

THE INFLUENCE OF CHAR STRUCTURE ON LOW TEMPERATURE COMBUSTION REACTIVITY

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INTRODUCTION

Coal char is a porous material with a structure which is intimately related to its combustion properties. In particular, the internal structure influences the degree of intraparticle diffusion limitations present at various temperatures. For fluid coals, the char structure is expected to depend on the extent of "reorganization" during the fluid stage, and should vary with the pyrolysis heating rate, the pyrolysis temperature and the holding time. On the other hand, coals which do not become fluid should produce chars with a structure similar to that of the original coal. It has been shown in a previous study¹ that the pyrolysis heating rate has an impact on the reactivity of fluid chars. Since reactivity was measured in the kinetic regime, this effect should not be related to the char physical structure, except for differences in internal surface area. However, the extent of rearrangement during the period when the char is fluid may well affect both the physical pore structure and the molecular order. The latter quantity will determine the active site concentration. In that previous study¹, the reactivity of low rank coals was found to be relatively independent of the time-temperature history, as long as the same degree of pyrolysis is reached. This is consistent with the fact that no important structure reorganization is expected to occur with these non-fluid coals.

The current study investigated the influence of the starting coal type (softening or non-softening) and of the char formation conditions on the onset of the pore diffusion regime. The reactivity of chars produced from fluid coals at different heating rates, and from non-fluid coals at low heating rate was measured isothermally with a TGA. Cumulative pore volumes and nitrogen surface areas were measured in order to be correlated with the behavior of the chars towards pore diffusion limitations.

The transition from zone I (kinetic regime) to zone II (combination of pore diffusion and kinetic regime) has been observed in a TGA apparatus by several researchers^{2,3,4,5}. The chars studied were, in all cases, produced at low heating rate, i.e., a few degrees per minute. Tseng and Edgar^{2,3} observed variations in the activation energy for lignite chars (from approximately 28 kcal/mol in the kinetic regime to 14 kcal/mol in the pore diffusion regime) and anthracite and bituminous coal chars (from about 33 kcal/mol to 22 kcal/mol). For an identical particle size of 650 μm , their results show that the lignite chars reach the pore diffusion regime at a much higher reaction rate (roughly an order of magnitude) than the bituminous or anthracite chars. This implies that the structure of the lignite char is probably more "open", thus retarding diffusion limitations. The values of the N_2 -BET surface areas at 0% burnoff were measured and were found to be of the order of 100 m^2/g for the lignite char, 15 m^2/g for the bituminous char and 1-2 m^2/g for the anthracite char. These values are consistent with the assumption of a more porous structure for the lignite chars. Su and Perlmutter⁴ studied chars produced at different heating rates (in the range 1 to 10 K/min), for different pyrolysis temperatures (873 to 1223 K) and for

different starting coals (anthracite and bituminous coals). They concluded that chars with different pore structures can be generated from the same coals by varying pyrolysis conditions: a higher final pyrolysis temperature or a slower heating rate generate chars of more compact structure. Floess et al.⁵ compared the behavior of a microporous sucrose char with a macroporous spherocarb char and observed that the reactivity of the former varied with particle size, while the latter did not display such an effect. They attributed the difference in behavior to the different structure of the chars (purely microporous versus microporous and macroporous), and in particular to the presence of large microporous domains in the sucrose char. As Hurt et al.⁶ pointed out, the degree of meso and macroporosity defines the size of the microporous regions, and consequently influences the degree of diffusion limitations in the micropores. In other words, for highly meso/macroporous chars, where the microporous regions are small, the micropores may not be diffusion limited before the meso/macropores themselves. This situation is similar to the one described in Thiele⁷ where, even if most of the reaction occurs in small micropores, the meso/macropores configuration is assumed to control intraparticle diffusion. Walker⁸ and Simons⁹ arrived at the same general conclusion, although using different approaches. Consequently, it is important to estimate the degree of micro and meso/macroporosity of a char in order to predict the degree of pore diffusion limitations.

