

Reactivity of Low-Temperature Chars: Significance of Char Active Surface Area as a Reactivity Parameter

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ABSTRACT

Contemporary char reactivity studies have focused primarily on coal chars prepared at severe (high-temperature) conditions. In this study, the reactivity of chars prepared at mild (low-temperature) conditions has been addressed. A thermogravimetric analysis system (TGA) was used to determine the reactivity of chars in air or O₂ using isothermal or nonisothermal techniques. Coal chars were prepared in a TGA or in a slow heating rate organic devolatilization reactor (SHRODR) at a temperature range between 500° and 950°C. The chars prepared by mild pyrolysis of coal at 500°C are shown to be highly reactive. Comparison of reactivities of low- and high-temperature chars shows that the low-temperature chars exhibit higher reactivity than both the parent coals and the high-temperature chars. Correlation between isothermal reactivity results (e.g., time) and nonisothermal reactivity data (e.g., temperature) has been obtained. Hydrogen contents of chars correlate well with the reactivity of the chars. The study considers the significance of oxygen chemisorption capacity as a reactivity parameter.

INTRODUCTION

The Morgantown Energy Technology Center (METC) in-house results demonstrated that relatively high-quality liquids (low sulfur, high H/C) can be produced by low-temperature devolatilization of coal (1). The major product in a devolatilization process is char. Thus the utilization of the by-product chars by gasification/combustion should significantly improve the overall economics of a process that uses devolatilization. A literature review (2) suggests that previous studies of char reactivity were aimed solely at chars prepared at severe conditions (e.g., high temperatures). Consequently, there is a dearth of reactivity data on coal chars prepared at mild temperatures (e.g., 500°C). The volatile matter content of low-temperature chars, which can be appreciable, however, may favor reactivity of these chars. Literature data do not present a clear picture of the relationship between char hydrogen content or char volatile matter and the reactivity of char.

BACKGROUND

Coal chars are composed of pseudo-graphitic building blocks (3). In coal chars, particularly those prepared at low temperature, the carbon crystallites are small in size and poorly aligned because of crosslinking. The edge sites and various imperfections in the carbon structure (including singly-bonded "dangling" carbons) are thought to be the "active sites" during gas reactions.

The reactions of char with oxygen have generally been described (4,5) as governed by the following controlling processes: (a) mass transfer (by diffusion) of O₂ to reaction sites; (b) chemisorption of oxygen on the carbon surface, reaction of chemisorbed oxygen with carbon to form products, and desorption of products from the carbon surface, and; (c) mass transport of the gaseous products from the carbon surface. In the absence of mass transport limitations, the intrinsic char reactivity is controlled by (a) char active surface area, and (b) catalysis by impurities.

Laine, et al. (6) measured the kinetics of the C-O₂ reaction on graphitized carbon black using a combination of mass spectroscopy and oxygen chemisorption; the measurements showed clearly that gasification rates depend upon the fraction of active surface area (ASA) unoccupied by a stable oxygen complex. Hennig (7) developed an etch decorative technique to follow the enlargements of vacancies in the basal plane of graphite during reaction of carbon with oxygen; and established the importance of carbon active sites in determining the reactivity. Radovic et al. (8,9,10) extended the concept of active sites to lignitic chars prepared at various conditions and observed that the reactivity results can be normalized better when char ASA was considered.

As previously stated, the active sites are considered as imperfections in carbon crystallite edges or dislocations. The influences of hydrogen present on char surfaces, especially on those prepared at low temperatures, on reactivity or oxygen chemisorption are not well-known. For low-temperature chars, surface heteroatoms (mainly hydrogen) may play an important role in their reactivity by generating nascent sites (sites formed by devolatilization or gasification). ASA determination by oxygen chemisorption does not account for surface heteroatoms such as hydrogen. Suuberg, et al. (11), questioned the significance of oxygen chemisorption as a means to monitor ASA; and argued that the concept of active sites was too broad, since the reactive sites may be quite different in low-temperature chars from those in high-temperature graphitic carbons.

