

EFFECTS OF COAL PREOXIDATION AND HEAT TREATMENT CONDITIONS ON RESULTING CHAR STRUCTURE OF CAKING COAL

D. J. Maloney* and R. G. Jenkins

Department of Materials Science and Engineering
The Pennsylvania State University, University Park, Pennsylvania, 16802

Introduction

When most bituminous coals are heated in the absence of air, they soften (i.e., become fluid), agglomerate, and, as gases and vapors are evolved, swell to form a coke. These properties can limit the utilization potential of certain coals because agglomerates can impede gas flow leading to poor mixing in reactors and, in the extreme case, eventual plugging. In addition, coals which pass through a plastic stage produce relatively unreactive chars (1,2). These factors can add substantially to the cost of a gasification process.

Coal agglomerating tendencies can be eliminated by mild oxidation of the raw coal prior to heat treatment. This method is very effective in removing the swelling and softening characteristics of caking coals (3). Also, under certain carbonization conditions, preoxidation can significantly enhance the subsequent reactivity of the resulting chars (2).

Recent studies at the Pennsylvania State University have been directed at understanding the effects of preoxidation on coal utilization potential under conditions of interest for entrained-flow gasification and pulverized coal combustion (rapid heating rate, short residence time). Studies were conducted on an eastern bituminous coal in an effort to evaluate the effects of preoxidation on devolatilization behavior (yield and kinetics), coal swelling and agglomerating tendencies, and resulting char structure and reactivity (4). This paper describes the changes in char structural features resulting from coal preoxidation and examines the relationship between char structure and subsequent gasification potential.

Experimental

The chars examined in this study were prepared from freshly mined and preoxidized samples of a strongly caking bituminous coal under widely varying pyrolysis conditions (heating rate and time). The parent sample was PSOC-1099, a HVA bituminous coal from the Pittsburgh No. 8 seam. All work described here was conducted on 200 x 270 mesh size fractions with mean particle diameters of 62 μm . Preoxidized coal samples were prepared by air oxidation of sized coal in a fluidized-bed furnace. Oxidation temperature, time, and weight gain were determined based upon complementary thermogravimetric studies of the air oxidation of each coal. Oxidation levels reported here are given as percent weight gain on oxidation (dry coal basis). The proximate analyses of the fresh and preoxidized coals used in this work are presented in Table 1.

Chars were prepared under rapid heating conditions ($\sim 10^4$ K/s) in an entrained-flow furnace at temperatures between 1073 and 1273K with residence times up to 0.27s. Slow pyrolysis (12 K/min) chars were prepared in a horizontal tube furnace at a temperature of 1273K with a soak time at final temperature of 1 h. Extensive analyses of the surface properties of the chars were performed. Char morphology was examined

* Present Address: U.S. DOE, Morgantown Energy Technology Center, P.O. Box 880, Collins Ferry Road, Morgantown, West Virginia, 26505.

TABLE 1
Proximate Analyses of Samples* Examined

Sample	Moisture Percent	Ash Percent	Volatile Matter Percent	Fixed Carbon Percent
PSOC-1099 (HVA bituminous coal)	1.3	10.6	34.0	54.1
PSOC-1099 (1 percent O ₂ added)	0.8	10.6	32.5	56.1
PSOC-1099 (2 percent O ₂ added)	1.0	10.5	31.6	56.9

* Proximate analyses were conducted on 200 x 270 mesh fractions of 62 μ m mean particle diameter.

using SEM. Total surface area was determined by CO₂ physisorption at 298K. Macro and transitional pore surface areas were determined by N₂ adsorption at 77K. Additional char structural information was obtained by ultimate analysis using a Perkin-Elmer Model 240 elemental analyzer. Char reactivities were determined in air at 668K using a thermogravimetric method described by Mahajan and co-workers (2,5). Complete details of all experimental procedures employed in this study are supplied in Reference 4.

