

EFFECTS OF PREOXIDATION ON PYROLYSIS BEHAVIOR AND RESULTANT CHAR STRUCTURE OF CAKING COALS

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INTRODUCTION

Coal gasification processes may be divided into two stages. They are, the initial rapid release of volatile matter and the relatively slow gasification of the residual char. These two processes are not, however, totally independent because the heat treatment conditions under which coal pyrolysis occurs determine, to a large extent, the structure and reactivity of the remaining char (1). The importance of understanding devolatilization kinetics has long been recognized (2-6). However, it is surprising to note that very little information is available in the literature regarding the structure and reactivity of the chars produced in these studies.

The work described here is concerned with the utilization of bituminous (caking) coals in dilute phase, rapid heating gasification and combustion systems. Two highly caking coals were pyrolyzed in an entrained flow tube furnace system and devolatilization kinetics determined for each coal at temperatures of 900 and 1000°C. Structural properties of the chars collected in this work were then analyzed. In addition, the effects of mild preoxidation of these coals upon their subsequent pyrolysis behavior were examined. Samples of each coal were oxidized to various levels prior to heat treatment. Devolatilization kinetics and structural properties of the chars produced were then analyzed. Results reported here follow the development of char structure with varying heat treatment conditions and examine changes in char morphology which occur on preoxidation of these coals. This work is of practical importance in future design considerations for dilute phase gasifiers and of particular interest in gasification schemes where agglomeration of caking coals can cause serious problems.

EXPERIMENTAL

Pyrolysis experiments were conducted in an entrained flow tube furnace somewhat similar to that described by Scaroni et al. (7,8) and Nsakala and coworkers (9). Briefly, a dilute-phase coal stream is entrained in a primary carrier gas, passed through a water cooled probe and then injected into the center of a preheated secondary gas stream. The secondary gas stream enters the reaction zone at a temperature slightly above the furnace wall temperature so that upon mixing the combined gas stream attains the desired reaction temperature ($\pm 10^\circ\text{C}$). The primary modes of coal particle heating are conduction from the gas and radiation from the furnace walls. Heating rates in excess of 10,000°C/s are estimated. Coal particles travel in a pencil stream down the axis of the furnace tube. Samples are collected and rapidly quenched ($> 10,000^\circ\text{C/s}$ quench rate) using a water cooled probe which is inserted up the axis of the furnace. Reaction times are varied by changing the position of the sampling probe relative to the injector. The operating conditions at each temperature studied are given in Table 1. Helium is used as the primary carrier gas and is adjusted to maintain isokinetic sample injection. The secondary gas is nitrogen.

Weight loss due to pyrolysis was determined using ash as a tracer. The proximate analyses of the samples used in this work are presented in Table 2. The coals examined were PSOC-1133 a LV coal from the Lower Kittanning seam in Pennsylvania

TABLE 1. OPERATING CONDITIONS

Operating Temperature °C	900	1000
Coal Feed Rate g/min	0.5	0.5
Mean Gas Velocity cm/s	97	105
Secondary N ₂ /Primary He (Mole Basis)	26.4	24.2

TABLE 2. PROXIMATE ANALYSES OF SAMPLES (200x270 mesh fractions)

Sample	Moisture, %	Ash, %	Volatile Matter, %	Fixed Carbon, %
PSOC-1099 (Raw Coal)	1.6	9.0	33.7	56.7
PSOC-1099 (1% O ₂ added)	0.9	12.6	32.5	64.0
PSOC-1133 (Raw Coal)	0.4	16.4	18.5	64.7
PSOC-1133 (0.5% O ₂ added)	1.1	19.3	17.6	62.0
PSOC-1133 (1% O ₂ added)	1.1	19.5	18.2	62.2

and PSOC-1099 a HVA coal from the Pittsburgh seam in Pennsylvania. All work was conducted on 200x270 mesh size fractions with mean particle diameter of 63 μ m.

