

Microstructural Variations of Three American Coals and Their High Temperature Chars

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Microstructure of a North Dakota lignite, a Washington subbituminous and a New Mexico bituminous coal and their chars produced by devolatilization in nitrogen at 1000 to 1300°C was investigated in this work using the CO₂ adsorption method conducted at 25°C. For each coal and char, specific surface area, micropore volume, micropore surface area, mean equivalent radius of micropores and characteristic energy of adsorption, as well as micropore volume distribution, were determined and tabulated, and their variations with devolatilization temperature studied and interpreted. It was found that, overall, specific surface areas, micropore volumes and micropore surface areas of chars decreased monotonically as devolatilization temperature was raised from 1000 to 1300°C, although most of these values were much larger than that of their parent coals. The micropore volume distributions obtained were interpreted and found to provide an interesting insight into the microstructural variations of coals and chars.

Introduction

It is well known that coals and their chars possess a complex intraparticle pore structure, similar to the structure of a tree [1], with micropores (4-12Å) expanding gradually into mesopores (12-300Å) and eventually macropores (>300Å) [2]. For most coals and chars, surface areas and thus active sites for gasification are provided mainly by micropores, although mesopores and macropores are also needed to serve as feeder pores for transportation of reactant molecules to the micropores. Depending on the gasification condition and other factors, the intraparticle diffusional resistance caused by this complicate pore structure may become rate limiting. Hence the reactivity of coals and their chars during gasification is closely related to their microstructures.

Changes in surface areas of coals during devolatilization have been investigated by several research workers [3-5]. They observed that specific surface area increased with increasing devolatilization temperature, passed through a maximum at about 600-700°C and decreased thereafter. However, the heating rates involved were less than 20°C/min, which were too slow to be of practical use for commercial gasifiers, particularly the entrained flow type.

In the present work, specific surface area, micropore volume distribution and other microstructural parameters of three American coals of different rank and their chars were determined. The chars were prepared by devolatilization in a nitrogen atmosphere at 1000-1300°C. The heating rates involved were over 100°C/sec. The effects of devolatilization temperature on the microstructure of coals and chars were studied and the results reported and interpreted.

Experimental

Three coals obtained from the Penn State Coal Sample Bank were used in this work. They are lignite (PSOC-1423P) from North Dakota (Hagel seam), subbituminous coal (PSOC-240) from Washington (Big Dirty seam) and high volatile C bituminous coal (PSOC-309) from New Mexico (#8 seam). The proximate and ultimate analyses of these coals are given in Table I.

A thermogravimetric analyzer (TGA), developed by Sears et al. [6] and further improved by Peng et al. [7], was used to prepare chars at atmospheric pressure and four different devolatilization temperatures, viz., 1000 to 1300°C at intervals of 100°C. The particle size range used in this study was -70 + 100 U.S. mesh (average particle size 177.5 μm). Devolatilization was carried out in nitrogen environment at the desired temperature for one minute. The chars thus obtained are called "N₂ chars" to distinguish them from the "in-situ chars" [7] obtained by devolatilization in steam. Work associated with the in-situ chars will be reported elsewhere.

One of the unique features of this TGA is that the micromotor located inside the TGA is capable of lowering the sample from less than 1500°C to extreme high temperature (up to 1700°C) in less than 10 seconds. The heating rates of the coal particles were in the range of 100 to 1000°C/sec depending on the operating conditions and the samples used [6]. All the chars produced were immediately put into air-tight vials and stored in nitrogen environment. Experiments under various operating conditions were repeated several times to check reproducibility of data. In all the cases tested the experimental errors were within $\pm 10\%$, most being within $\pm 2\%$.

Microstructural properties of the three coals and their high temperature chars were determined by gravimetric adsorption method using CO₂ as an adsorbate. Char samples produced in the TGA were used without further classification by their particle sizes, although they were outgassed overnight at 110°C and 10⁻³ torr to remove moisture which might otherwise block entrances to some micropores.

The apparatus for measuring CO₂ adsorption gravimetrically consisted of a Cahn R-100 electronic microbalance, a mechanical vacuum pump, a U-tube manometer and two pressure detectors. For each series of adsorption runs, the system was maintained at 25°C and at preselected pressures ranging from 60-700 torr. At each CO₂ pressure, the weight-gain curve of the sample was continuously recorded in a strip-chart recorder until adsorption equilibrium was reached. For each run, the time required to reach equilibrium varied, depending on the type of coal involved. For the lignite and its chars, 8-10 hours were normally needed. On the other hand, it took about 24 hours for the subbituminous coal but only 2-3 hours for its chars to reach equilibrium. For the bituminous coal, the times needed were only 4-5 hours for coal but about 24 hours for chars.