Results

Figures 1 and 2 are scanning electron micrographs of chars prepared from fresh and pre-oxidized samples (2.5 percent oxygen added) of PSOC-1099 after heat treatment of 0.23 s at 1273K. Chars prepared from the fresh HVA coal, Figure 1, were thin-walled transparent structures commonly referred to as cenospheres (6-8), the mean diameters of which were more than twice that of the starting coal. This represents a ~10-fold increase in volume. During pyrolysis the sample shown lost 51 percent of its starting material (daf). Under the conditions employed in this work, cenospheres were fully developed during the first 0.1 s of heating time after which no observable changes in macroscopic properties were evident. When carbonized under slow heating conditions, this coal formed a fused swollen coke.

As illustrated in Figure 2, the preoxidized coal did not form the cenosphere structures observed in Figure 1. Preoxidized coal char particle sizes were similar with those observed for the parent sample prior to carbonization. Char particle shapes, however, were altered considerably. Particle surfaces were rounded with little evidence of the sharp, well-defined fracture surface characteristic of the starting coal. This indicates that the preoxidized coal passed through a fluid state during rapid heating. All pre-oxidized samples examined in the present study formed chars of similar size and shape during rapid pyrolysis. In contrast to this behavior, the preoxidized coal exhibited no signs of thermoplastic behavior when carbonized under slow heating conditions.

Figure 3 illustrates the development of char surface area (CO₂ area) as a function of heat treatment time at temperatures of 1073 and 1173K for chars produced from the fresh HVA coal. Char surface areas remained constant during the first 0.05 s of heat treatment after which surface areas increased with time. The CO₂ surface area for the parent coal was 170 m²/g. At each heat treatment temperature, a more than two-fold increase in surface area occurred during the pyrolysis process. At 1073K, the maximum char surface area obtained was 360 m²/g (daf char); while at 1173K, the maximum char surface area was 465 m²/g. The sigmoid-shaped curves shown in Figure 3 suggest that char surface areas were approaching maximum values. This observation is supported by the results of Radovic (9) and others (10-14).

The N_2 surface area determined for the fresh coal was $2.7 \text{ m}^2/\text{g}$. N_2 surface areas determined for the corresponding char samples were less than $2 \text{ m}^2/\text{g}$ for all the chars examined. These areas approximate the theoretical limits calculated for cenospheres of the size and weight produced in this study.

Generally, N_2 surface areas determined for coals or char samples are considerably lower than the corresponding CO_2 surface areas. N_2 adsorption kinetics (at 77K) on microporous materials are limited by activated diffusion and, therefore, N_2 adsorption gives an estimate of macro and meso porosity (15). CO_2 (at 298K), however, is accessible to surfaces present in macro, meso, and micro pores.

Figure 4 illustrates the development of char surface area as a function of weight loss during pyrolysis. Surface areas exhibited little change during the early stages of pyrolysis. After 25 percent weight loss, however, char areas increased rapidly up to a weight loss of approximately 45 percent. Subsequent weight loss, up to 50 percent, had little effect on resulting surface areas. It is of interest to note that the weight loss level at which surface areas began to increase coincided roughly with the initiation of cenosphere growth (4).

CO_2 surface areas determined for the untreated and preoxidized coal samples and selected chars generated from these samples are presented in Table 2.

TABLE 2
Comparison of CO_2 Surface Areas
Determined for Fresh and Preoxidized
Coals and Their Corresponding Chars

		Surface Areas m^2/g (daf basis)			
Carbonization Temperature (K)	Raw	1073	1173	1273	1273
Carbonization Time (s)	Coal	0.27	0.25	0.23	3600*
Sample					
PSOC-1099 (untreated)	170	360	465	465	88
1.2 percent oxygen added	160	290	480	475	
2.5 percent oxygen added	150	320	500	522	188

* Slow heating conditions (12 K/min) followed by 1 h soak time at 1273K.