In order to assess differences in pore structures, multiple techniques such as gas adsorption (for surface areas and pore size distribution measurements), helium pycnometry (densities) and mercury intrusion (macropores distribution) can be used. White et al.¹⁰ performed a comprehensive study on representative US coal chars (from lignite to bituminous) in order to determine surface area, pore size and volume distribution, and density. The chars were prepared at high heating rate in a flat flame burner (in the presence of oxygen), which is representative of char formation in pulverized coal combustion processes. They observed large variations in properties between the original coals and the corresponding chars: increase by two to three-fold for CO₂-DP surface area, by 20-200-fold for N₂-BET surface area, by 5-10-fold for pore volume, by three to four-fold for porosity. However, the differences between the chars produced from different coals were not very important, and varied by less than a factor of 2 for surface area, less than a factor of 2 for pore volume, and less than 15% for porosity. All of the chars were fairly porous (porosity of about 0.6-0.7) with most of the pore volume in macropores, and had N₂ surface areas of about 100-200 m²/g and CO₂ surface areas of about 200-500 m²/g.

More significant variations between the chars studied in the present work were expected, due to the widely different char formation conditions used.

EXPERIMENTAL

Coal Samples - The coals used are from the Argonne Premium Coal Sample Program. The original coal particle size fraction is -100 mesh.

Char Preparation - The chars prepared in the TGA were produced by heating at 30°C/min in helium up to the pyrolysis temperature. In the case of non-fluid, non-agglomerating chars, the isothermal combustion cycle was done immediately after the pyrolysis cycle (without removing the sample from the TGA). In that case, the coal sample size was approximately 10 mg, which corresponds to a char sample of 4 to 7 mg. For fluid coals, since the particles have agglomerated during low heating rate pyrolysis, the char was prepared in larger quantity (150 mg) and was separated into different size fractions. The char average particle size was measured with an ISI Scanning Electron Microscope. The same procedure was applied to the char

prepared in an entrained flow reactor (EFR).

Isothermal Reactivity Measurements - The reaction rates at low temperatures were measured isothermally using a Dupont 951 TGA. The reaction rate is constantly monitored during the entire burnoff process. All experiments were performed using an oxygen partial pressure of 17.2 kPa, a total flow rate of 240 cc/min, and a char sample size of 4 to 10 mg. For the chars prepared in advance in the TGA or the EFR, the char sample was heated under a helium atmosphere at 30°C/min up to the combustion temperature, and the oxygen was introduced after 15 minutes to allow equilibrium.

Nitrogen Adsorption Measurements - Adsorption isotherms in nitrogen were obtained using the dynamic, continuous flow method. The measurements were made using a Quantasorb instrument (Quantachrome Corp.). From the adsorption isotherm, the cumulative pore volume was calculated. The nitrogen surface areas were obtained using the BET equation (single point).

RESULTS AND DISCUSSION

Reactivity Measurements - Chars from the fluid coal Pittsburgh No. 8 were produced at low heating rate in a TGA (Pitts8 TGA) and at high heating rate in an entrained flow reactor (Pitts8 EFR). In order to evaluate the influence of coal rank on pore structure, a char from a Zap lignite was also produced at low heating rate in the TGA (Zap TGA). A char from a demineralized Zap was produced under the same conditions for comparison (Zapd TGA). Table I gives a summary of the properties of the chars studied.

Isothermal measurements of reactivity were obtained for each char over a wide range of temperature, which covered usually 3 orders of magnitude in reactivity. The reported rate was taken at 35% burnoff in all cases, in order to avoid any uncertainty in the calculation of the reaction rate because of the relatively high weight increase due to oxygen adsorption at lower burnoff levels. As shown in Fig. 1, a leveling off of the rate is observed for all chars at a rate of approximately 1 g/g.min. This behavior is due to external mass transfer resistances in the TGA, and would not occur under typical pulverized coal combustion conditions. The Zap TGA char was also found to ignite, which is indicated by the presence of a discontinuity in the reactivity.

As shown in Fig. 1, at low temperature all the chars studied indicated a similar activation energy, which fell in the range of 28 to 34 kcal/mol. The Arrhenius plots for the low heating rate, fluid char Pitts8 TGA showed a gradual change in activation energy, from approximately 28 kcal/mol at low temperature, to 22 kcal/mol at higher temperature. This behavior is observed for the two different particle sizes studied, 150 μm and 800 μm . Following the Thiele⁷ model, the observed change in activation energy is believed to represent the transition from regime I (kinetic) to regime II (pore diffusion). However, features relative to the effect of particle size in each regime need to be clarified. In particular, the fact that, at low temperature (i.e. in the kinetic regime), the 150 μm particle size presents a reactivity higher than the one from the 800 μm particle size requires some explanation. This phenomenon has been observed by other researchers^{5,11}. van Heek and Mühlen¹¹ proposed that the enrichment of product gases inside the larger particles caused by too small diffusion coefficients or too large flow resistances is responsible for the inhibition of the reaction rate. On the other hand, at higher temperatures (in the pore diffusion regime), the variation in rate between the two size fractions is smaller than expected: since the two particle sizes differ by about a factor of 5, the same factor should be obtained between the reaction rates. However, only a factor of 2 is found. A possible explanation of this effect may

