

REACTIVITY IN AIR OF CHARS PRODUCED FROM A LIGNITE
CONTAINING VARIOUS CATIONS

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The combustion of coal is practiced widely throughout the world. In the United States in 1982, for example, almost 600 million tons of coal were burned for electricity production (1). Nevertheless, many fundamental aspects of coal combustion are not well understood. It has been established, however, that at least two general processes occur during combustion: pyrolysis or devolatilization of the coal due to an applied thermal stress and heterogeneous combustion of the remaining char according to carbon-oxygen reactions. The relative importance of each process to the overall combustion of a particular coal is not easy to measure experimentally and is even more difficult to predict a priori.

In the sequence of events that is coal combustion, heterogeneous char combustion, which is usually referred to as char burnout, necessarily occurs last. This has led to the deduction that the char burnout is the rate determining step in the overall process. This argument then provides that to burn coal more effectively and efficiently, it is necessary to understand the mechanism, and thereby be able to affect the rate of the char-oxygen reaction.

While it is true that the rate of release and combustion of the volatiles in most practical systems are fast compared to the rate of the C-O₂ reactions, the yield of volatiles, which determines the amount of char which must be burned heterogeneously, is equally important in determining the char burnout time. Hence, an alternative to increasing the rate of the C-O₂ reaction is to decrease the required extent of the C-O₂ reaction by reducing the yield of char. Both aspects of the combustion of a range of coals have been addressed in the current project, but coverage in this paper is restricted to the properties of lignites which affect the yield of volatiles and the char reactivity, both of which may affect the overall combustion rate of lignites.

The heterogeneous reaction rate of a coal char with a reactant gas is influenced by such parameters as the inherent char reactivity, which is related to the number of carbon active sites, the rate of transport of the reactant gas to the active surface area and the presence of potentially catalytic inorganic species. Jenkins et al. (2,3) have shown that the air reactivity of coal chars is dependent upon the pyrolysis conditions under which the chars were prepared. As the severity of the pyrolysis conditions was increased, the number of carbon active sites in the char was found to decrease, hence, the reactivity decreased. In addition, coal char reactivity was shown to be rank dependent; chars produced from lignites being more reactive than those from higher rank coals.

The high reactivity of lignite chars has been attributed, in part, to the presence of ion exchangeable cation on the original coals. These are predominantly alkali and alkaline earth metals (4), some of which are excellent catalysts for the C-O₂ reaction (5,6). Their presence on low rank coal chars, as distinct from discrete mineral phases, has been shown to increase reactivity (7). However, as the severity of the pyrolysis or reaction conditions increases, the metals lose their catalytic activity due primarily to a loss of dispersion via sintering. This occurs as the holding time at temperature or the reaction temperature itself

increases (8). The objective of the current work was to determine the effect of the presence of cations, namely calcium and magnesium, on the pyrolysis of a lignite under combustion conditions and on the subsequent reactivity of partially burned chars.

Experimental

The ion exchangeable cations on a Texas lignite, PSOC 623, were removed by acid washing in 0.04 N HCl. Alkaline earth metals, Ca and Mg, were back exchanged onto the acid washed samples using 1 M metal acetate solutions. Details of the exchange procedure have been outlined previously (9). Cation contents of the prepared samples were measured by atomic absorption spectroscopy.

The raw and modified lignite samples were pyrolyzed and partially combusted in an entrained-flow reactor at an initial reactor (gas and wall) temperature of 1173 K. A description of the reactor and its mode of operation have been provided elsewhere (10).

Reactivity data were generated on chars produced under either a N₂ or air atmosphere at various residence times in the entrained flow reactor using a Fisher Thermogravimetric Analyzer (Model 260 F). The reactivities were obtained isothermally in air at atmospheric pressure and a temperature of 533 K.

For these conditions and by using only 2 mg of char spread thinly on a Pt pan, heat and mass transfer effects should not mask the reaction rate. Hence, the reported reactivities are believed to be intrinsic, chemically controlled rates. The gasification reactivities are taken from the maximum slope of the TGA recorder plot, normalized to the initial weight of dry ash free char.

Results and Discussion

The ultimate analysis of the raw lignite and the proximate analyses of the raw and modified samples are shown in Table 1. The raw lignite contained 1.8 wt% cations on a dry basis, predominantly Ca (1.4%) and Mg (0.26%) with trace quantities of Na, K, Ba and Sr. The acid washing reduced the cation content to less than 0.01 wt%. The two cation-loaded samples chosen for comparison in the present study contained 1.9 wt% Ca and 1.6 wt% Mg, respectively.