Preoxidized samples were prepared in a fluidized bed furnace. Samples of sized coal (200x270 mesh) were fluidized in nitrogen and brought to reaction temperature (175°C). The fluidizing gas was then switched to air and the samples were oxidized for various predetermined times. Oxidation times were determined based upon thermogravimetric studies of the air oxidation of each coal. It is assumed that oxidation rates in the thermobalance and fluidized bed systems are equivalent. This assumption is valid if one insures that the O₂ partial pressure in each system is the same and that there are no bed diffusion effects in the thermobalance system. Operating conditions were selected to meet these requirements. Oxidation levels reported here are given as % weight gain on oxidation (dry coal basis).

RESULTS AND DISCUSSION

Typical weight loss versus time curves for devolatilization of PSOC-1133 (LV coal) are presented in Figure 1. This plot shows weight loss is essentially complete within the first 100 msec of residence time. The same behavior was observed for the HVA coal examined in this study. These results are in good agreement with that of Badzioch and Hawksley (10). In similar experimental systems it is often assumed that pyrolysis occurs isothermally (7-10), however, this assumption cannot be made for the coals analyzed here.

Figure 1 also shows the maximum weight loss for devolatilization at 900°C is greater than at 1000°C. Similar observations have been reported by Menster et al. (11,12). These authors suggest a possible explanation for this behavior which involves a competition between bond breaking reactions (which result in volatile formation) and secondary recombination or polymerization (char forming) reactions,

Figures 2 and 3 demonstrate the effects of preoxidation on devolatilization behavior. Oxidation appears to have little effect on the rate of pyrolysis, however, devolatilization occurs so rapidly that the time resolution of this system may be inadequate to distinguish such effects. Preoxidation reduces the yield of volatile material in all cases examined. This corresponds with a sharp decrease

in the amount of condensible products (tars) collected.* Increases in the level of oxidation prior to pyrolysis result in a progressive reduction in the yield of volatile material. Devolatilization curves for preoxidized coals all have the same characteristic shape. Weight loss passes through a shallow minimum with residence time. Further study of this behavior is in progress.

Figure 4 shows an electron micrograph of PSOC-1133 char collected after 330 msec residence time at 1000°C. Coal structure has undergone extensive physical changes during the pyrolysis process. These chars are thin walled transparent structures commonly called cenospheres (13), the average diameter of which is three times that of the starting coal. This represents a > 20 fold increase in volume. Similar results are obtained at 900°C and for PSOC-1099 at each temperature studied. Under the pyrolysis conditions employed in this work cenospheres are fully developed during the early stages of pyrolysis (< 40 msec) after which no detectable changes in macroscopic properties are observed.

Figure 5 is a micrograph of a preoxidized coal char (PSOC-1133, 1% oxygen added) collected after 330 msec residence time at 1000°C. These chars do not form the cenosphere structures exhibited by the unoxidized coals. Char particles are rounded in shape indicating that the coal passes through a plastic transition during carbonization but no significant swelling is observed.

SUMMARY

The sharp contrast in macroscopic properties of the chars collected in this study give rise to several important questions regarding char gasification. Varying heat treatment conditions and coal feed stocks give rise to chars of widely varying structure. In order to understand the behavior of these materials in subsequent gasification steps a more detailed analysis of char structure is required. At present microstructural properties (surface areas, porosities) of the chars generated in this study are being examined in an effort to better understand the relationship between char structure and heat treatment conditions. Results of this work will be available shortly.

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* Tar yields were not measured quantitatively in this work, however, the differences in the amounts of condensible materials collected in the filtering systems were substantial enough to warrant the above comment.

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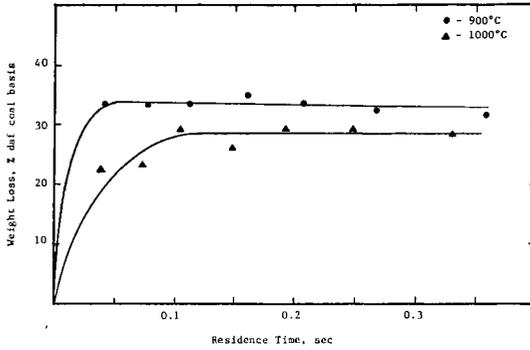