Preoxidation had little effect on the surface area of the coal sample prior to carbonization. During pyrolysis, preoxidation had a mild effect on resulting char surface area, however, no specific pattern was evident. After heat treatment at 1073K, surface areas of chars prepared from preoxidized coals were less than that observed for the corresponding unoxidized coal char. At carbonization temperatures of 1173 and 1273K, preoxidized coal formed chars with slightly higher surface areas than the corresponding chars prepared from the unoxidized coal. When slow heating conditions and extended heat treatment times were employed, preoxidation led to a significant increase in resulting char surface area. Following extended hold times at elevated temperatures, char surface areas were greatly reduced when compared with char surface areas observed for the rapidly heated (short time) samples.

The carbon and hydrogen percentages obtained from ultimate analysis provide some useful information concerning changes in char composition as a function of carbonization

conditions. The C/H ratios presented in Figures 5 and 6 show that as carbonization temperatures and times were increased, hydrogen was preferentially removed from the char samples. As the temperature of carbonization was increased, the rate of hydrogen evolution relative to carbon evolution increased significantly. The preoxidized coal behavior was similar to that of the fresh coal. Under comparable carbonization conditions, no significant differences were observed in the C/H ratios determined for chars derived from the fresh and preoxidized coal samples.

Preoxidation effects on char composition are illustrated more clearly in Figure 7. Over 80 percent of the hydrogen present in the fresh HVA coal sample was removed during 0.23 s of heat treatment at 1273K. Less than 50 percent of the original carbon was removed in the same time interval. Preoxidation reduced the quantities of both hydrogen and carbon liberated during comparable heat treatments.

The relative gasification potential of the chars produced in this study were evaluated by examining the reactivities of selected samples during gasification in one atmosphere of air (20 kPa O₂). The reactivity parameter reported here is $\tau_{0.5}$, which, at a given reaction temperature, is the time corresponding to a fractional burn-off of one-half. Mahajan, Yarzab, and Walker (5) demonstrated the utility of this parameter for correlating char reactivity data for gasification in air, steam, and CO₂.

Table 3 shows the reactivity parameters, $\tau_{0.5}$, determined for chars generated from PSOC-1099 as a function of carbonization temperature and preoxidation level. The carbonization times employed were the maximum residence times attainable at each furnace operating temperature. These were 0.27 s at 1073K, 0.25 s at 1173K, and 0.23 s at 1273K. The reactivity parameters reported are the mean values determined from three replicate reactivity tests. Typically the standard deviation from the mean was less than ± 10 percent.

TABLE 3
Comparison of Air Reactivities at 668K
for Chars Prepared from PSOC-1099 as a Function of
Carbonization Temperature and Preoxidation Level

Furnace Temperature (K)	Reactivity Parameter $\tau_{0.5}$ min		
	No Oxygen Added	1.2% Oxygen Added	2.5% Oxygen Added
1073	33	32	36
1173	46	46	46
1273	69	64	66

As carbonization temperature was increased from 1073K to 1273K, the subsequent char reactivity decreased by a factor of two. This was true for chars prepared from both the unoxidized and preoxidized parent samples. Preoxidation had no apparent effect on subsequent char reactivity. Values of $\tau_{0.5}$ determined for chars prepared from unoxidized and preoxidized coals were equivalent within the limits of reproducibility of the reactivity measurement.

Discussion

Nsakala and co-workers (16,17) and Radovic (9, 18) examined lignite coal chars generated under rapid heating, short residence time conditions. Each of these investigators reported increases in char surface areas, determined by CO_2 adsorption, of 200 to $300 \text{ m}^2/\text{g}$. The results presented here concur with these findings. Nsakala, et al. (16, 17), also reported significant increases in N_2 surface area during pyrolysis of a lignite. Similar increases in N_2 area were not observed for the bituminous coal examined in the present study.

Mahajan, et al. (2), reported that surface areas of chars produced from preoxidized coals were several times larger than those prepared from fresh coal samples. These investigators examined coals of similar rank and employed preoxidation conditions comparable with those used in the present study. They employed slow heating conditions (10 K/min) and extended soak times (1 h) at final temperature (1273K) during the carbonization process. When slow heating conditions (12 K/min to 1273K, followed by 1 h soak time at 1273K) were employed in the present study, chars produced from the unoxidized coal had CO_2 surface areas significantly lower than the chars produced from the preoxidized coal (Table 2). However, under rapid heating conditions, preoxidation had only a slight effect on resulting char surface area. It is apparent from the results shown here that preoxidation effects on resulting char area were greatly diminished when employing rapid heating conditions and short carbonization times.