result from finding out where the diffusion limitations take place in the particle. If we consider the char to be formed by microporous grains (or regions) surrounded by meso or macropores, diffusion limitations can occur either in the grains (if these are large) or in the meso/macropores (in the case of small microporous grains). In other words, for a char with large microporous regions, the diffusion parameter $D_{\text{micro}}/L_{\text{micro}}^2$ (where D_{micro} is the effective diffusivity and L_{micro} is the diffusion distance in the microporous grains) is lower than the corresponding parameter $D_{\text{meso/macro}}/L_{\text{meso/macro}}^2$ for the meso/macropores, where $L_{\text{meso/macro}}$ represents a distance of the order of the particle size. In such a case, particle size effects may not be present, or would be weak, until the particle size is small enough (i.e. of the size of the microporous regions), in which case the diffusion distance is effectively reduced. The fact that a very low N_2 surface area of 0.5 m²/g at 0% burnoff is found for that char would also be consistent with this assumption, since it implies that few meso and macropores are present. In such a case, the microporous regions could be fairly large.

In contrast with the low heating rate char, Pitts8 TGA, the char produced at high heating rate Pitts8 EFR, did not show much change in activation energy (i.e. did not reach the pore diffusion regime) before entering the external diffusion limitation regime. Its N_2 surface area (at 0% burnoff) was also found to be higher (4 m²/g versus 0.5 m²/g) than the one from Pitts8 TGA. This behavior is consistent with the findings of Su and Perlmutter⁴ that low heating rate chars have a more compact structure. The lignite and demineralized lignite chars Zap TGA and Zapd TGA behaved similarly to the Pitts8 EFR. Their surface areas (84 m²/g and 100 m²/g respectively) were also much higher than the ones from either of the Pittsburgh No. 8 chars.

Pore structure characterization - In an attempt to characterize the pore structure of the chars studied, nitrogen adsorption measurements were performed. Nitrogen adsorption is done at the temperature of liquid nitrogen (77 K). Adsorption is assumed to occur in the mesopores but not in the micropores (at least in the case of 0% burnoff chars) because of activated diffusion. However, since the micropores open up at higher burnoffs, those also adsorb nitrogen in the case of partially combusted chars.

The N_2 adsorption data at 0% burnoff provide useful information on the number and accessibility of the mesopores of the char. Since mesopores probably constitute the main pathway for oxygen to penetrate into the particle, their characterization is an important step in order to predict diffusion limitations. Fig. 2 shows the adsorption isotherms for the Pitts8 EFR and the Pitts8 TGA at 0% burnoff. Pitts8 EFR char produces an isotherm of type IV (characteristic of the presence of pores in the transitional range) while Pitts8 TGA produces an isotherm of the types II or III (non porous). Also, the adsorbed volume is larger in the case of the Pitts8 EFR than for the Pitts8 TGA. The adsorption isotherm for Zap TGA char is shown in Fig. 3, and is characteristic of a porous material with numerous mesopores. Fig. 4 gives the cumulative pore volume for the three chars. These results confirm, in the case of the high heating rate Pitts8 EFR, the presence of more mesopores than in the low heating rate Pitts8 TGA char and are consistent with the assumption that the latter possesses larger microporous regions than the former. Also, as expected, the structure of the Zap TGA char is much more porous than the chars from the fluid coals. This is consistent with the results from Tseng and Edgar^{2,3} who found that for the same particle size, a bituminous char entered the diffusion limited regime before a lignite char. A more quantitative correlation of the pore volume with the degree of diffusion limitations will require additional data in the pore diffusion limited regime for the highly porous chars.

It is well known that the N_2 adsorption pattern changes significantly after a few percent of burnoff.