The effect of inherent inorganic constituents on char reactivity varies with coal rank. It is known that reactivity of chars prepared from lignites are markedly influenced by the inherently present well-dispersed metal cations. However, the reactivity of chars prepared from bituminous coals is not significantly influenced by the inorganic matter inherently present in chars, perhaps because of the discrete (lumped) nature of these minerals. Indeed, the reactivity of acid demineralized chars appeared to be slightly greater compared to the mineral-matter-containing chars (9). The effects of the demineralization process on the coal organic structures are not well known. It was shown (12) that commonly used demineralization procedures (13) markedly reduced the swelling of a plastic coal.

OBJECTIVES

The overall objectives of this study are the following: (a) quantify the reactivities of coal chars prepared at mild (low-temperature, 500°C) and severe (high-temperature, e.g., 950°C) conditions, (b) compare the reactivities of coals of various ranks with the corresponding low-temperature chars, (c) study the influence of char/coal hydrogen content on reactivities, (d) investigate the significance of oxygen chemisorption capacity as an index of char reactivity. Some preliminary results on each of these areas are presented.

EXPERIMENTAL

The coals were devolatilized either in a thermogravimetric analysis system (TGA) or in a slow heating rate organic devolatilization reactor (SHRODR), which allowed preparation of larger amounts of samples for characterization. In these units, chars were prepared at 20°C/min (TGA) or at 12.5°C/min (SHRODR). Descriptions of the TGA and SHRODR systems are available (1,14).

The analyses of coals and chars prepared at various conditions are presented in Tables 1A and 1B. As shown in Tables 1A and 1B, several high-volatile bituminous coals were used for devolatilization and reactivity studies. The Pittsburgh No. 8 coal pyridine extracted residue (subsequently water washed and vacuum dried at 200°C to remove pyridine) was also pyrolyzed at 500°C. In a TGA, the weight loss of a small amount of sample due to reaction is continuously monitored as a function of temperature. TGA has been shown to be useful for comparing reactivities of various feedstocks. To monitor the reactivity of the coal/char, isothermal and nonisothermal

reactivity techniques were used. The isothermal approach has been used to monitor char reactivity by others (8,10,15). Smith (4), Wagoner and Duzy (16), Wagoner and Winegartner (17) used derivative TGA profiles (DTA) for comparing relative reactivities of various coals, coal chars, or petroleum cokes under specified conditions.

TABLE 1A: Characterization Data for Raw Coals

	Pittsburgh No. 8 (hvAb)	Illinois No. 6 (hvCb)	Kentucky No. 8 (hvAb)
<u>Proximate</u> (As Received)			
Moisture	0.57	4.05	0.10
Ash	7.27	8.41	7.03
Volatile Matter	37.86	36.3	35.46
<u>Ultimate</u> (dry-ash-free basis, daf)			
C	83.75	69.3	86.35
H	5.46	4.75	5.41
N	1.56	1.32	1.53
S	2.15	3.2	1.21
O (By Difference)	7.08	10.26	5.50
H/C (atomic)	0.78	0.82	0.75
Heating Value (As Received) (Btu/lb)	13,976	12,523	14,256

TABLE 1B: Characterization Data for Chars

Sample/Preparation Condition	daf basis			
	C	H	N	H/C (Atomic)
Pit 8, TGA 500°C	79.7	3.02	1.67	0.45
Pit 8, SHRODR 500°C	84.4	3.05	2.15	0.43
Pit 8, TGA 650°C	83.8	1.98	2.12	0.28
Pit 8, TGA 750°C	86.0	1.20	1.77	0.17
Pit 8, TGA 950°C	90.4	0.52	1.64	0.07
Pit 8, Pyridine	79.82	2.65	2.79	0.40
Extracted residue 500°C				
Ill 6, SHRODR 500°C	89.2	3.06	2.57	0.41
Kentucky 8 SHRODR 500°C	91.14	1.66	1.81	0.22

In this study, the sample size used for a reactivity run was 2 mg or less. The gas flow rate for the reactants (O₂ or air) was 120 cc/min. The isothermal reactivities reported were independent of gas flow rate and, thus, the expressed rates are free from external mass transfer limitations. The char particle size was <74 μm. At these conditions, kinetically controlled reactivity results were obtained. The nonisothermal reactivity studies were performed at a heating rate of 100°C/min in air. In an attempt to measure the concentration of available carbon sites, oxygen chemisorption capacity of chars was determined. Chemisorption was carried out at ~200°C and 0.1 MPa O₂ for ~15 hours using the TGA.