Specific surface areas were determined by means of the Dubinin-Polanyi (D-P) equation [8-10]:

$$\ln W = \ln W_0 - D \ln^n(P/P_0) \quad (1)$$

where W is the weight of CO_2 adsorbed per unit weight of sample at pressure P . P_0 is the vapor pressure of CO_2 , whose value is 63.5 atm at 25°C [10], and the corresponding W is designated as W_0 . D and n are constants determined from experimental data. For most of the cases, n is equal to 2.0. The molecular cross-sectional area of CO_2 at 25°C was taken as $25.3 (\text{\AA})^2$ [10]. The relative pressure employed in all measurements was less than 0.015 to avoid capillary condensation [11]. Properties related to micropore, such as micropore surface area, mean micropore volume, mean equivalent radius of micropore and adsorption characteristic energy [12], as well as micropore volume distribution, were calculated by the Medek's method [12].

Results and Discussion

The data obtained from the gravimetric adsorption experiments for the three coals used in this work and their high temperature chars are presented as adsorption isotherms in Figures 1-3, and as linear plots of Equation (1) with $n = 2$ in Figures 4-6. All the data shown in Figures 4-6 fall on straight lines with correlation coefficients of each linear least squares fit greater than 0.99, thus reassuring the suitability of using the D-P equation for CO_2 adsorption on these coals and chars at 25°C and the choice of $n = 2$ [10,12].

The effect of devolatilization temperature on the intraparticle structure of coals and chars is vividly demonstrated by the equilibrium isotherms presented in Figures 1-3. For each coal, as the devolatilization temperature is raised from 1000°C to 1300°C , the amount of CO_2 adsorbed per gram of char decreases monotonically. Furthermore, with the exception of chars produced from the caking coal (PSOC-309, bituminous) at temperatures above 1200°C , all the other chars exhibit significantly higher capability to adsorb CO_2 than their parent coals.

Shown in Tables 2-4 are specific surface areas, micropore surface areas, micropore volumes and mean equivalent radii of micropores of coals and chars calculated from the data presented in Figures 1-6 using the methods mentioned in the previous section. For each char, extent of devolatilization expressed in terms of percentage of coal (DAF basis) devolatilized was also included in the tables. Micropore volume distributions of the three coals and their chars were also calculated and plotted in Figures 7-9. For convenience of comparison, some of the data given in Tables 2-4 are also plotted in Figure 10.

The plots in Figure 10 clearly illustrate that, for each coal, the specific surface area of the char obtained by devolatilization at 1000°C is larger than that of its parent coal; whereas the opposite is true for the mean equivalent radius of the micropores. This will be explained later. Furthermore, as the devolatilization temperature is raised from 1000°C to 1300°C , the overall trend for each coal appears to be that of a reduction in specific surface area and an enlargement of micropore size. The only exception is the reduction of pore size for chars prepared from the caking coal (PSOC-309 bituminous) at 1300°C . As expected, extent of devolatilization of each coal increases with increasing devolatilization temperature. The adsorption characteristic energy of micropores, on the other hand, shows little variation, being in the range of 9-13 KJ/g-mole for the chars and coals tested.

A close examination of the data on specific surface area, micropore volume and micropore surface area of chars reveals a striking similarity in their dependence on devolatilization temperature. This is true for all the three coals used in this work. This similarity is obviously related to our observation mentioned before on adsorption isotherm and extent of devolatilization.

Briefly speaking, coals are composed of aromatic and hydroaromatic layers terminated at their edges by various functional groups. Different functional groups are cross-linked to each other, causing poor alignment between layers and creating micropores of molecular dimensions. Some of them are closed, while most are open to mesopores and macropores, leading to a pore-tree structure. When coals are heated in an inert atmosphere, volatile matter is released, dead pores open up and the previously open pores enlarge in size, all leading to increased pore volume and surface area. Concurrent with these, some crosslinks between aromatic layers are broken, thus allowing them to align in a more orderly fashion and resulting in a loss of pore volume and surface area.