In order to evaluate those variations, Pitts8 TGA and the Pitts8 EFR chars were produced at 10% and 35% burnoff respectively. Although the degree of burnoff of the two chars is different, it can be reasonably assumed that the internal structure does not vary significantly between 10 and 35% burnoff. The combustion temperature was chosen to be sufficiently low as to be in the kinetic regime. Under these conditions, the pore structure is expected to vary uniformly through the whole particle. It should be noted that this may not be how the structure changes when burnoff is performed at higher temperature, i.e., in the pore diffusion regime (in that case burnoff occurs mostly at the exterior of the particle, with the interior not being modified). Fig. 5 presents the adsorption isotherm for the Pitts8 TGA at 10% burnoff and the Pitts8 EFR at 35% burnoff. The two chars produce an adsorption isotherm characteristic of a microporous structure¹², with most of the pores being smaller than about 20 Å. In that case, the Kelvin equation cannot be utilized to calculate the pore size distribution. The value of the N_2 surface area also increased dramatically, from 0.5 to 98 m²/g for the Pitts8 TGA char and from 4 to 310 m²/g for the Pitts8 EFR. These results indicate that the structure of both coal chars is mostly microporous. However, the degree of meso and macroporosity (which is important to estimate for transport processes) cannot be evaluated easily from these measurements. Also, since the burnoff was performed in the kinetic regime, it does not give a representation of the structure obtained when the combustion is done under more severe conditions. Additional data from chars combusted at high temperatures (i.e. in the pore diffusion regime) is needed. This point will be addressed in more detail in a future publication.

CONCLUSIONS

From this study it can be concluded that low heating rate, fluid chars are less macroporous than high heating rate, fluid chars or lignite chars. This conclusion is consistent with the observation that the low heating rate, fluid chars enter the pore diffusion regime earlier than the other chars. It was also shown that char structural parameters such as surface area and cumulative pore volume can be correlated with the behavior of the char towards pore diffusion limitations. However, additional data obtained in the pore diffusion regime is necessary in order to establish a quantitative correlation between structural properties and the onset of diffusion limitations for a wide range of chars.

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TABLE I Char Properties

Char	Coal	Reactor	Heating Rate (°C/s)	Final Temp.(°C)	Char Particle Size (μm)	N ₂ Surface Area (m ² /g)
Pitts8 TGA	Pitts 8	TGA	0.5	900	800 ± 200* 150 ± 50	0% BO:0.5 10% BO:98
Pitts8 EFR	Pitts 8	EFR	5000	1100	130 ± 30	0% BO:4 35% BO:310
Zap TGA	Zap	TGA	0.5	900	80 ± 40	0% BO:84
Zapd TGA	Zap	TGA	0.5	900	60 ± 20	0% BO:100

* In that case, the combustion cycle was performed immediately after the pyrolysis. The particle size is approximate, since the chars showed a cenospheric agglomerated structure.

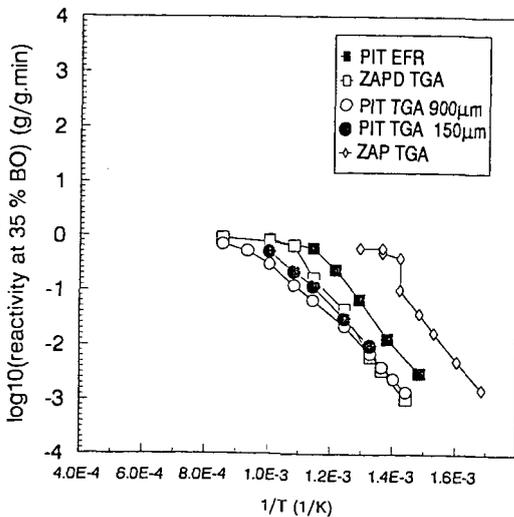


Figure 1. Measured Reactivity at 35% Burn-off of PITTS8 TGA, PITTS8 EFR, ZAP TGA, ZAPD TGA Chars as a Function of 1/T.