Weight Loss Rate Data

Weight loss rate data for pyrolysis in N₂ and combustion in air at 1173 K are shown in Figure 1 for raw and acid washed lignite. The same data for the Ca and Mg loaded lignite are shown in Figure 2. Details of the model for predicting residence times have been provided by Tsai and Scaroni (10). In addition, an analysis is provided which estimates particle and gas temperature excursions from the initial furnace temperature of 1173 K due to the superimposition of endothermic heats of pyrolysis and exothermic heats of combustion. The essence of the analysis is that the lignite particles are being heated to the furnace (gas and wall) temperature for at least 0.1 s. Upon ignition, particle temperatures exceed gas temperatures for a short period (< 0.1 s) by in excess of 200 K. Hence, the weight loss rate data in Figures 1 and 2 are for nonisothermal pyrolysis and combustion for about 0.15 s.

The data shown in Figures 1 and 2 have been discussed previously (9) and can be summarized as follows. The presence of ion exchangeable cations suppresses the evolution of volatiles during pyrolysis. This is attributed to an increase in secondary char forming reactions primarily involving tars. Such reactions are catalyzed by Ca and Mg (11). In an air atmosphere, however, catalysis of the C-O₂

reaction by Ca for a short time increases the weight loss by the Ca loaded lignite to above that of the acid-washed sample. No such rapid rate of weight loss occurs for the Mg-loaded coal since Mg is not a good catalyst for the C-O₂ reaction. At longer residence times, weight loss rates are similar for the raw, acid-washed and Ca-loaded samples, and slightly larger for the Mg loaded sample. This implies that catalysis of the C-O₂ reaction is no longer occurring. Loss of catalytic activity by Ca at high temperature has been ascribed to loss of dispersion due to sintering (7). Hence, comparing the behavior of the raw and acid washed samples, the increased weight loss due to short-lived but significant catalysis of the C-O₂ reaction by the presence of cations on the raw lignite simply compensates for the reduced yield of volatiles because of their presence.

TGA Reactivity Data

Maximum reactivities in air at 533 K of partially combusted chars are shown in Figure 3 as a function of weight loss in the entrained flow reactor. For each form of the lignite, reactivities decrease with increasing weight loss in the reactor up to about 85-90%. For higher weight losses, reactivities are low and approximately constant at < 0.1 mg/mg h. A decreasing reactivity indicates a loss of carbon active sites, whereas a constant reactivity may indicate a constant active site concentration or control of the reaction rate by oxygen diffusion to the active surface area though an ash barrier formed from the mineral matter in the coal.

Maximum char reactivities at 50, 75 and 90% weight loss and the time required to reach each level of weight loss for the variously treated lignites are given in Table 3. Note that 50% weight loss exceeds the level reached by pyrolysis in N₂. For residence times less than 0.10-0.13 s, reactivities at each level of weight loss decrease in the order Ca > Raw > Mg > acid-washed. This is in accordance with the order predicted by catalysis of the C-O₂ reaction. For residence times greater than 0.10-0.13 s, reactivities are low and approximately the same. This implies an absence of significant catalysis, possibly due to temperature induced sintering of the metals. Ignition of the particles with an attendant temperature increase occurs within this time range.

The significance in relating TGA reactivity data to weight loss in the entrained flow reactor is seen by comparing the data in Table 3 for the cation containing samples. After a weight loss of 50%, reactivities decrease in the order Ca > Raw > Mg while the additional time required to reach 90% weight loss in the entrained flow reactor increases in the order Ca < Raw < Mg. In this region of the weight loss curve where heterogeneous char combustion is occurring, catalysis of the C-O₂ reaction may be important implying that chemical reactivity controls the weight loss rate. Although different conditions prevail, TGA data may give a qualitative indication of behavior in this region. It is difficult to interpret the data for the acid washed lignite in this manner, however. Work is continuing to explain this apparent anomaly.

For residence times greater than 0.13 s in the entrained low reactor, which correspond to weight losses in excess of 85-90%, weight loss rates are low and approximately constant at 3.8×10^{-4} g/cm²s (expressed per unit external surface area). There is no apparent effect of the presence of cations in this region of the weight loss curve. It has been suggested previously that this may indicate physical rate control of the reaction mechanism (9). The TGA reactivity data can now be used to help determine the reaction Zone.