RESULTS AND DISCUSSION

Isothermal Reactivity Results

The reactivity of char is generally expressed by the relationship, $R = -1/M_c \frac{dM_c}{dt}$. 1)

where dM_c/dt = instantaneous slope of burn-off curve

M_c = dry-ash-free (daf) basis char weight at time, t

In isothermal TGA studies, in the absence of catalysis, the rate is a function of concentration of reactants. Assuming the reactivity is first order for carbon (ASA), the char reactivity can be expressed by

$$\frac{dM_c}{dt} = -k M_c P_{O_2}^n \quad (\text{ASA}) \quad \begin{array}{l} P_{O_2} = \text{partial pressure of oxygen;} \\ n = \text{true reaction order} \\ \text{ASA} = \text{total active surface area} \end{array} \quad 2)$$

The intrinsic (in the absence of mass or heat transfer limitations) reaction rate constant k is given by, $k = A e^{-E/RT_p}$; where E = true activation energy, kJ/mole; T_p = particle temperature, K.

Equation 1 can be expressed in terms of fractional conversion, x :

$$M_c = M_i (1-x) \quad \text{or,} \quad x = \frac{(M_i - M_c)}{M_i} \quad 3)$$

$$R = \left(\frac{1}{1-x}\right) \frac{dx}{dt} = k P_{O_2}^n \quad (\text{ASA}) \quad 4)$$

where, M_i = initial daf char mass.

During a TGA run, T_p and P_{O_2} were held constant so that changes in the reactivity R with conversion could only be attributed to changes in ASA and k .

$$R = \left(\frac{1}{1-x}\right) \frac{dx}{dt} \propto k \quad (\text{ASA}) \quad 5)$$

The maximum rate of char reactivity (R_m , daf) widely used in literature (8,9,10,15), has been used as an index of char reactivity. Arrhenius relationships for the reactivity (R_m) of chars prepared at various peak devolatilization temperatures (PDT) are presented in Figure 1. The higher the PDT of the coals, the lower the reactivity of the resulting char; i.e., the highest R_m was noted for the char prepared at 500°C. This behavior is consistent with the trends available in the literature (10), although no data are reported for the low-temperature chars. The lower observed reactivity for the high-temperature chars are attributable to the loss of reactive sites and/or reactive functional groups (or hydrogen) on char surface at elevated temperatures.

The preliminary results show that the reactivity of low-temperature chars, like high-temperature chars, can be expressed by Arrhenius relationships. The activation energies of the low- and high-temperature chars are comparable. The observed activation energy of 130 kJ/mole is consistent with the literature results noted for various chars (10).

Significance of Oxygen Chemisorption Capacity as a Reactivity Parameter

The oxygen chemisorption data (e.g., percent O₂ uptake presented as m²/g, daf) were used to normalize the reactivity (at 400°C) results (Table 2) for chars prepared at low- and high-temperature conditions. For comparison, data on chars prepared at 500°C from various bituminous coals are also presented. Values for the active surface area, i.e., that surface area occupied by dissociatively chemisorbed oxygen atom (Table 2) were determined assuming a value of 0.08 nm² for the area occupied by each oxygen atom. The reactivity of different chars at 400°C showed variations by a factor of 13 (on g reacted/g initial material per h, basis). When the reactivity data are normalized on ASA basis (e.g., g/m²ASA.h), the variations in reactivity were reduced to a factor of 4. These findings are consistent with results reported by Radovic, et al. (8-10). These results provide credence that ASA as determined by oxygen chemisorption is a relevant reactivity parameter for low-, as well as high-temperature chars.