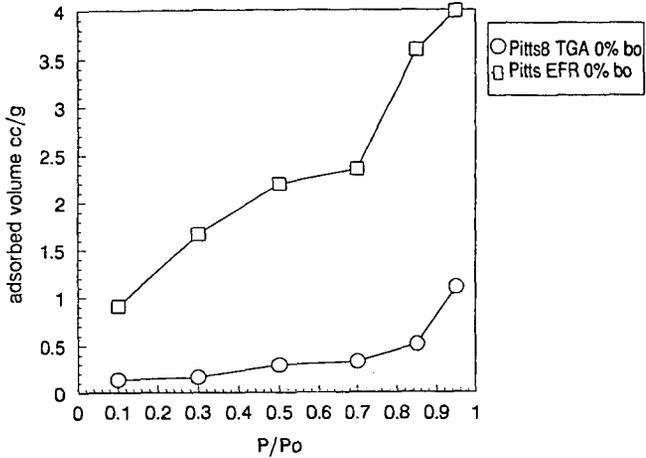


Figure 2. Nitrogen Adsorption Isotherms for PITTS8 EFR and PITTS8 TGA Chars.

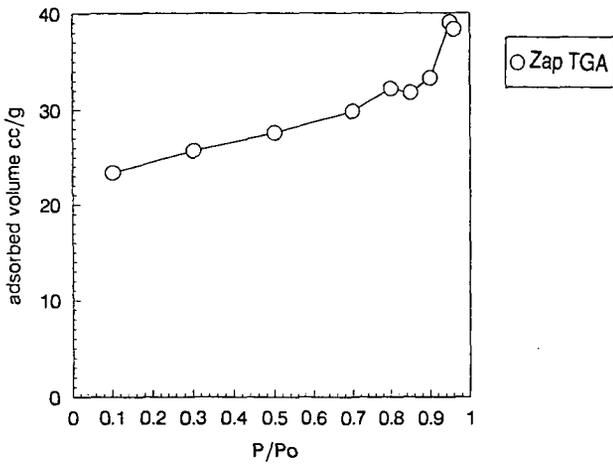


Figure 3. Nitrogen Adsorption Isotherm for ZAP TGA Char.

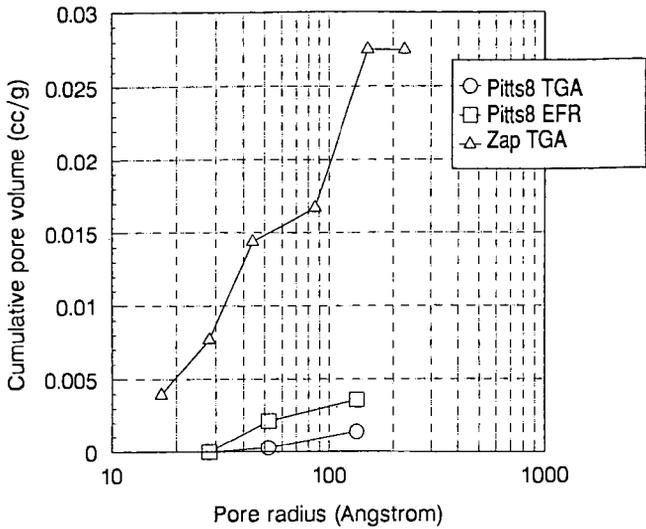


Figure 4. Cumulative Pore Volume for PITTS8 EFR, PITTS8 TGA and ZAP TGA Chars.

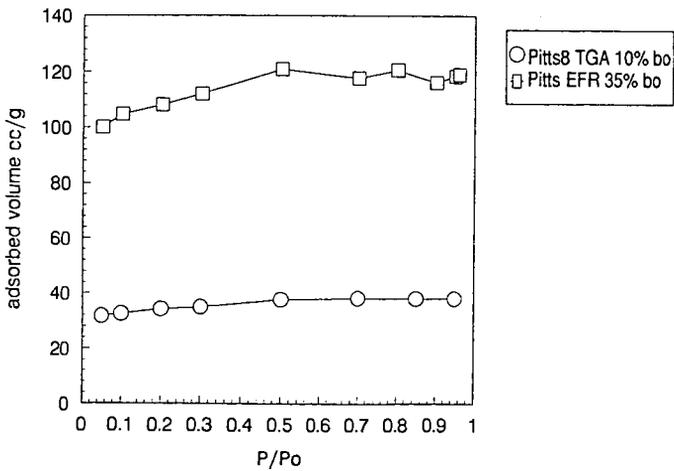


Figure 5. Nitrogen Adsorption Isotherms for PITTS8 EFR at 35% Burn-off and PITTS8 TGA at 10% Burn-off.