

TEMPERATURE-PROGRAMMED DESORPTION STUDIES OF COAL CHAR GASIFICATION

Anthony A. Lizzio and Ljubisa R. Radovic
Department of Materials Science and Engineering
Fuel Science Program
The Pennsylvania State University
University Park, PA 16802

INTRODUCTION

In recent years, it has become increasingly clear that the understanding of char gasification kinetics requires more detailed information about the nature of the surface intermediates (carbon-oxygen complexes) formed during reaction. The first step in char (carbon) gasification is the dissociative chemisorption of reactant gas molecules (O_2 , CO_2 , H_2O) on the active sites of carbon, located at the edges of, and imperfections within, the turbostratic carbon crystallites [1]. A distribution of activities is known to exist among these carbon active sites [2,3]; some sites are more active than others. The sites which are important for predicting gasification rates are thought to be the ones that have intermediate activity, i.e., the ones that are sufficiently active to chemisorb dissociatively the reactant gas, but not to the extent that a stable C-O complex is formed [4,5]. Temperature-programmed desorption (TPD), an experimental technique widely used in the field of heterogeneous catalysis [6] and recently applied in coal char gasification studies [7-10], may be used to discern the nature of this distribution. TPD spectra provide useful information not only on the extent [11,12] but also on the energetics of desorption of C-O complexes from the char surface. In order to gain new insights into char gasification kinetics, it should prove beneficial to analyze TPD spectra, both qualitatively and quantitatively, with respect to factors which are known to significantly influence rates of gasification, e.g., nature of reactant gas, level of conversion (or extent of reaction), and the presence of inorganic impurities. The main objective of this study is to characterize the energetic heterogeneity of surfaces of coal chars, and carbons in general, and to relate it to their observed catalyzed and uncatalyzed gasification behavior in O_2 and CO_2 .

EXPERIMENTAL

The coals used in this study include a high volatile A Illinois #6 bituminous coal (PSOC 1098) and a North Dakota lignite (PSOC 246) [13]. Demineralized coal samples (Dem) were obtained by washing the raw coal with HCl and HF; essentially all the inorganic constituents were removed. The demineralized lignite was subsequently ion-exchanged with Ca^{+2} (designated as PSOC 246 Dem Ca sample) using a 1.5 M solution of calcium acetate [4]. All coal chars were prepared under identical pyrolysis conditions (900 °C, 10 °C/min, 0.5 h). A polymer-derived carbon, Saran char [4], and a graphitized carbon black, Graphon [3], both extensively studied in the literature, were also used.

Temperature-programmed desorption experiments were carried out in a flow-thru, fixed-bed reactor system. A quadrupole mass spectrometer (Dycor, model M100) was used to continuously monitor the evolution of CO , CO_2 , H_2O , H_2 and O_2 . Direct sampling of the effluent stream from a quartz reactor, operated at atmospheric pressure, was done through a 50 μm ID capillary tube. The partial pressure data were collected by an IBM PC and stored in a Lotus 1-2-3 worksheet for future analyses. A typical TPD experiment began with *in situ* partial gasification of the char in 1 atm air or 1 atm CO_2 . Relatively low reaction temperatures were chosen to ensure uniform, kinetically controlled rates (typically, 0.01-0.05 h^{-1}). After reaching the desired conversion, the sample (200-400 mg) was cooled in the reactant gas to a temperature at which no significant gasification occurred, e.g., 120 °C.

The reactant gas was flushed from the system with high-purity argon (99.9995%). Once the concentrations of O₂, CO and CO₂ returned to baseline levels, the sample was heated in flowing argon (47 cm³/min) at a constant heating rate of 5 °C/min to a final temperature of 1000 °C. This temperature was held for 2 h, in most cases, to achieve complete desorption of CO and CO₂ from the char surface. After each TPD experiment, the mass spectrometer was calibrated to permit a quantitative analysis of the partial pressure data. All TPD spectra were expressed per unit weight of carbon (200 mg) to allow direct comparison of peak heights.

RESULTS

Typical TPD spectra are shown in Figure 1. In all figures, the units on the ordinate and the abscissa are ppm and °C, respectively. In all figures and Table 1, the samples are designated by their name, reactant gas used, gasification temperature (°C), and level of conversion (X_C) achieved. The parameters obtained by analyzing the TPD spectra include the absolute amount of oxygen adsorbed on the char surface (wt % O), the relative amounts of CO and CO₂ evolved, given as the CO/CO₂ ratio, and the CO and CO₂ peak temperature(s), T_{pCO} and T_{pCO2} (°C). Table 1 lists the values of these parameters for all the TPD spectra referred to in this paper.

