MASTER

EFFECTS OF PREIGNITION ON PULVERIZED-COAL COMBUSTION

SECOND QUARTERLY REPORT

FOR THE PERIOD

1 JANUARY 1981 - 31 MARCH 1981

GIRARD A. SIMONS and G. KOTHANDARAMAN

PREPARED FOR THE

U. S. DEPARTMENT OF ENERGY
DIVISION OF ENERGY TECHNOLOGY
UNDER CONTRACT DE-AC22-80PC-30293

APRIL 1981

PHYSICAL SCIENCES INC.
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ACKNOWLEDGEMENT

The authors are grateful to the Coal Research Section, the Pennsylvania State University, for supplying the coals used in these studies.

1. INTRODUCTION

The current research program is directed to study the effects of preignition on pulverized coal combustion. The objectives of the program are to:

- 1) optimize the reactivity of the coal char with respect to variations in the pore structure that occur during pretreatment;
- 2) develop a porous transport theory that can be used to extract the dominant primary and secondary chemical reactions from existing pyrolysis data.

The research program consists of the following four tasks:

- 1) a theoretical study to determine the optimum pore structure for maximum char reactivity;
- 2) experimental studies of pore structure evolution during pyrolysis;
- 3) a theoretical description of pore structure evolution and porous species transport during pyrolysis which is coupled to the experimental studies;
- 4) utilization of the porous species transport model to determine the dominant primary and secondary pyrolysis chemistry from existing laboratory data.

This report summarizes the technical progress accomplished on Tasks 1, 2 and 3 during the current quarter. Details of the technical progress are described in Sections 2, 3, and 4, respectively, and a brief summary is given in Section 5.

2. OPTIMUM PORE STRUCTURE

2.1 Introduction

This section reports theoretical studies of how to maximize the reactivity of char with oxygen by varying the porous structure of the char. These studies utilize the pore tree model^{1,2} for species transport³ and char reactivity.^{4,5} The work is in two parts: first, the reactivity is optimized with respect to char characteristics such as porosity, internal surface area, pore aspect ratio and pore size range; and secondly, the sensitivity of the reactivity to the pore size distribution is examined. These characteristics are expected to vary primarily due to different heating profiles as the coal is heated to the combustion temperature.

2.2 Optimization with Respect to Char Characteristics

Details of this study are reported in the first quarterly progress report.⁶ The results indicate that the most important char characteristic is the porosity. Internal surface area is much less important (except below 800 K) and pore aspect ratio is totally unimportant.

2.3 Optimization with Respect to the Pore Distribution Function

The pore tree model^{1,2} for char structure was developed from a pore size distribution function. Each pore that reaches the exterior surface of the char sample is depicted as the trunk of a tree. The number of tree trunks whose radius is between r_p and $r_p + dr_p$ is denoted by $4\pi a^2 \bar{g}(r_p) dr_p$ where a is the radius of the char sample and $\bar{g}(r_p)$ is the number of pores per unit area. The pore distribution function is given by¹

$$\bar{g}(r_p) = \frac{\theta}{2\beta\pi r_p^3}$$

where θ is the porosity and β is $\ln(r_{\max}/r_{\min})$, where $r_{\max}$ and $r_{\min}$ are the maximum and minimum pore radii, which have known values.¹

Asserting that the trunk of each tree is associated with an internal surface area denoted by $S_T(r_p)$, compatibility between $\bar{g}(r_p)$ and the total internal surface area requires that S_T be proportional to r_p^3 (see Ref. 2). The net reactivity associated with each pore tree may be limited by the kinetic rate acting upon the surface area S_T , or by diffusion through the trunk of the tree. It was determined³ that the smallest pore trees tend to be kinetically limited while the larger trees tend to be diffusion limited. The diffusion limited pores are controlled either by continuum diffusion ($r_p > \text{mean free path}$) or Knudsen diffusion ($r_p < \text{mean free path}$).

Figure 1 illustrates the relative fraction of the total oxidation rate occurring in the pores controlled by the kinetics, continuum diffusion or Knudsen diffusion. The calculation was made for a 100 μ diameter char particle that is 75% porous and being oxidized in air at 1 atm. Note that below 700 K, all pores are kinetically limited. At 800 K, the largest pores become limited by continuum diffusion. Only 60% of the total oxidation rate occurs in kinetically limited pores while the remaining 40% occurs in pores limited by continuum diffusion. At 2000 K, 70% of the total oxidation rate is controlled in Knudsen diffusion limited pores. Surprisingly, 15% of the total oxidation rate is still kinetically limited. A very small fraction of the smallest pore trees see the exterior surface of the char particle directly and they account for a finite fraction of the oxidation rate. The main point to be deduced from Fig. 1 is that all three physical processes are occurring simultaneously during the oxidation of a pulverized fuel.