TABLE 2: Comparison Of Reactivities and Active Surface Areas For Various Chars

Sample/ Preparation Condition	ASA (at 200°C) (m ² /g)	R _m (400°C) (g/g/h,daf)	k, 400°C x 10 ³ (g/m ² ASA.h)
Pittsburgh No.8/TGA 500°C	253.5	3.3 (highest rate)	13.0
Pittsburgh No.8/TGA 650°C	150	1.2	8.0
Pittsburgh No.8/TGA 750°C	103	0.73	7.0
Pittsburgh No.8/TGA 950°C	70	0.26 (lowest rate)	3.7
Pittsburgh No.8 (Extracted)/TGA 500°C	251	3.2	12.7
Illinois No.6/SHRODR 500°C	157.5	1.26	8.0
Kentucky No.8/SHRODR 500°C	170.4	1.32	7.8
L. Kittanning/TGA 500°C (PSOC 1197; lvb)	158.7	1.14	7.2

Nonisothermal Reactivities

For dried char/coal samples (i.e., no moisture), the weight loss as a function of temperature is governed by the following events: (a) intrinsic gas solid reaction at low (10 percent) conversion, (b) at elevated temperature, the mass transfer of oxygen to the char limiting the intrinsic reactivity. However, with increased conversion and pore enlargement, the weight loss may shift between intrinsic reactivity limited to mass transport limited regions (4,5).

Nonisothermal reactivities of chars prepared at low- and high-temperatures were compared (Figure 2). As with the isothermal technique, the reactivity of the high-temperature chars were significantly lower than the low-temperature chars as was evident by a lower maximum rate of weight loss and increased temperature where the maximum rate peaked.

There are two primary schools of thought in the literature (5) on char oxidation mechanisms: (a) homogeneous combustion of volatiles formed during devolatilization is followed by slower heterogeneous oxidation of char, and (b) direct heterogeneous combustion of coal or char dominates. The results show that the latter mechanism prevails. For example, the mild pyrolysis chars (prepared at 500°C) demonstrated significant burn-off at 500°C, a temperature where little volatile matter is formed (Figures 2 and 3). The greater reactivity of the mild pyrolysis chars than that of the corresponding parent coals or the high-temperature chars can be attributed to

(a) easier accessibility of reactants into the chars structure compared to the parent coals, (b) the greater concentration of active surface area in the low-temperature chars as compared to the high-temperature chars, or (c) both.

Comparison of Reactivities of Coals and Chars

Nonisothermal reactivity measurements were performed in air to determine the reactivities of low- (500°C) and high-temperature (750°C) chars compared (Figure 3) to the parent coals. For the three high volatile bituminous coals (Pittsburgh No. 8, Illinois No. 6, and Kentucky No. 8), the maximum reaction rates of chars (prepared by pyrolysis at 500°C) were greater than the parent coals (Figures 3A, 3B, and 3C). By contrast, the maximum rates of weight losses for the char prepared from a low volatile coal (PSOC 1197, lower Kittanning seam coal, Pennsylvania) by pyrolysis at 500°C were lower than the corresponding parent coal (data not shown). It is suggested that highly agglomerated chars prepared from the HVA coals prevented diffusion of oxygen into the structure, and thus caused lower reactivity.

Reactivity of Preoxidized and Solvent Extracted Coals

It was hypothesized that preoxidized HVA bituminous coals, which do not become fluid, may demonstrate increased reactivity over untreated coals. A preoxidized (at 150°C for 6 days) Pittsburgh No. 8 coal was reacted nonisothermally in air. The maximum reaction rate for the preoxidized coal was greater than the untreated coal, but smaller than the char prepared at 500°C (Figure 3A and 4A). A comparison of nonisothermal (DTA) plots for the raw Illinois No. 6 and the preoxidized coal is presented in Figure 4B. It is interesting to note that the temperature of maximum rate of weight loss is shifted to elevated temperatures for the preoxidized coal. It is possible that upon preoxidation, some carbon sites for this coal are occupied by a stable oxygen complex which desorb at a higher temperature, causing an increase in the temperature of maximum burn-off rate. It is well-known that solvent extraction of bituminous coals destroys the plasticity of the residue during subsequent pyrolysis. To prevent coal swelling, the Pittsburgh coal was extracted with pyridine to remove materials that cause coal plasticity. The extracted coal also reacted nonisothermally in air. However, the maximum reactivity of the extracted residue was still lower than that of the char prepared at 500°C (Figure 4C). These results show that the char prepared at low temperature (500°C) is significantly more reactive than the preoxidized or solvent-extracted coal.