Effect of Reactant Gas. Figure 2 and Table 1 show that significantly more C-O complexes are formed during gasification in air than in CO₂. Table 1 also shows that the chars in Figure 2 adsorbed about the same amount of oxygen after partial gasification in air; however, significant differences in the amount of adsorbed oxygen are observed after partial gasification in CO₂. In comparison with gasification in air, peak temperatures are seen to increase by about 300 °C after partial gasification of the PSOC 1098 and Saran chars in CO₂; on the other hand, T_{pCO} and T_{pCO2} do not change as much for the PSOC 246 Dem Ca char. It is interesting to note that the amount of CO₂ evolved from the PSOC 1098 and Saran chars after partial gasification in CO₂ (see Figures 2b,d) is significantly smaller than that evolved from the PSOC 246 Dem Ca char (see Figure 2f).

Effect of Conversion Level. Figures 3 and 4 show the TPD spectra for the three chars reacted in air and CO₂, respectively, to three levels of conversion. In all cases the amount of adsorbed oxygen increases with conversion (see Table 1 and Figure 5). In addition, Table 1 shows that the CO/CO₂ ratio decreases monotonically with conversion in air, particularly for the PSOC 1098 and Saran chars.

Effect of Inorganics. Figure 6 shows the effect of mineral matter on the TPD spectra of the partially gasified bituminous coal char. It is seen that some of the peaks disappear upon demineralization and can thus be assigned to the presence of inorganics in the chars. For comparison, Figure 7 shows the TPD spectra of partially gasified Graphon and Saran char. Both are known to be essentially free from the catalytic effects of inorganic impurities. Figure 8 shows the effect of inorganics (i.e., discrete minerals as well as cations, and Ca in particular) on the TPD spectra of the partially gasified lignite char.

DISCUSSION

Before interpreting the TPD spectra in terms of the extent of adsorption on, and energetics of desorption from, the char surface, experimental artifacts and possible complicating effects (such as mass transport limitations and secondary reactions) need to be considered. It should be noted that a mass 28 fragment of CO₂ (about 5% of the mass 44 signal) was always produced in the mass spectrometer. The TPD spectra shown in this paper were not corrected for this. Therefore, extraneous peaks appear in CO evolution profiles when the concentration of CO₂ is very large (e.g., see Figures 1a and 3b,c,i). In addition, the frequent appearance of a small shoulder in the CO spectra of coal chars at 1000 °C is an experimental artifact due to the rather abrupt halt in the temperature rise upon reaching

the final desorption temperature. The possibility of interparticle diffusional limitations was investigated by varying the sample size (100-1500 mg) and the carrier gas flow rate (10-100 cm³/min); peak temperatures for CO and CO₂ evolution varied by no more than 10 °C. The possibility of intraparticle diffusional effects and/or secondary reactions of desorbed species was not tested directly. However, Otake [14] has shown that a heating rate of 5 °C/min is satisfactory for resolving the CO and CO₂ desorption peaks in a TPD spectrum of a microporous char. In addition, he provided evidence that the rates of CO and CO₂ desorption were governed solely by the decomposition of C-O complexes on the surface and not also by secondary reactions involving the desorbed species. Hall et al. [10] have recently interpreted the observed effect of heating rate variations (20-300 °C/min) on the relative amounts of CO and CO₂ desorbed from some coal chars in terms of secondary reactions of desorbed species. One of their arguments favoring this interpretation is the decreasing CO/CO₂ ratio with increasing conversion of a subbituminous coal char in air. An alternative interpretation of this behavior, also observed in our study (see Figure 3 and Table 1) and elsewhere [15], is that the probability of formation of CO₂, through interaction of adjacent and/or mobile C-O complexes, increases with increasing surface coverage. Furthermore, at our relatively low heating rate, the concentration of CO in the pores should be sufficiently low to prevent significant occurrence of secondary reactions. The TPD spectra obtained in this investigation are thus considered to be representative of the original state of C-O complexes on the char surface.