Physically, any system that is controlled by three competitive processes may be optimized. It is noted from Ref. 3 that the total oxidation rate is expressed as the sum of three moments of the distribution function $\bar{g}(r_p)$. They are the r_p^3 , r_p^2 and $r_p^{3/2}$ moments of $\bar{g}(r_p)$ for kinetically limited, Knudsen diffusion and continuum diffusion, respectively. In abbreviated form, the task is to maximize $\dot{M}$ (carbon removal/time) with respect to $\bar{g}(r_p)$:

Fig. 1 Relative contribution from the limiting processes for a 100 μ diameter, 75% porous char particle in air @ 1 atm.

$$\begin{aligned}
M = & a_1 \int_{r_{\min}}^{r_1} S_T(r_p) \bar{g}(r_p) dr_p \\
& + a_2 \int_{r_1}^{r_2} r_p^2 \bar{g}(r_p) dr_p \\
& + a_3 \int_{r_2}^{r_{\max}} r_p^{3/2} \bar{g}(r_p) dr_p, \quad (1)
\end{aligned}$$

where a_1 , a_2 and a_3 are independent of r_p and

$$S_T(r_p) \propto r_p^3. \quad (2)$$

To examine the sensitivity of the reactivity to $\bar{g}(r_p)$, a perturbation to the $1/r_p^3$ distribution is constructed. The function $\bar{g}(r_p)$ is expanded as

$$\bar{g}(r_p) = \bar{g}_0(r_p) + \bar{g}_1(r_p)$$

where

$$\bar{g}_0(r_p) = \frac{\theta}{2\beta\pi r_p^3}$$

and $\bar{g}_1(r_p)$ is chosen such that the total porosity and total internal surface area is invariant. Only the distribution of porosity and surface area with pore size are allowed to vary.

Before choosing a representative form for $\bar{g}_1(r_p)$, it must be noted that the surface area of a pore tree, $S_T(r_p)$, is also a function of the distribution function $\bar{g}(r_p)$. However, for simplicity, it is assumed that

changes in the shape of the pore tree are negligible compared to changes in the size distribution of the trees. Hence, S_T proportional to r_p^3 is retained. Since this choice of $S_T(r_p)$ is consistent with $\bar{g}_o(r_p)$, the $S_T(r_p)$ moment of $\bar{g}(r_p)$ is approximated by the integral of $S_T(r_p)\bar{g}_o(r_p)$. This ensures that the total internal surface area (the integral of $S_T(r_p)\bar{g}(r_p)$ over all r_p) is invariant with $\bar{g}_1(r_p)$. The "exact" expression for $S_T(r_p)$ is derived in Section 4 and it is shown that the errors introduced by the above approximation are negligible.

It has been assumed that the surface area within a pore tree and hence, the total internal surface area of the char, is invariant with $\bar{g}$. The function $\bar{g}_1(r_p)$ must be chosen such that the total porous volume is also invariant. An analysis of pore combination² within the same constraint suggests

$$g_1(r_p) = \frac{-Q\bar{g}_o}{\beta} \left[\ln(r_p/r_{\min}) - \ln(r_{\max}/r_p) \right],$$

where Q is an adjustable coefficient ($-1 \leq Q \leq 1$). The distribution of porosity with pore size is demonstrated in Fig. 2. The normalized porous volume between $r_{\min}$ and r_p is illustrated parametrically as a function of Q . The total porous volume between $r_{\min}$ and $r_{\max}$ is invariant with Q and the variation in the porosimetry profiles between $Q = +1$ and $Q = -1$ is consistent with available mercury porosimetry data for coals⁷ and chars.⁸

The char reactivity model^{3,4} has been modified for arbitrary Q and numerical results indicate that a tailored pore structure can readily increase char reactivity by a factor of two. Illustration of the results is presented in Figs. 3 and 4. The $Q = -1$ chars are generally more reactive than the $Q = +1$ chars. At high temperatures and large particle sizes, no enhancement with Q is observed. Under these conditions, the char reactivity is limited by diffusion through the external boundary layer. Similarly, at low temperatures (≈ 500 K), the reactions are kinetically limited and no enhancement with Q can occur because the internal surface area

Fig. 2 Normalized pore volume distribution.

Fig. 3 Enhanced reactivity of 100 μ particles.

Fig. 4 Enhanced Reactivity of 1 mm particles

is invariant with Q . At intermediate temperatures, char reactivity is limited by gaseous diffusion through the pores. Since the large pores have better diffusional properties, the $Q \rightarrow -1$ chars are more reactive because they possess a relatively greater number of large pores. This is a general interpretation and may be applied to char gasification as well as char oxidation.

An example of char gasification with CO_2 or H_2O is illustrated in Fig. 5. The intrinsic gasification rates are assumed to be 10^{-5} times the oxidation rates ($e_f = 10^{-5}$). The $Q = -1$ chars are typically twice as reactive as the $Q = +1$ chars. Below 1000 K the char gasification is kinetically limited and there is no enhancement with Q . However, above 1000 K, the reaction is limited by gaseous diffusion through the porous structure and the char reactivity may be enhanced by increasing the relative number of the large pores ($Q \rightarrow -1$). Empirical methods of controlling the value of Q are currently under investigation. Although no definitive results are yet available, the present theory does suggest a potential payoff in terms of enhanced char reactivity.

