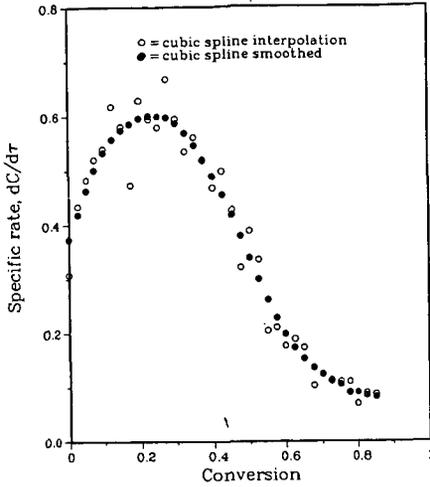


Figure 5: Application of cubic spline interpolation technique and cubic spline smoothed technique.

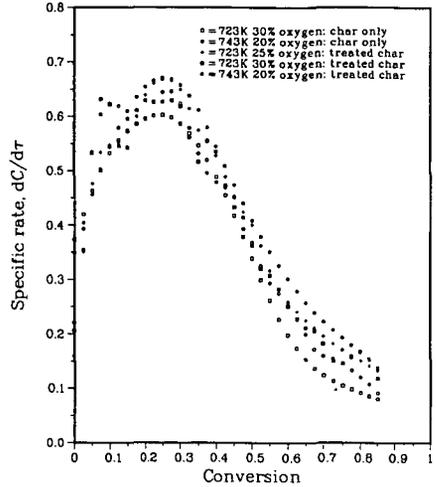


Figure 6: Effect of CaCl_2 on the combustion characteristic curve of char under chemical control.

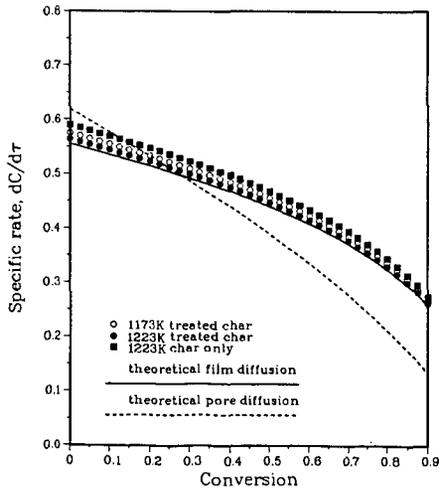


Figure 7: Effect of CaCl_2 on the combustion characteristic curve of char under diffusional control.

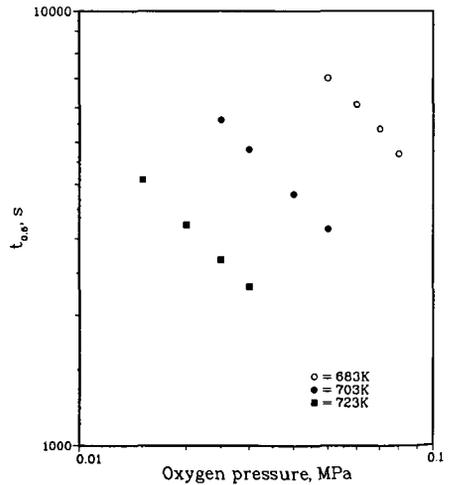


Figure 8: The reaction order of char.

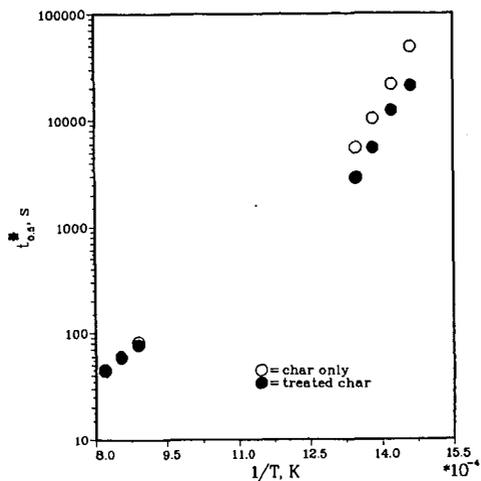


Figure 9: The effect of CaCl_2 on the char activation energy.

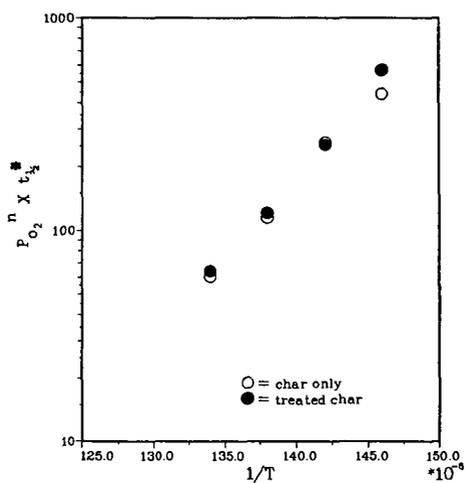


Figure 10: Comparison of the reactivity of char in the presence and absence of CaCl_2 .