Correlations of Reactivity Results With the Char Hydrogen or H/C

Figures 5A and 5B correlate the reactivity (at 400°C) of the chars with the char H/C (atomic) or the hydrogen contents. The results show that the higher the char H/C (atomic) or hydrogen content, the greater the reactivity. The results suggest that the hydrogen rich portions of coal char are preferentially oxidized relative to carbon. Snow, et al. (18) studied the influence of hydrogen content on the oxidation of carbon blacks and observed that the higher the hydrogen content, the higher the reactivity (15,18). The significantly greater reactivity of the low-temperature chars compared to the high-temperature chars is attributable, at least in part, to the greater hydrogen contents of these chars. Hydrogen removal by oxidation leaves behind highly reactive "nascent" carbon sites (19). Walker, et al. (19,20) proved that removal of complexes from carbon surfaces enhanced the reactivity of carbons in carbon dioxide.

Correlations Between Isothermal and Nonisothermal Reactivity Data

Comparisons of the isothermal reactivity parameter (e.g., time for a given burn-off) with nonisothermal reactivity data (e.g., temperature for the same burn-off) have been made. Data in the Arrhenius forms are presented in Figures 6A (for 10-percent conversion, $T = 0.1$), 6B ($T = 0.3$), and 6C ($T = 0.4$). The activation energy (E_{act})

at low conversion ($T = 0.1$) is calculated to be ~ 130 kJ/mole, comparable to the isothermal case (Figure 1). At greater conversion ($T = 0.2$ to 0.4), the E_{act} reduced from 102 kJ/mole ($T = 0.3$) to 75 kJ/mole (at $T = 0.4$). This suggests that at low conversion, the weight loss is dominated by the intrinsic char oxygen reaction which has an $E_{act} \sim 130$ kJ/mole. At higher conversions (i.e., higher temperatures), however, the mass transfer of O_2 limits the weight loss. It is known that mass transfer process has a lower activation energy (4,5). Thus, at higher conversion ($T = 0.2$ to 0.4), the E_{act} is significantly reduced. The nonisothermal reactivity results (i.e., temperature) at low (10 weight percent) conversion can be correlated somewhat with the char active surface area (Figure 7), suggesting that active surface areas of these chars play an important role in determining the reactivity.

The influences of added inorganics on coal devolatilization and product yield/composition have been discussed (1,12,21). It was observed that addition of a hydrated dolomite [$Ca Mg (OH)_4$] at a low concentration (~ 5 weight percent) significantly reduced gaseous H_2S yield while the liquid quality was improved (i.e., reduced S content). A comprehensive study on the influence of various additives introduced prior to devolatilization on the reactivity is in progress. Figures 6A, 6B, and 6C presents some data (i.e., temperatures) derived from non-isothermal heating of a char prepared by co-pyrolysis of coal with dolomite.

There are several simplifications inherent in this study. The results presented in Table 2 (e.g., the absolute values of the reported ASA) should be interpreted with caution. As discussed previously, the ASA is a measure of available sites present on char surface. The analysis, in essence, demonstrates a trend that illustrates the principle of char reactivity. The actual reactivity mechanisms are complicated by the observations that (a) oxygen chemisorption capacity is a function of both the temperature and pressure of chemisorption, and (b) the measured oxygen uptake depends on whether it occurs in the presence or absence of concurrent gasification. A significant portion of sites on coal chars can be occupied by hydrogen, which may preferentially react with oxygen at low conversion, opening up new carbon active sites. However, the trends shown in Table 2, based on somewhat arbitrary conditions of chemisorption, illustrate the utility of oxygen chemisorption technique as an index of char reactivity.

SUMMARY AND CONCLUSIONS

(a) For char oxidation, the activation energy of 130 kJ/mole, comparable to literature data, was observed for both low- and high-temperature chars. This suggests that the chemistry of gas solid reactions follow comparable mechanisms for both low- and high-temperature chars. (b) The low-temperature chars prepared from various coals (at $500^\circ C$) appear to be more reactive (determined nonisothermally) than the parent coals. These low-temperature chars are also more reactive than the parent preoxidized coals or the solvent extracted residue. (c) The reactivity of various chars can be correlated with the H/C or char hydrogen contents. (d) The weight loss during nonisothermal reactivity at low conversion (10 percent) is limited by intrinsic gas-solid reactions. At elevated temperatures (or higher conversions), however, mass transfer limits the weight loss as is evident by lower activation energies for the process. (e) Finally, the char active surface area serves as a significant parameter for normalizing isothermal reactivity results. In addition, at low conversion, the non-isothermal reactivity parameter of chars can be correlated to the active surface area as determined by oxygen chemisorption.