In general, at lower devolatilization temperature, the release of volatiles predominates; while at higher temperature, structure alignment becomes dominant, as the volatile release becomes small. Hence, it is expected that over a certain temperature range, the pore volume and surface area of coal chars will go through a maximum. The temperature at which the maximum occurs depends mainly on the parent coals [13]. As mentioned before, according to a number of studies conducted by several researchers [3-4] over a temperature range of 200 to 1200°C, the maximum usually falls around 600-700°C. Since the range of devolatilization temperature in this work is well above 600-700°C, our observation of decreasing specific surface area and micropore volume with increasing devolatilization temperature is thus consistent with those reported previously.

The changes in micropore volume distributions during the course of devolatilization should reflect the major changes in the porosity of coals and chars, because most of their pore volumes are contributed by micropores. Therefore, it is worthwhile to examine more closely the micropore volume distribution frequency curves presented in Figures 7-9. It is obvious that the area under each curve represents total micropore volume per gram of sample, whose dependence on devolatilization temperature, as mentioned before, is similar to that of specific surface area.

The significant increase in micropore volume from coal to char devolatilized at 1000°C is clearly demonstrated by comparing the corresponding distribution curves shown in Figures 7-9. For all the three coals involved, the curves for chars are much higher and wider, suggesting the creation of new micropores, the enlargement of open pores and the opening up of previously closed pores. Of particular interest are the extensions of the curves for the 1000°C chars beyond the lower limit of the curves for coals and their steep ascents in that region of extremely fine pores. The former implies the generation of new, extremely small micropores, and both together account for the reason why the 1000°C chars have smaller mean radii.

As devolatilization temperature increases from 1000 to 1300°C, the general trend is the reduction of the micropore volume of chars produced.

Although this holds for all the three coals involved, the behavior of the bituminous coal, a caking coal, is strikingly different from that of the other two coals, as mentioned before. While the micropore volume of the bituminous coal chars reduces rapidly down to a value well below that of the original coal, the values of the micropore volumes of the lignite and the subbituminous coal chars stay within the range of 0.12-0.17 cm³/g, which is well above that of their parent coals (see Tables 2-4). Furthermore, for the latter two coals, most of the reduction in micropore volume is due to the decrease in the number of micropores at the lower end of the distribution as shown clearly in Figures 7 and 8; whereas for the bituminous coal chars the reduction appears to be quite uniform across the whole range of micropores. The reason for this difference is worthy of further exploration.

As strong caking coal, such as the bituminous coal used in this work, is heated, it invariably passes through a softening stage. During that period, parts of the coal substance decompose and produce metastable fluid material which acts as a plasticizer and softens the mass. This unstable material, known as metaplast [14,15], primary tar or thermobitumen [16], consists of mainly heavy hydrocarbons with high viscosity and tends to seal up the micropores. The liberation of volatile matter against the sealing up leads to an initial expansion of micropores and thus an increase in the micropore volume of the resultant char (semicoke). As the temperature rises further, the semicoke, the thermobitumen and the primary volatile products start to decompose and/or polymerize. These secondary reactions eventually resolidify the plastic mass causing shrinkage of pores as well as pore blockage. The latter is due to the production of cracked carbon which deposits on the entrance of the pores. The higher the temperature, the more cracked carbon is produced and deposited uniformly throughout the whole range of the micropores, thus leading to a micropore volume smaller than that of its parent coal.

As for weak caking coal, such as the subbituminous coal used here, the plastic range is not very noticeable and the production of thermobitumen may not be significant. Hence the cracked carbon produced, though not sufficient to cover the whole range of micropores, does manage to deposit first on a portion of the finer micropores leading to a gradual reduction of the number of ultrafine micropores (see Figure 8), as pyrolysis temperature increases to 1300°C. As a result, the micropore volumes of chars decrease, but their mean equivalent radii of micropores increase. This is exactly what the data in Table 3 indicate.

In summary, the microstructural data of the three coals and their high temperature chars have been presented in this paper. In addition, the characteristics of the data have also been investigated, particularly with respect to their relation with the devolatilization temperature, and the meaning of the data interpreted.