TGA reactivities at 533 K for these chars were approximately constant at 6.1×10^{-4} g/cm²s. Extrapolating these data to the entrained-flow reactor operating temperature of 1173 K using the Zone II Activation Energy of 21.7 kcal/mole as determined by Young (12), produces a reactivity of 4.4×10^{-4} gm/cm²s. This is

similar to the experimentally measured reactivity of 3.8×10^{-4} g/cm²s, and is considerably less than the value calculated for Zone III control, 7.7×10^{-2} g/cm²s.

Arrhenius parameters are currently being generated in the TGA for the C-O₂ reactions appropriate for the current chars. This will eliminate the need to use Arrhenius parameters generated by others. However, if the data of Young are appropriate for use in this situation, the implication is that the same reaction zone does not exist in the TGA and entrained flow reactor, the former being Zone I, and the latter Zone II.

Summary

TGA reactivity data of partially combusted chars have been used to elucidate the char burnout stage of pulverized coal combustion. The absence of a significant effect of cations on char reactivity at high levels of burnoff implies the absence of catalysis of the C-O₂ reaction. This was ascribed to sintering of the metal cations following ignition. The char particles then burn out slowly under Zone II control, the chars having relatively low inherent reactivities.

Acknowledgments

The lignite was supplied by W. Spackman from the PSU-DOE Coal Sample Bank and Data Base. Financial support for Bruce Morgan was obtained from the Coal Cooperative Program and MRI Fellowship Program at Penn State.

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Table 1
ULTIMATE AND PROXIMATE ANALYSES FOR THE RAW AND MODIFIED LIGNITE

<u>Ultimate Analysis</u>				<u>Proximate Analysis</u>				
	C	H	N	S	O (by diff)	% H ₂ O	% Ash (dry)	VM(daf)
% (daf)	70.1	5.0	1.7	1.4	21.8	10.8	15.9	59.7
						7.8	10.7	54.9
						5.3	13.7	57.6
						6.8	12.0	57.1

Table 2
CATION CONTENTS OF THE RAW AND MODIFIED LIGNITE

<u>Raw</u>	<u>Ca</u>	<u>Mg</u>	<u>Na</u>	<u>K</u>	<u>Ba</u>	<u>Sr</u>	<u>Total</u>	<u>Acid</u>		<u>Ca</u>	<u>Mg</u>
								<u>Washed</u>	<u>Loaded</u>		
wt % (dry)	1.4	0.26	0.03	0.03	0.03	0.02	1.8	<0.01	1.9	1.6	1.6
meq/g (dry)	0.7	0.2	0.01	0.01	0.002	0.002	0.9	~0	1.0	1.3	1.3

Table 3
TIME TO REACH AND MAXIMUM CHAR REACTIVITIES AT VARIOUS LEVELS OF
WEIGHT LOSS IN ENTRAINED FLOW REACTOR AT 1173 K

Weight Loss in Entrained Flow Reactor at 1173 K	Maximum Char Reactivity, mg/mg h (daf) (Time to reach weight loss, ms)			
	<u>Co-loaded</u>	<u>Raw</u>	<u>Mg-loaded</u>	<u>Acid-washed</u>
50	2.1 (80)	0.8 (65)	0.6 (90)	0.4 (50)
75	1.2 (95)	0.7 (85)	0.4 (125)	0.3 (70)
90	<0.1 (110)	<0.1 (145)	<0.1 (290)	0.1 (140)