ACKNOWLEDGEMENTS

The assistance of E. Newton and M. Rutherford, undergraduate student trainees at METC through Oak Ridge Associated Universities (ORAU) Program, who performed the TGA experiments, is acknowledged. J. Kovach and L. Headley made meaningful inputs in various aspects of this study.

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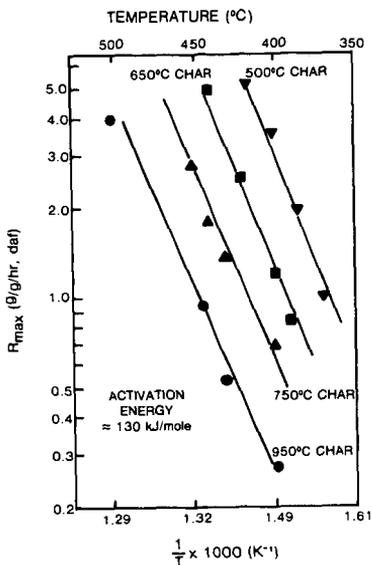


FIGURE 1. Arrhenius Relationships Between Chars (Prepared at Various Conditions) and Their Reactivities

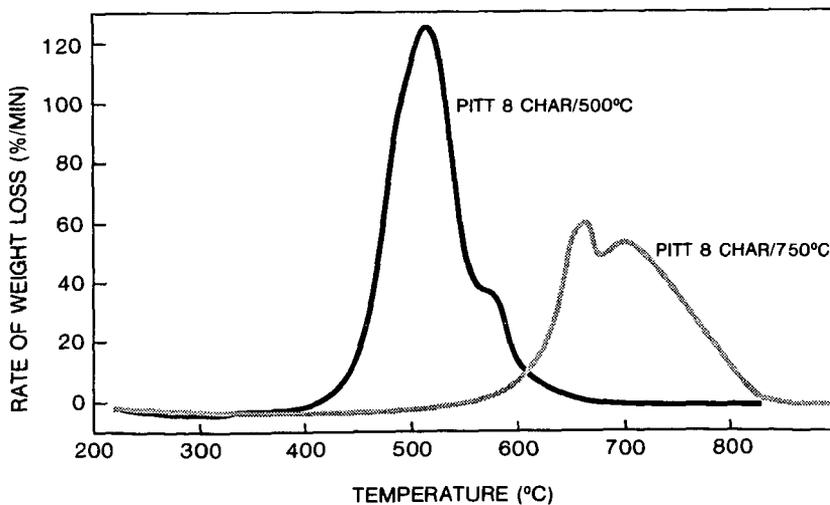


FIGURE 2. DTA Plots for Low- and High-Temperature Chars. (Air Flow Rate 120 cc/min)