Acknowledgements

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Table 1. Characteristics of Coals Used

	N.D. Lignite (PSOC-1423P)	Wash. Subbituminous (PSOC-240)	N.M. Bituminous (PSOC-309)
Proximate Analysis (wt%, as received)			
Moisture	29.53	18.21	10.09
Ash	5.75	18.39	18.32
Volatile Matter	31.76	32.00	33.80
Fixed Carbon	32.96	31.40	37.79
Ultimate Analysis (wt%, DAF)			
Carbon	69.80	72.59	77.08
Hydrogen	4.41	5.79	5.75
Nitrogen	1.35	1.41	1.70
Sulfur	1.14	1.30	1.02
Chlorine	0.00	0.01	0.00
Oxygen (diff.)	23.30	18.90	14.46

Table 2. Microstructural Parameters of Lignite (PSOC-1423P) and Its Chars

Sample	Coal	Char	Char	Char	Char
Devolatilization Temperature (°C)	NA	1000	1100	1200	1300
% Devolatilization (DAF basis)	NA	53.5	61.7	69.1	71.7
Specific Surface Area (m ² /g)	238	511	498	434	468
Micropore Surface Area (m ² /g)	223	496	462	399	421
Micropore Volume (x10 ² cm ³ /g)	7.7	16.6	16.2	14.1	15.2
Mean Equivalent Radius of Micropore (nm)	0.69	0.67	0.70	0.71	0.72
Adsorption Characteristic Energy (KJ/g-mole)	11.9	13.1	11.5	11.2	10.5

Table 3. Microstructural Parameters of Subbituminous Coal (PSOC-240) and Its Chars

Sample	Coal	Char	Char	Char	Char
Devolatilization Temperature (°C)	NA	1000	1100	1200	1300
% Devolatilization (DAF basis)	NA	58.3	60.4	65.6	69.3
Specific Surface Area (m ² /g)	198	499	472	451	382
Micropore Surface Area (m ² /g)	181	470	445	415	341
Micropore Volume (x10 ² cm ³ /g)	6.4	16.2	15.3	14.7	12.4
Mean Equi. Radius of Micropore (nm)	0.71	0.69	0.69	0.71	0.73
Adsorption Characteristic Energy (KJ/g-mole)	11.0	12.0	12.1	11.2	10.2

Table 4. Microstructural Parameters of Bituminous Coal (PSOC-309) and Its Chars

Sample	Coal	Char	Char	Char	Char
Devolatilization Temperature (°C)	NA	1000	1100	1200	1300
% Devolatilization (DAF basis)	NA	46.3	53.4	52.3	59.0
Specific Surface Area (m ² /g)	117	401	304	109	21
Micropore Surface Area (m ² /g)	106	373	272	95	19
Micropore Volume (x10 ² cm ³ /g)	3.8	13.0	9.9	3.6	0.7
Mean Equi. Radius of Micropore (nm)	0.72	0.70	0.73	0.75	0.69
Adsorption Characteristic Energy (KJ/g-mole)	10.7	11.6	10.3	9.4	12.0

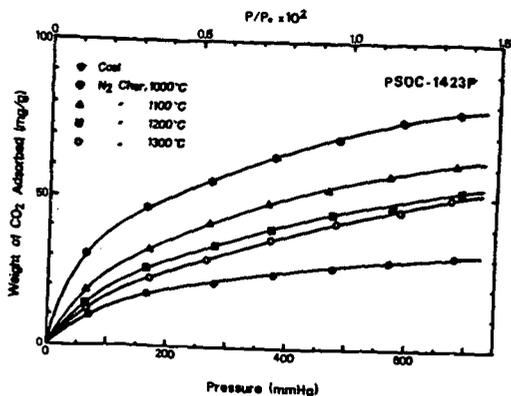


Figure 1. Isotherms of CO₂ Adsorption on Lignite (PSOC-1423P) and its chars at 25°C

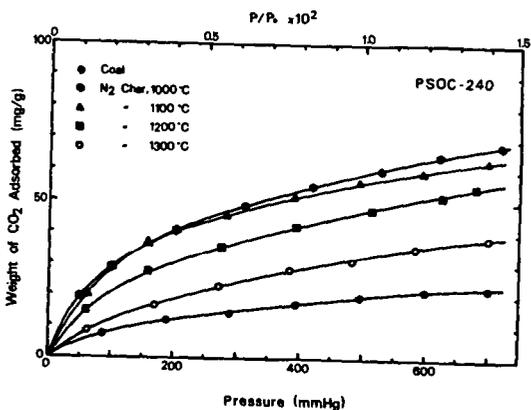


Figure 2. Isotherms of CO₂ Adsorption on Subbituminous coal (PSOC-240) and its Chars at 25°C