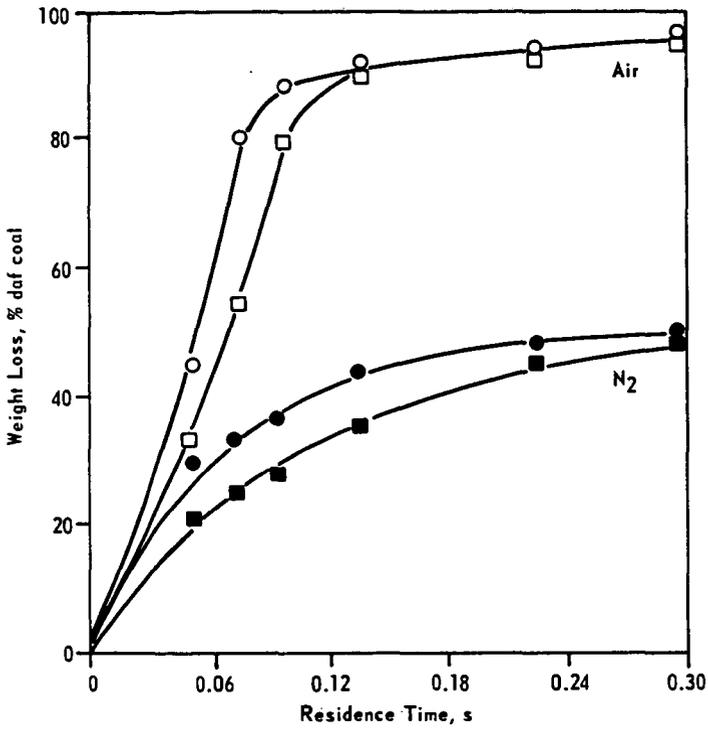


Figure 1. WEIGHT LOSS RATE IN AIR AND N₂ FOR RAW (□, ■) AND ACID-WASHED (○, ●) LIGNITE IN ENTRAINED FLOW REACTOR AT 1173 K

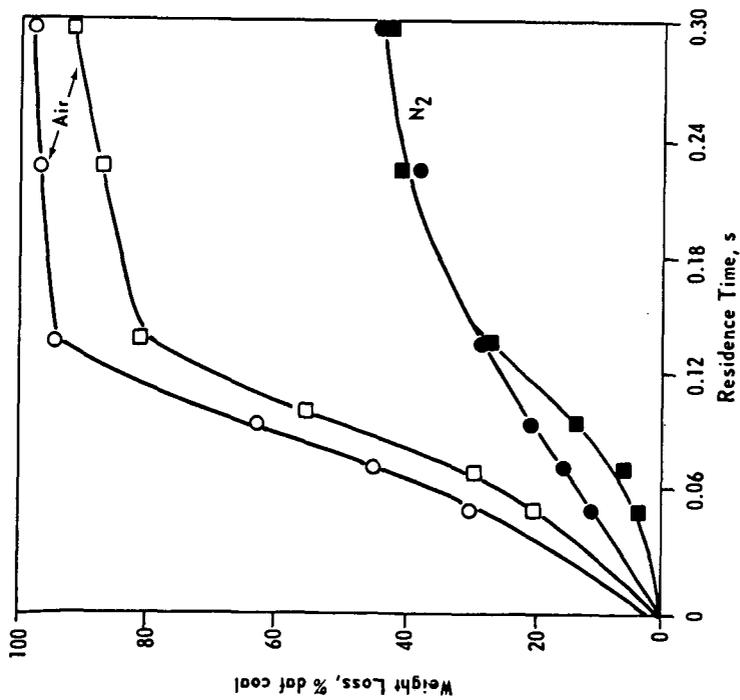


Figure 2. WEIGHT LOSS RATE IN AIR AND N₂ FOR Ca (○, ●) AND Mg (□, ■) LOADED LIGNITE IN ENTRAINED FLOW REACTOR AT 1173 K

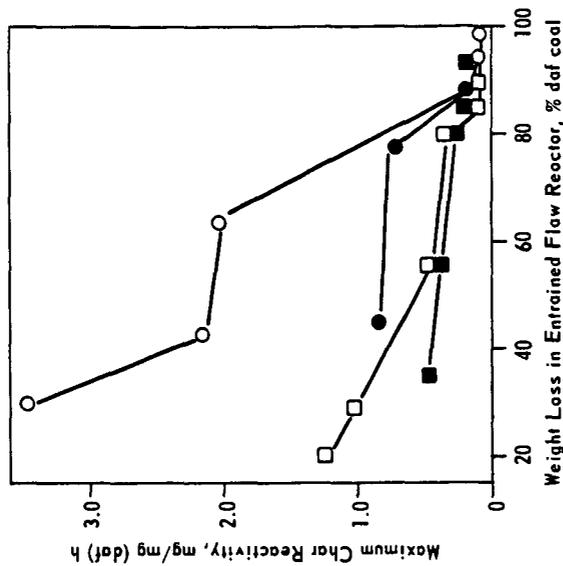


Figure 3. TGA REACTIVITIES IN AIR AT 533 K OF CHARs PRODUCED FROM Ca-LOADED (○), RAW (●), Mg-LOADED (□) AND ACID WASHED (■) LIGNITE AS A FUNCTION OF WEIGHT LOSS BY PARTIAL COMBUSTION IN ENTRAINED FLOW REACTOR AT 1173 K