Figure 1. WEIGHT LOSS AS A FUNCTION OF RESIDENCE TIME FOR PSOC-1133

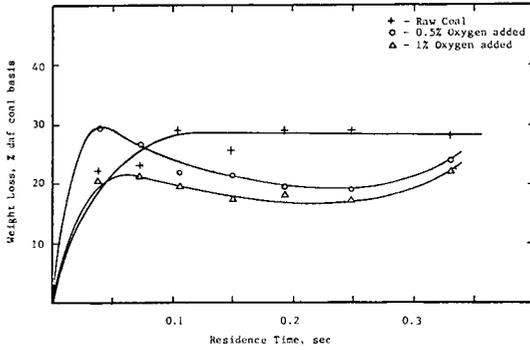


Figure 2. WEIGHT LOSS VERSUS RESIDENCE TIME AS A FUNCTION OF PREOXIDATION LEVEL FOR PSOC-1133

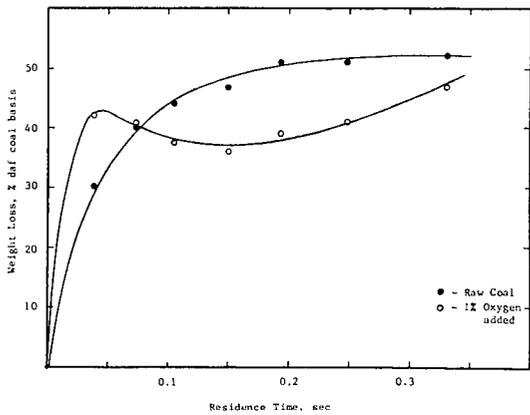


Figure 3. WEIGHT LOSS VERSUS RESIDENCE TIME AS A FUNCTION OF PREOXIDATION LEVEL FOR PSOC-1099

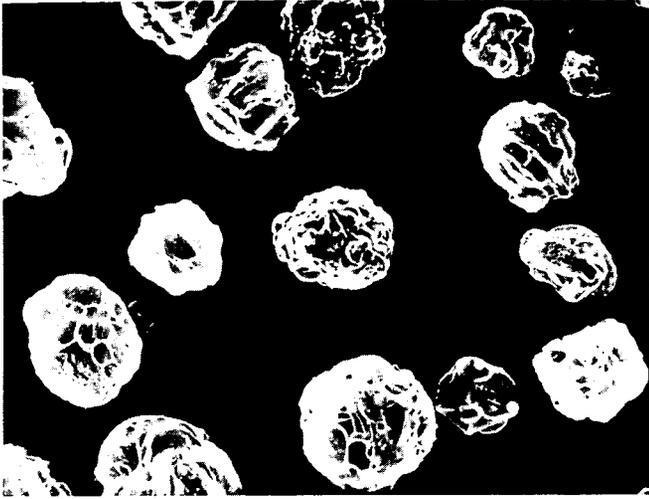


Figure 4. SCANNING ELECTRON MICROGRAPH OF PSOC-1133 CHAR
330 msec Residence Time at 1000°C

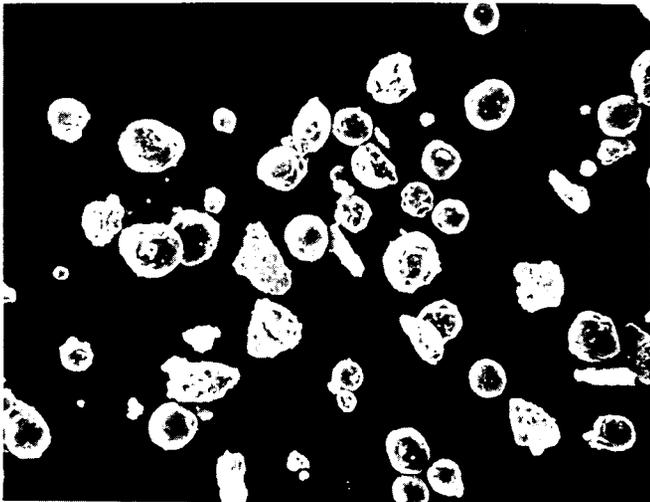


Figure 5. SCANNING ELECTRON MICROGRAPH OF A PREOXIDIZED COAL CHAR
(PSOC-1133 1% Oxygen Added) 330 msec Residence Time at
1000°C