Decreases in char reactivity with increasing heat treatment temperature were reported previously for coal chars (1,9,18) and other disordered carbonaceous solids (19). Jenkins and co-workers (1) examined chars prepared under slow heating conditions (10 K/min heating rate, 2 h soak time at final temperature). They reported that char reactivities during air gasification decreased by as much as 10 times when carbonization temperature was increased from 873K to 1273K. Radovic (9,18) examined reactivities of chars prepared from a lignite under rapid heating, short contact time carbonization conditions similar to those employed in the present study. He observed a decrease by a factor of 10 when carbonization temperature was increased from 975K to 1275K.

Jenkins, et al. (1), suggested that the effect of temperature on subsequent char reactivity could be explained on the basis of the concentration and accessibility of active sites. Firstly, they observed that the lower temperature chars had a significantly higher level of macro and transitional porosity (estimated from N_2 adsorption) and, thus, a more open or accessible pore structure than did the higher temperature chars. Secondly, they noted that the chemical nature of the char surface changed with changing carbonization temperature. Lower temperature chars had a higher hydrogen content than did the higher temperature chars. They suggested that hydrogen was preferentially removed during air gasification leaving behind nascent carbon active sites which are more reactive to oxygen. The chars generated in this study were essentially void of surface area associates with macro and transitional pores. Char reactivities exhibited no correlation with the micropore areas determined for these chars. Considering these results, it is probable that char reactivities were more strongly influenced by the amount of hydrogen remaining in the char. This suggestion is supported by the elemental composition data presented in Figures 5 through 7.

Mahajan and co-workers (2) observed that under slow heating conditions (10 K/min, 1 h soak at 1273K) preoxidation markedly enhanced subsequent char reactivity (by a factor of up to 40). The results of this study suggest that preoxidation effects on resulting char surface area and reactivity are greatly diminished when rapid heating conditions and short carbonization times are employed. In support of this observation, selected coal and char samples were carbonized under conditions comparable with those used by Mahajan and co-workers (2). Chars were prepared from the fresh HVA coal and

preoxidized (2.5 percent oxygen added) coal. In addition, the 1273K chars (0.23 s carbonization time) prepared by rapid heating of these samples were recarbonized under slow heating conditions. The reactivity parameters determined for these chars are presented in Table 4. Increasing hold times at the final carbonization temperature (1273K) from 0.23 s to 3600 s led to a seven-fold decrease in reactivity for the chars prepared from the unoxidized coal. When comparable hold times were employed, heating rate had little effect on subsequent char reactivity. Chars prepared from preoxidized coals were about a factor of two more reactive than the corresponding chars prepared from the unoxidized coal. The important factor in determining the subsequent char reactivity was the hold time at final temperature and not the heating rate.

TABLE 4

Effect of Carbonization Conditions on Subsequent Reactivity
of Chars Prepared from Raw and Preoxidized Samples of PSOC-1099

Char Preparation Method	Heating rate Hold Time at 1273K	Reactivity Parameter t0.5 min		
		30,000 K/s	0.2 K/s	30,000 K/s*
Parent Sample				
Raw (unoxidized)		69	450	490
2.5 percent oxygen added		66	300	260

* Chars were prepared in the entrained-flow furnace under rapid heating conditions and were recarbonized by heating at 0.2 K/s and holding for 3600 s at 1273K.