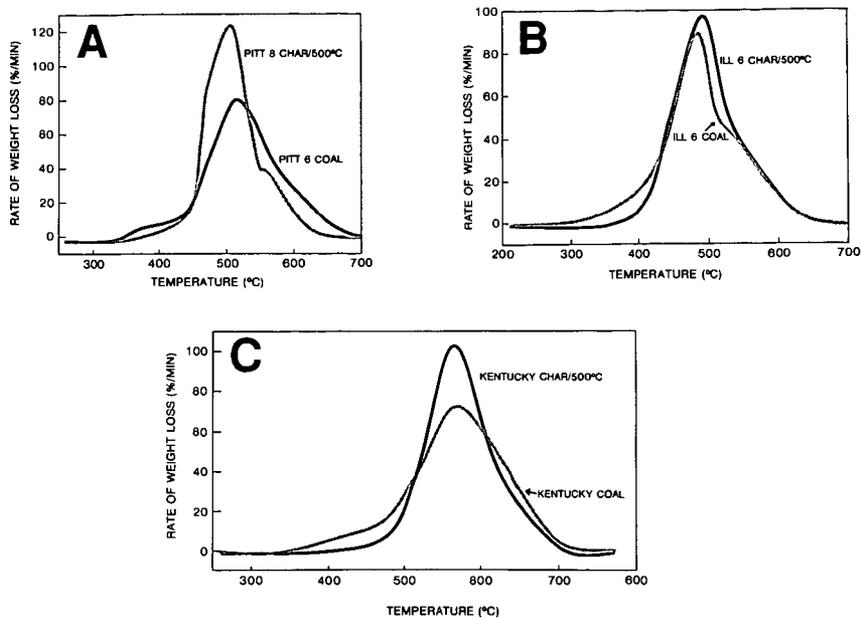


FIGURE 3. Comparison of DTA Curves for Coals with the Corresponding Low-Temperature Chars. (A) Pittsburgh No. 8, (B) Illinois No. 6, and (C) Kentucky No. 8. (Air Flowrate 120 cc/min)

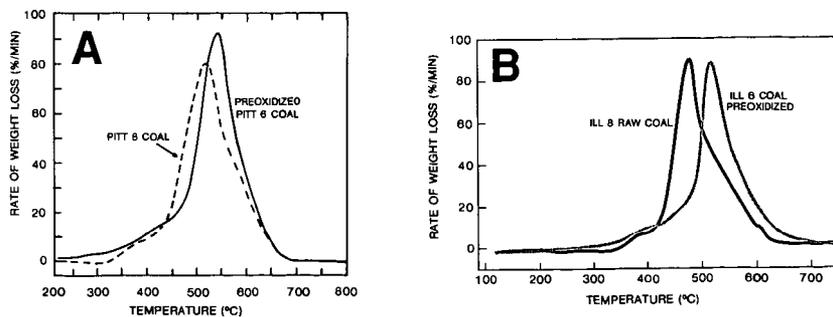


FIGURE 4. Comparison of DTA Curves for the Coals with the Corresponding Preoxidized Coals (A) Pittsburgh No. 8, (B) Illinois No. 6

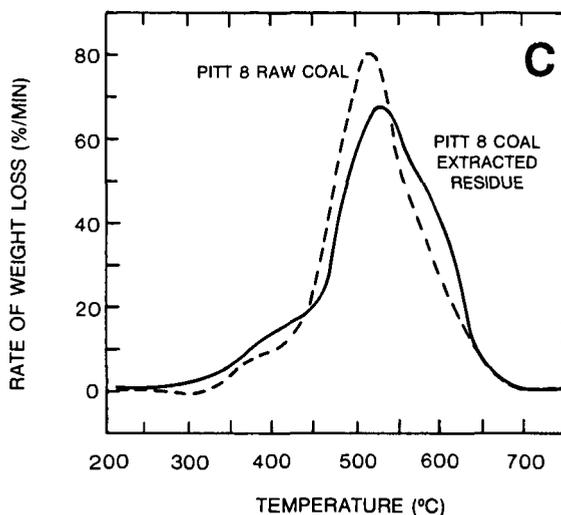


FIGURE 4. Comparison of DTA Curves for the Coals with the Corresponding Preoxidized Coals (C) Comparison of DTA Plots of Raw Pittsburgh No. 8 Coal with the Corresponding Pyridine Extracted Residue. (Air Flow Rate 120 cc/min)

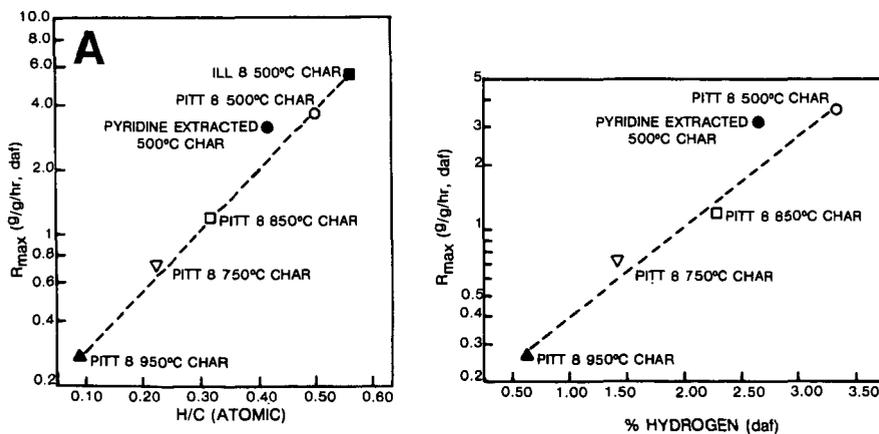


FIGURE 5. The Correlation Between Char Reactivity at 400°C (Isothermal) with (A) H/C (Atomic) or (B) Percent Hydrogen (daf) of the Chars