Char Reactivity and TPD Spectra. It is well known that the low-temperature oxygen chemisorption capacity of an unreacted char is a good index of its gasification reactivity, particularly for the purpose of comparing chars whose reactivities differ by more than a factor of 2-3 [4]. However, this concept has failed to explain the gasification behavior of partially reacted chars [5,15]. A quantitative interpretation of reactivity profiles, i.e., of variations in rate with conversion for a given char, was recently concluded to require not only the knowledge of the extent of chemisorption of oxygen but also an understanding of the energetic heterogeneity of the char surface [5,16]. It should be realized that the total amount of C-O complex evolved in a TPD experiment includes the "stable" complex as well as the reactive surface intermediate [17]. The concept of "stable complex" as an inhibitor of carbon gasification, shown to be valid at low pressures [18], is an oversimplification when applied to gasification at higher pressures [19-21]. In fact, the monotonic increases in the amount of oxygen adsorbed with conversion, well substantiated here and elsewhere [15, 21-23], correlate well with the often observed increasing specific gasification rate with conversion [16,17,24]. This correlation is thought to be the result of the fact that some C-O complexes are reaction intermediates. It can also be interpreted as a result of (a) a decrease in the desorption activation energy with increasing surface coverage [14,20], (b) an "activating" effect of the complex on the surrounding carbon atoms [21], or (c) the increase in the ratio of edge (active or reactive) carbon atoms to basal-plus-edge (total number of) carbon atoms in the turbostratic structure of the char as gasification proceeds [16]. Ultimately, however, reactivity profiles are probably best understood by measuring directly the reactive surface area of the chars [16,24].

In this study, an attempt was also made to correlate the reactivity of each char with the amount of oxygen adsorbed during gasification. Figures 2a,c,e and Table 1 show that, even though the three chars have vastly different reactivities in air (the catalyzed reaction of PSOC 246 Dem Ca being the fastest and the uncatalyzed reaction of Saran char being the slowest [4]), these differences cannot be explained using the total amount of C-O complexes formed during gasification (the majority of which is known to be the "stable" complex). Figures 2b,d,f and Table 1 show that a better qualitative correlation exists between the total amount of C-O complex and reactivity for these chars partially gasified in CO₂; similar results were obtained by Kyotani et al. [8] for various coal chars gasified in steam. It is interesting to note [18] that as much as 85% of the total C-O complex formed on the surface of Saran char after partial gasification in CO₂ is the reactive surface intermediate.

A comparison of TPD spectra obtained after partial gasification in air, at relatively low temperatures, and in CO₂, at higher temperatures, is also useful (see Figure 2). After partial gasification in CO₂,

only relatively stable C-O species, which decompose above 700 °C and yield predominantly CO, remain on the surface, in agreement with the findings of Keleman and Freund [25] for a glassy carbon. The fact that greater amounts of oxygen on the surface are observed after gasification in air is consistent with the view that the C-O₂ reaction is much faster than the C-CO₂ reaction because of a more facile dissociation step [26]. Ahmed and Back [22] have observed a decrease in the amount of surface oxygen with increasing temperature after partial gasification (and subsequent low-temperature oxygen chemisorption) in the same gas (O₂); they have attributed this to a "minor variation in the procedure for preparation" of their carbon films. In fact, having in mind that low-temperature oxygen chemisorption provides little additional surface coverage for chars previously gasified in O₂ [5], this effect is indeed expected [27].

Catalysis and TPD Spectra. A comparison of the TPD spectra of the as-received bituminous and lignite chars, together with those of the relatively pure carbon materials (chars prepared from the demineralized coals, Saran char and Graphon), may provide useful information about the effect of inorganics on the energetic heterogeneity of coal char surfaces.

The amount of oxygen adsorbed on partially oxidized Graphon is about an order of magnitude lower and T_{pCO} and T_{pCO₂} are about 100 °C higher than for the much more reactive Saran char (see Figures 7a,b and Table 1). The significantly smaller CO/CO₂ ratio for Saran char (see Table 1) is attributed to the fact that a relatively larger portion of its total surface is covered with C-O complexes, thus favoring CO₂ formation. From Figures 6a,b, the appearance of a clearly resolved high-temperature peak in the CO desorption spectrum and a low-temperature peak in the CO₂ desorption spectrum of the as-received bituminous coal char is seen to be due to the presence of inorganics, even though they have no catalytic effect [28] (see also Figures 1a, 2a, 3a-c). Hall et al. [10] recently observed similar behavior for a subbituminous coal char reacted in O₂, but attribute it to the "catalytic effect of the mineral matter." It is interesting to note the remarkable similarities in the TPD spectra of the demineralized bituminous coal char, Saran char and Graphon (see Figures 6b and 7).