Mahajan and co-workers (2) attributed the enhancement of char reactivity as a result of preoxidation to the large increases in micropore surface areas they observed for these chars. Under rapid heating, short contact time, carbonization conditions similar increases in surface area and char reactivity were not observed. However, when carbonization times were extended, preoxidation effects became evident. These results provide some insight concerning the role which oxygen plays in the carbonization process. From the work of Jenkins, et al. (1), and others (10-14), it is known that increasing the severity (time, temperature) of carbonization conditions results in a sealing up or closing of char porosity. This annealing process reduces the accessibility and quantity of active gasification sites present in the char. The results of this study and the work of Mahajan, et al. (2), suggest that preoxidation inhibits the annealing process and, thereby, leads to the production of more reactive coal chars. This inhibition does not become manifest in the initial stages of the carbonization process.

Acknowledgments

Funding for this work was provided by the Cooperative Program in Coal Research at the Pennsylvania State University and by the U.S. Department of Energy under Contract No. DE-AC01-79ET14882. Additional support was supplied by a Mining and Mineral and Mineral Fuels Conservation Fellowship. Elemental analyses were generously supplied by the United Technologies Research Center under the direction of Dr. James D. Friehaut.

References

1. Jenkins, R. G., S. P. Nandi, and P. L. Walker, Jr., Fuel, 52, 288, 1973.
2. Mahajan, O. P., M. Komatsu, and P. L. Walker, Jr., Fuel, 59, 3, 1980.
3. Maloney, D. J., R. G. Jenkins, and P. L. Walker, Jr., Fuel, 61, 175, 1982.
4. Maloney, D. J., Ph.D. Thesis, The Pennsylvania State University, 1983.
5. Mahajan, O. P., R. Yarzab, and P. L. Walker, Jr., Fuel, 57, 643, 1978.
6. Newall, H. E., and F. S. Sinnatt, Fuel, 3, 424, 1924.
7. Newall, H. E., and F. S. Sinnatt, Fuel, 5, 335, 1926.
8. Newall, H. E., and F. S. Sinnatt, Fuel, 6, 118, 1927.
9. Radovic, L. R., Ph.D. Thesis, The Pennsylvania State University, 1982.
10. Chiche, P., S. Durif, and S. Pregermain, Fuel, 44, 5, 1965.
11. Miura, S., and P. L. Silveston, Carbon, 18, 93, 1980.
12. Razouk, R. I., F. Z. Saleeb, and A. M. Youssef, Carbon, 6, 325, 1968.
13. Toda, Y., Fuel, 52, 94, 1973.
14. Toda, Y., Fuel, 52, 99, 1973.
15. Walker, P. L., Jr., Phil. Trans. R. Soc. Lond., A300, 65, 1981.
16. Nsakala, N., R. H. Essenhigh, and P. L. Walker Jr., Fuel, 57, 605, 1978.
17. Nsakala, N., Ph.D. Thesis, The Pennsylvania State University, 1977.
18. Radović, L. R., P. L. Walker, Jr., and R. G. Jenkins, Fuel, 62, 849, 1983.
19. Blake, J. H., G. R. Bopp, J. F. Jones, M. G. Miller, and W. Tambo, Fuel, 46, 115, 1967.