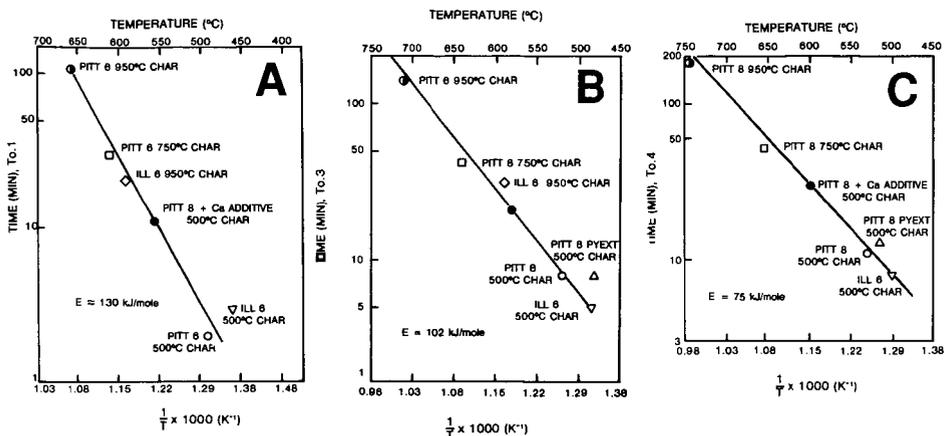


FIGURE 6. Correlation of Reactivity Results Obtained Using Isothermal (i.e., Time) and Nonisothermal (Temperature) Techniques at (A) 0.1 Conversion, (B) 0.3 Conversion, and (C) 0.4 Conversion. Isothermal experiments were performed at 400°C; nonisothermally, a heating rate of 100°C/min was utilized. To.1 signifies 10 percent conversion.

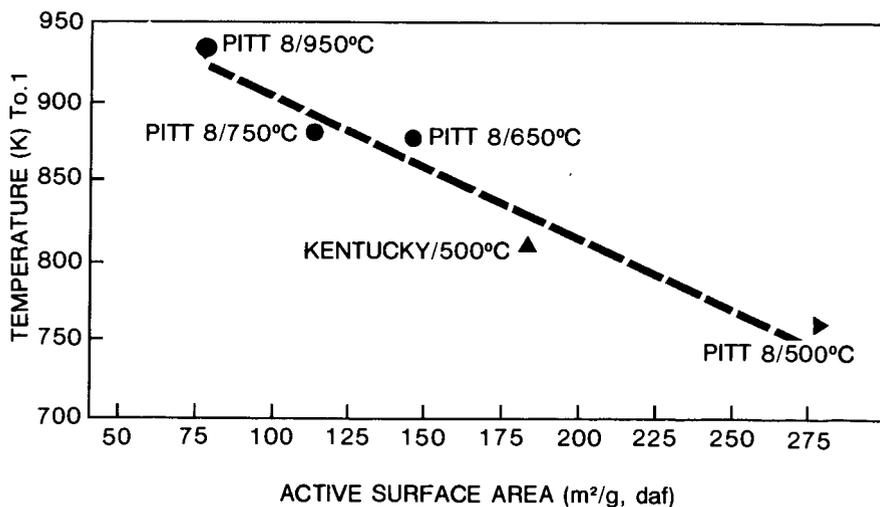


FIGURE 7. Correlation Between Nonisothermal Reactivity Parameter (i.e., Temperature) with the Char Active Surface Area as Determined by Oxygen Chemisorption. To.1 signifies temperature at which 10 percent conversion occurred when char was heated nonisothermally at 100°C/min in air.