The relatively high gasification reactivity of lignite chars compared to those obtained from higher-rank coals has been attributed to the catalytic effect of highly dispersed CaO on the char surface [29]. Figures 8a-c suggest that the catalytic effect of CaO in air cannot be clearly detected in TPD spectra. Demineralization of the lignite and subsequent Ca⁺² exchange result in no significant difference in the CO and CO₂ desorption spectra or the amounts of oxygen on the surface. Figure 3 shows, however, differences in the evolution of CO and CO₂ spectra with increasing conversion for the catalyzed (3g-i) vs. the noncatalyzed (3a-c and 3d-f) reaction.

Figures 8d-f show quite a different situation for the lignite char gasified in CO₂. The CO desorption spectrum of the demineralized sample (see Figure 8e) exhibits only one peak, typically found in spectra of uncatalyzed chars (see Figures 2b,d, 4a-c). Two CO peaks are observed for the Ca-exchanged sample (see Figure 8f), in agreement with the results of Kapteijn et al. [30]. It is tempting to attribute the lower-temperature peak to the interaction of the adsorbed oxygen with the catalytic sites and the higher-temperature peak to its interaction with the carbon active sites [30]. A very sharp intermediate CO peak appears in the spectrum of the as-received lignite char (see Figure 8d); it may be tentatively attributed to a catalytic species other than Ca, e.g., Na or K [8]. The sharp CO₂ peak (see also Figures 2f, 4g-i), not observed after partial gasification of uncatalyzed chars in CO₂, is attributed to the decomposition of CaCO₃ [8].

SUMMARY AND CONCLUSIONS

Temperature-programmed desorption was used to determine the extent and energetics of desorption of carbon-oxygen complexes from coal char surfaces; an attempt was made to relate this to their observed gasification behavior. The potential usefulness of this technique stems from the fact that

stable complex formation is considered to be not only an inhibiting process but also an intermediate step in the mechanism of carbon gasification. Very significant differences in the extent of oxygen adsorption and the CO and CO₂ desorption spectra were found depending on the reactant gas used, level of conversion achieved and the presence of inorganic impurities. In general, a better qualitative correlation between the extent of oxygen adsorption and the kinetics of both catalyzed and uncatalyzed gasification was observed after partial gasification in CO₂. The establishment of better quantitative correlations is being sought by further analysis and possible deconvolution of the TPD spectra.

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Table 1
Quantitative Analysis of TPD Spectra