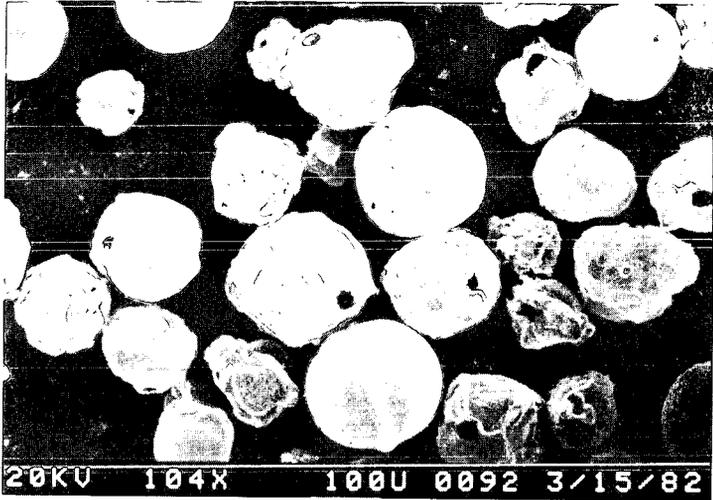


FIGURE 1. SCANNING ELECTRON MICROGRAPH OF THE CHAR PRODUCED FROM PSOC-1099 FOLLOWING HEAT TREATMENT AT 1273 K FOR 0,23 s

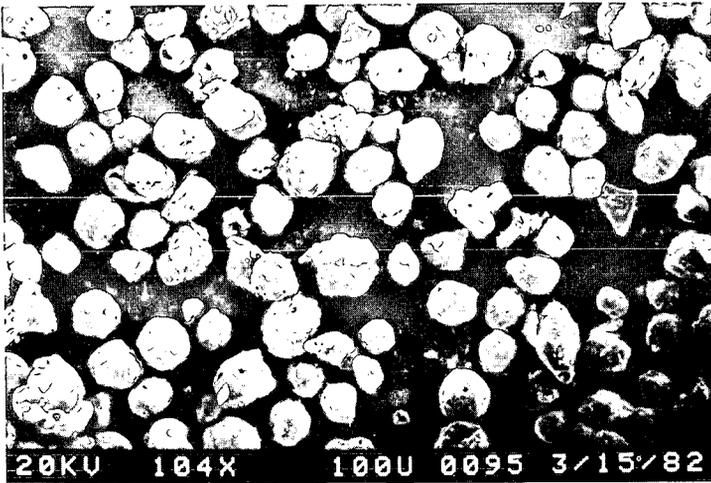


FIGURE 2. SCANNING ELECTRON MICROGRAPH OF THE CHAR PRODUCED FROM PREOXIDIZED PSOC-1099 (2,5% OXYGEN ADDED) FOLLOWING HEAT TREATMENT AT 1273 K FOR 0,23 s