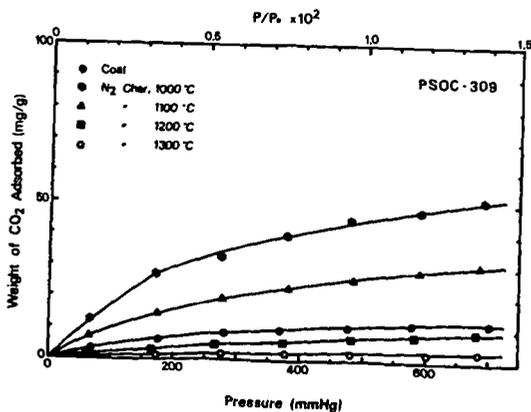


Figure 3. Isotherms of CO₂ Adsorption on Bituminous Coal (PSOC-309) and its Chars at 25°C

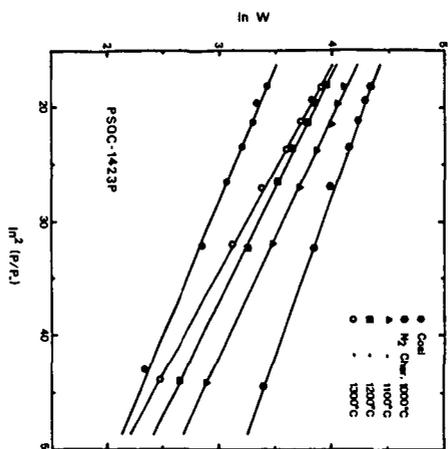


Figure 4. Linear Plots of the Isotherms from Figure 1 — Lignite

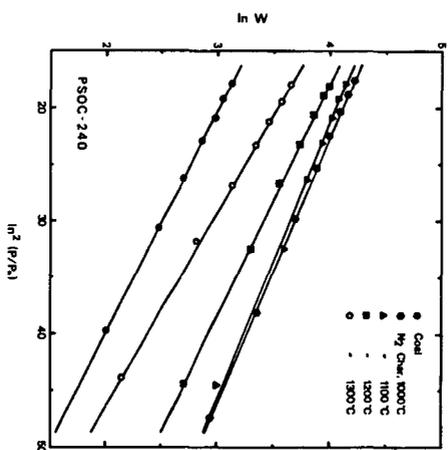


Figure 5. Linear Plots of the Isotherms from Figure 2 — Subbituminous Coal

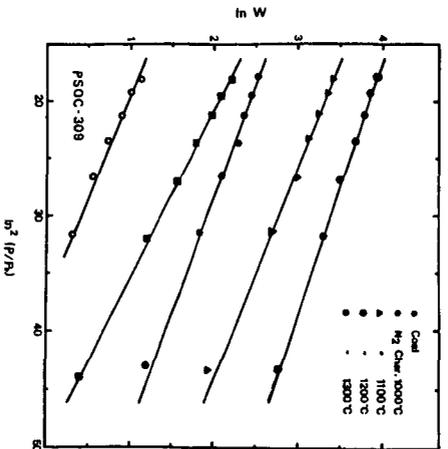


Figure 6. Linear Plots of the Isotherms from Figure 3 — Bituminous Coal

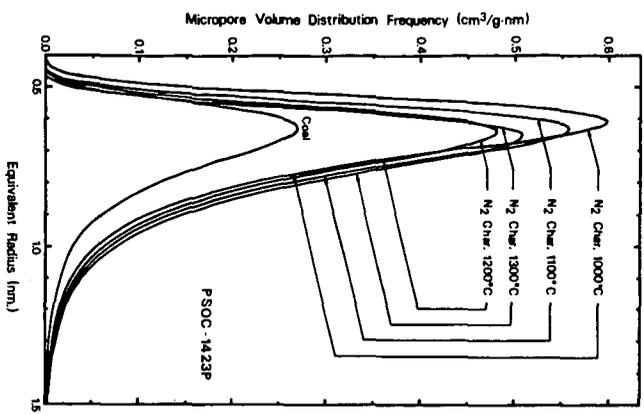


Figure 7. Micropore Volume Distributions of Lignite and Its Char.