Fig.	Char, Gas, °C, X _C	wt% O	CO/CO ₂	Tp _{CO}	Tp _{CO₂}
1a	PSOC 1098, O ₂ , 350, 0.75	30.7	1.9	640,830	520,680
1b	Saran, O ₂ , 388, 0.72	25.3	3.1	640	560
2a	PSOC 1098, O ₂ , 350, 0.20	13.8	2.4	670,820	490,650
2b	PSOC 1098, CO ₂ , 865, 0.20	2.8	9.6	910	640,810
2c	Saran, O ₂ , 388, 0.20	12.9	5.9	640	540
2d	Saran, CO ₂ , 860, 0.20	0.3	—	910	—
2e	PSOC 246 Dem Ca, O ₂ , 315, 0.20	14.4	2.0	730	460,600
2f	PSOC 246 Dem Ca, CO ₂ , 680, 0.20	7.6	3.1	720	700
3a	PSOC 1098, O ₂ , 350, 0.06	8.9	2.8	830	480,650
3b	PSOC 1098, O ₂ , 350, 0.54	23.8	2.4	640,840	500,670
3c	PSOC 1098, O ₂ , 350, 0.93	37.0	1.0	620,810	510
3d	Saran, O ₂ , 388, 0.05	5.5	7.0	660,810	530
3e	Saran, O ₂ , 388, 0.38	20.5	4.8	640	540
3f	Saran, O ₂ , 388, 0.90	26.8	2.8	630	590
3g	PSOC 246 Dem Ca, O ₂ , 315, 0.05	9.1	2.0	810	480,610
3h	PSOC 246 Dem Ca, O ₂ , 315, 0.50	20.1	2.0	710	540,650
3i	PSOC 246 Dem Ca, O ₂ , 315, 0.85	41.2	1.5	700	580,690
4a	PSOC 1098, CO ₂ , 865, 0.13	2.0	9.1	880	610,790
4b	PSOC 1098, CO ₂ , 865, 0.42	4.7	17.7	920	630,820
4c	PSOC 1098, CO ₂ , 865, 0.73	8.2	16.3	950	680,850
4d	Saran, CO ₂ , 860, 0.13	0.3	—	890	—
4e	Saran, CO ₂ , 860, 0.47	0.4	—	910	—
4f	Saran, CO ₂ , 860, 0.85	0.9	—	900	—
4g	PSOC 246 Dem Ca, CO ₂ , 680, 0.05	5.6	3.3	770	680
4h	PSOC 246 Dem Ca, CO ₂ , 680, 0.40	10.4	2.7	730,870	730
4i	PSOC 246 Dem Ca, CO ₂ , 680, 0.72	15.5	1.7	770,890	760
6a	PSOC 1098, O ₂ , 350, 0.30	17.8	2.4	640,850	490,660
6b	PSOC 1098 Dem, O ₂ , 350, 0.33	15.6	4.6	640	480,640
7a	Graphon, O ₂ , 580, 0.82	1.3	13.3	720	640
7b	Saran, O ₂ , 388, 0.26	13.5	5.2	640	530
8a	PSOC 246, O ₂ , 315, 0.33	13.3	2.0	720,800	610
8b	PSOC 246 Dem, O ₂ , 315, 0.37	16.5	2.5	750	460,610
8c	PSOC 246 Dem Ca, O ₂ , 315, 0.35	17.1	2.3	720	490,630
8d	PSOC 246, CO ₂ , 680, 0.42	8.8	2.3	720,770,850	720
8e	PSOC 246 Dem, CO ₂ , 680, 0.36	6.4	4.4	860,	860 670
8f	PSOC 246 Dem Ca, CO ₂ , 680, 0.40	10.4	2.7	730,	870 730

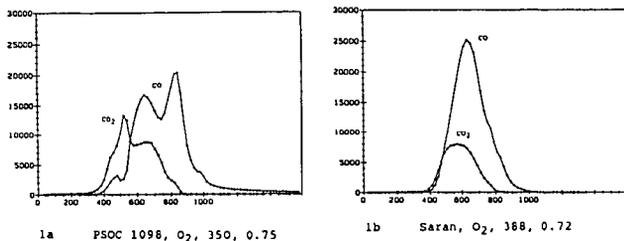


Figure 1. Typical TPD Profiles for the Bituminous Coal Char and Saran Char Reacted in 1 atm Air.

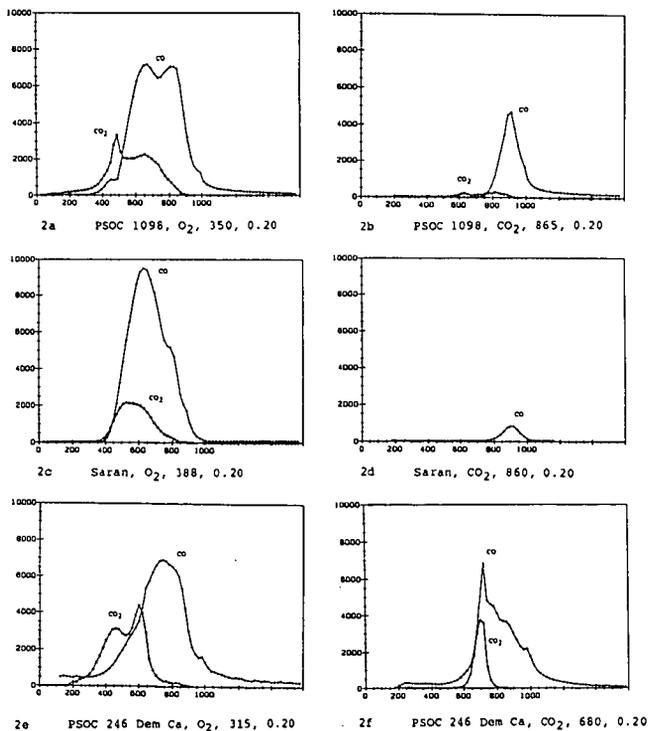


Figure 2. Effect of Reactant Gas on TPD Profiles of Chars Reacted in 1 atm Air and 1 atm CO₂ to 20% Conversion.