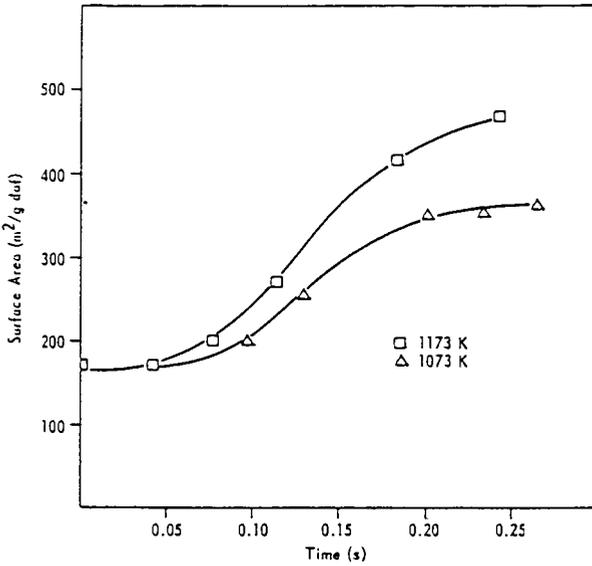


Figure 3. EFFECTS OF CARBONIZATION TIME AND TEMPERATURE ON RESULTING CO₂ SURFACE AREA FOR CHARs PREPARED FROM PSQC-1099

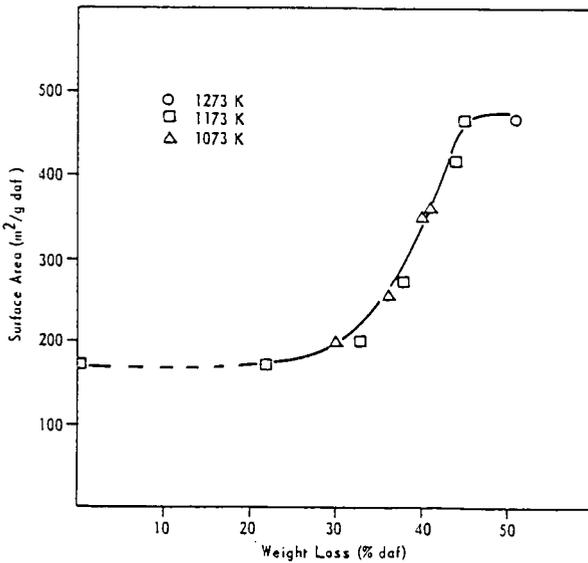


Figure 4. EFFECT OF PYROLYSIS YIELD ON RESULTING CO₂ SURFACE AREA FOR CHARs PREPARED FROM PSQC-1099

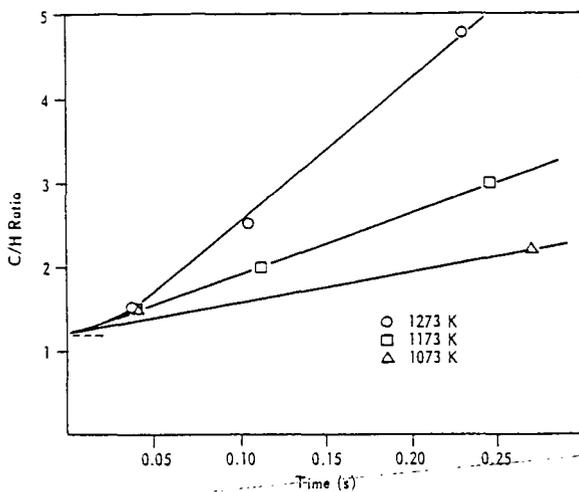


Figure 5. EFFECTS OF CARBONIZATION TIME AND TEMPERATURE ON RESULTING ATOMIC C/H RATIOS FOR CHARS PREPARED FROM PSOC-1099

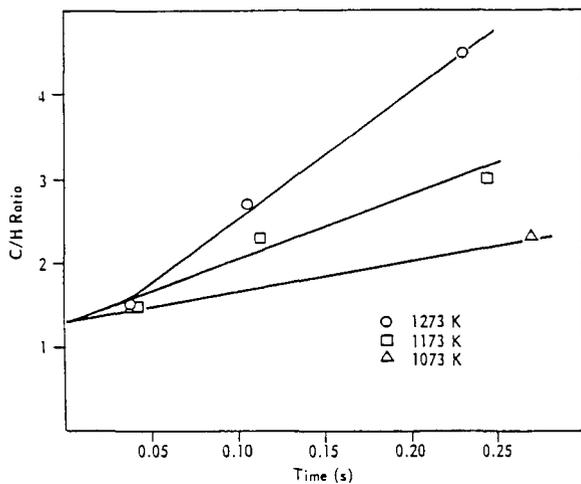


Figure 6. EFFECTS OF CARBONIZATION TIME AND TEMPERATURE ON RESULTING ATOMIC C/H RATIOS FOR CHARS PREPARED FROM PREOXIDIZED PSOC-1099 (2.5% Oxygen Added)

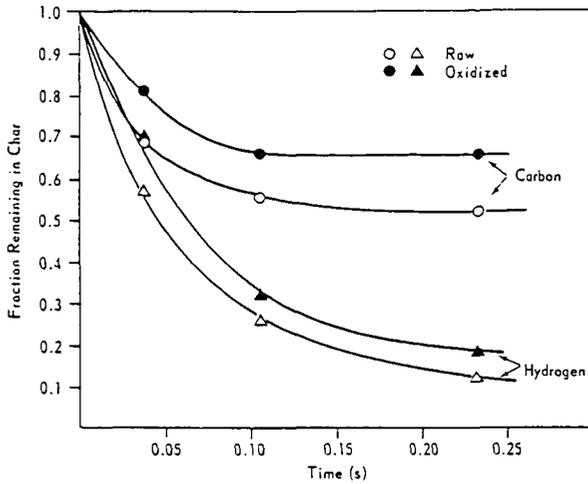


Figure 7. WEIGHT FRACTIONS OF CARBON AND HYDROGEN REMAINING IN CHARS AS A FUNCTION OF TIME AT 1273 K FOR RAW AND PREOXIDIZED (2.5% Oxygen Added) SAMPLES OF PSOC-1099