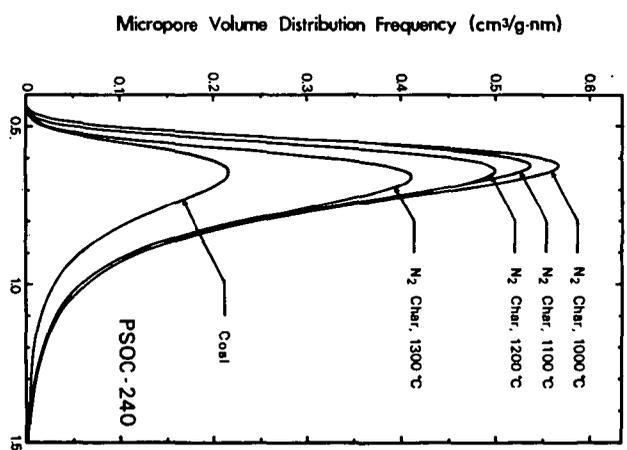


Figure 8. Micropore Volume Distributions of Substitutional Coal and Its Char.

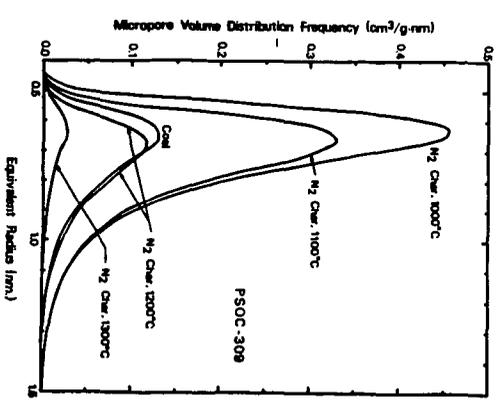


Figure 9. Micropore Volume Distributions of Substitutional Coal and Its Char.

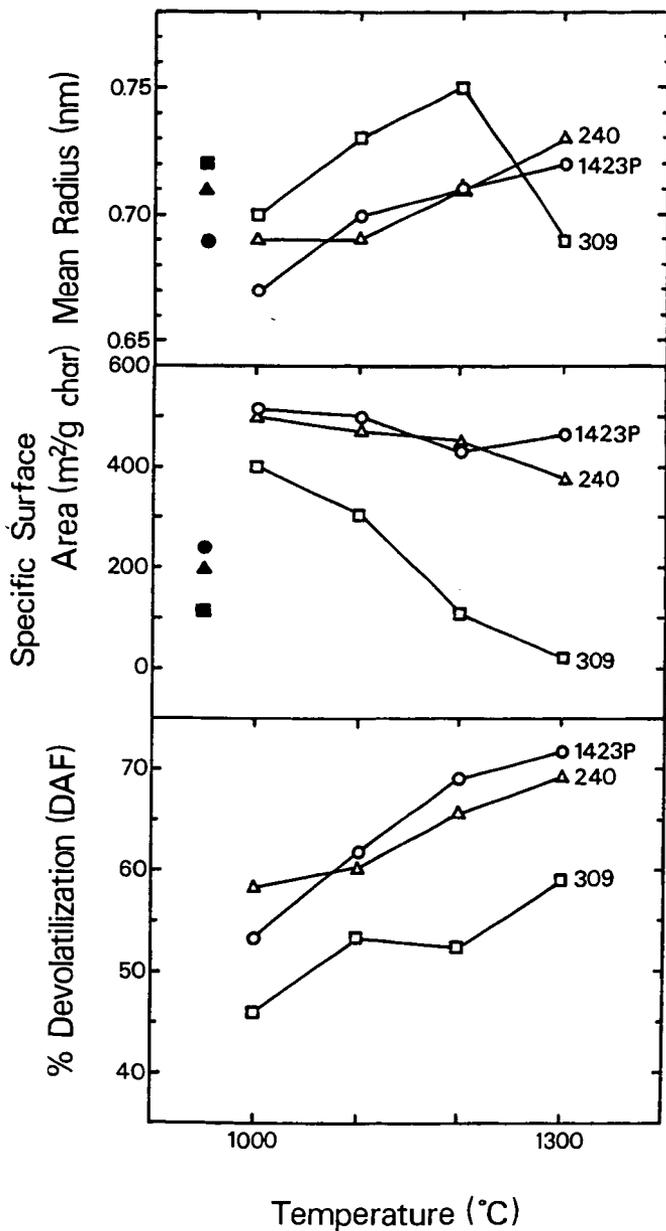


Figure 10. Effect of Devolatilization Temperature on the Microstructure of Coals and Chars (● Lignite; ○ Lignite Char; ▲ Subbituminous Coal; △ Subbituminous Coal Char; ■ Bituminous coal; □ Bituminous Coal Char)