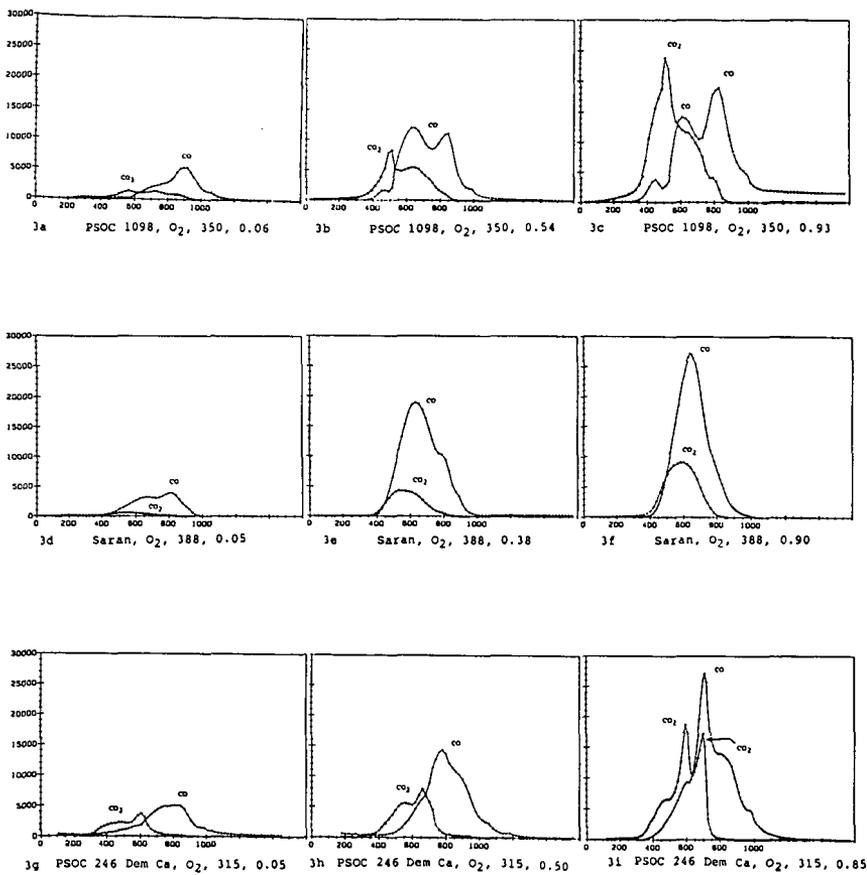


Figure 3. Effect of Conversion Level on TPD Profiles of Chars Reacted in 1 atm Air.

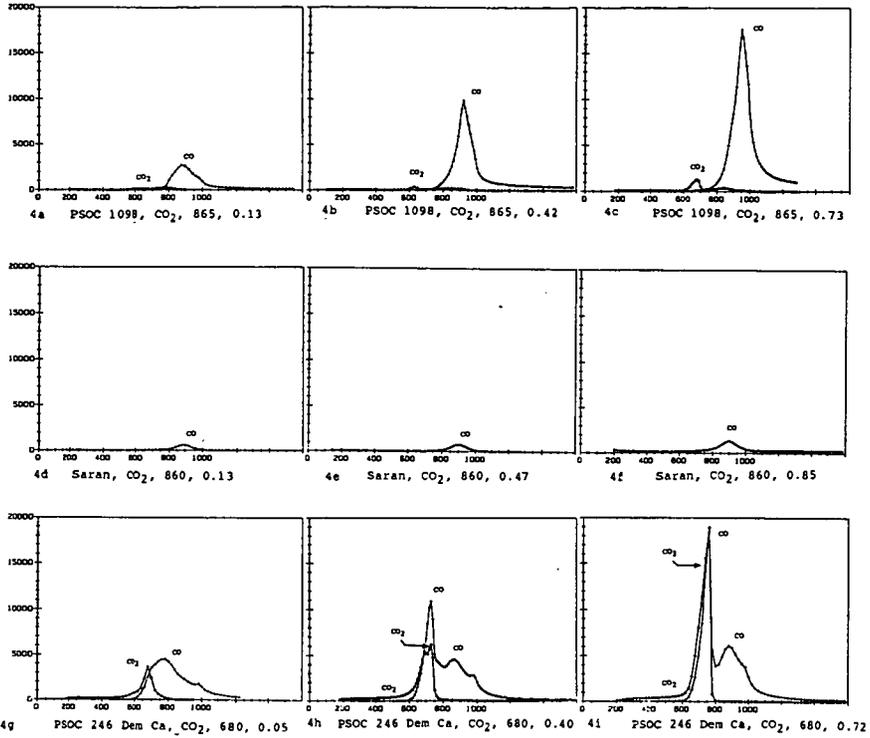


Figure 4. Effect of Conversion Level on TPD Profiles of Chars Gasified in 1 atm CO_2 .

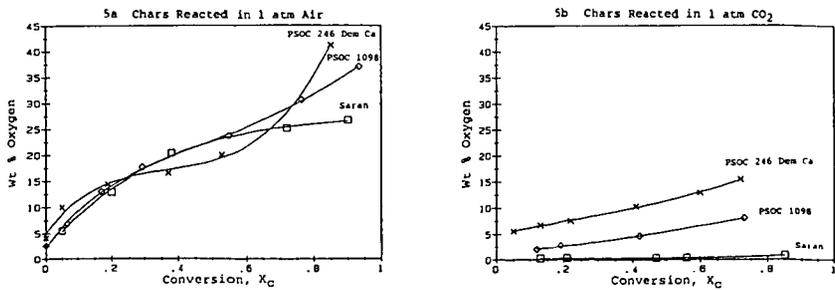


Figure 5. Effect of Reactant Gas and Conversion Level on Oxygen Uptake by Chars Partially Gasified in 1 atm Air and 1 atm CO_2 .

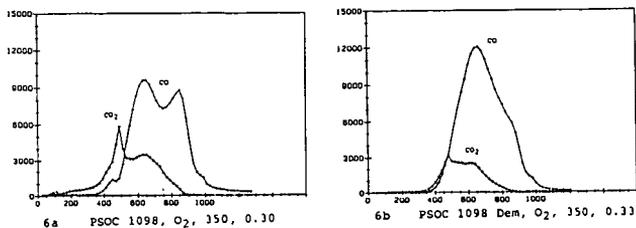


Figure 6. Effect of Mineral Matter on TPD Profiles of the Bituminous Coal Char Reacted in 1 atm Air.

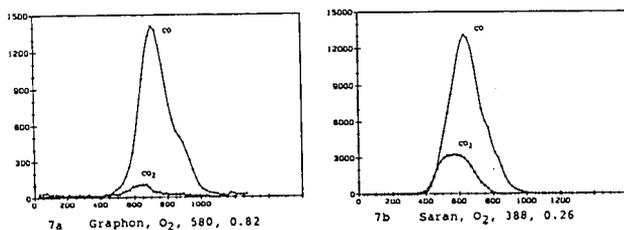


Figure 7. Representative TPD Profiles For Uncatalyzed Chars Reacted in 1 atm Air.

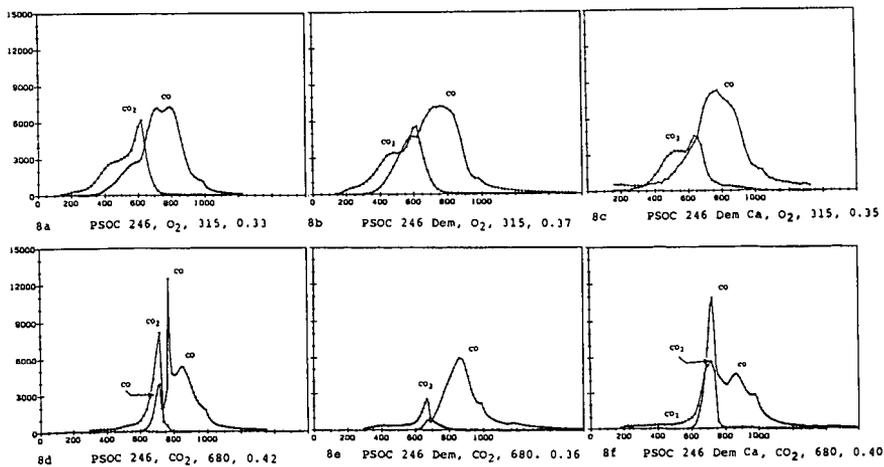


Figure 8. Effect of Mineral Matter and Calcium on TPD Profiles of A Lignite Char Reacted in 1 atm Air and 1 atm CO₂.