Fig. 5 Enhanced reactivity of gasification reactions.

3. EXPERIMENTAL STUDIES

3.1 Introduction

The present experimental program consists of assembling a bench-scale pyrolysis reactor and determining the pore-structure development within the coal during pyrolysis. The results will be used for optimizing the char reactivity by heat treatment. In a typical experiment, coal particles will be heated to various final temperatures at different heating rates. The volatiles evolved will be analyzed for product composition. The resulting char will be collected and subjected to analysis for pore distribution within the char. The range of experimental conditions to be covered is given in Table 3.1. During the first quarter of this program, the design of the pyrolysis reactor was completed. The details of the design were presented in the first quarterly report.⁶ During this quarter, the pyrolysis apparatus has been constructed and some preliminary experiments on pyrolysis have been performed.

A brief description of the pyrolysis apparatus is given in Section 3.2. The results of the experimental determination of the power requirements for heating the stainless steel screen to various final temperatures are presented in Section 3.3. The results of the preliminary experiments on pyrolysis are described in Section 3.4. Finally, a brief discussion of the results outlined in Section 3.4 is given in Section 3.5.

3.2 Description of Pyrolysis Apparatus

The apparatus consists of a 325 mesh stainless steel screen folded into a pocket that holds the coal particles, a screen holder, a power source for heating the screen and a vessel for enclosing the screen assembly. A photograph displaying the pressure vessel, the screen and the screen holder is shown in Fig. 6. The stainless steel screen used in the following characterization experiments is 325 mesh, 20 cm x 5 cm, folded once and spot welded along two edges so that it forms a pocket of 20 cm x 2.5 cm. A chromel-alumel thermocouple of 75 μ diameter is spot welded to the center of the screen. The screen is held between the poles of a

TABLE 3.1
Range of Experimental Conditions

Parameter	Range
Coal type	Lignite to bituminous
Particle size	100 to 1000 μ
Final temperature	800 to 2000 K
Heating rate	1 to 10,000-K/s
Pressure	1 to 20 atm
Atmosphere	He and O ₂

Fig. 6 Photograph of the pyrolysis apparatus.

screen holder which also serves to conduct electric current. A ceramic honeycomb manufactured by Corning Glassworks⁹ is placed on top and bottom of the screen insuring thermal contact of the particles with the screen while allowing gaseous products to escape. The screen holder is designed such that the dimensions of the screen can be varied. The screen is heated by an electric current. The entire screen assembly is enclosed in a pressure vessel equipped with electrical feed-through and several ports for the diagnostics. The vessel is connected to a vacuum pump and a gas feed line which enable one to evacuate the vessel and fill it with an inert gas such as helium. As described in the first quarterly report, a convenient source of electrical power for heating 1 g of coal to 2000 K at heating rates of 10^4 K/s is a bank of automobile batteries. However, for our initial experiments in characterizing the screen, the 110 V line voltage with a step down transformer was used as the power source. The results of these experiments are described in the next section.

3.3 Power Requirements and Uniformity of Surface Temperature

The power required to heat the stainless steel screen to a desired final temperature at steady state was determined experimentally. The screen surface temperatures were measured both by thermocouples and by photodiode detection of the emission from different locations on the hot screen. For these experiments a 325 mesh stainless steel screen of 20 cm x 5 cm, folded once and spot welded to dimension of 20 cm x 2.5 cm was used.

The final temperatures attained by the stainless steel screen as a function of applied power, in vacuum and at a pressure of one atmosphere of helium are shown in Fig. 7. Also shown in Fig. 7 are the calculated curves assuming the heat losses are due to radiation from the screen for emissivities of 0.73 and 0.61. The calculated curve for emissivity of 0.73 compares well with the data taken at one atmosphere pressure. The data obtained in vacuum compares well with the curve for the emissivity of 0.61. At a pressure of 1 atmosphere, the loss mechanisms are conduction through the gas and radiation. In vacuum, the loss mechanism is radiation.

Fig. 7 Variation of steady state temperature of SS screen with input power.

Comparing the experimental data at one atmosphere with those in vacuum, one observes that the contribution to the heat loss due to conduction is approximately 20%. Thus, the major loss mechanism is radiation even at a pressure of one atmosphere. The value of 0.61 obtained for the emissivity of stainless steel is high compared with the value of 0.27 quoted in the Handbook.¹⁰ This increased value of emissivity can be attributed to the presence of oxides on the surface, which have emissivities of 0.7 to 0.9.

In order to determine the temperature of the screen at various locations on the surface, the emission at 6665 Å was monitored using an EG&G photodiode and a 6665 Å⁰ filter with a bandwidth of 200 Å. The viewing area of the screen was small compared to the dimensions of the screen. Treating the hot screen as a black body, the radiation emitted at a temperature, T, is given by

$$R_{\lambda}^0 d\lambda = \frac{2\pi hc^2}{\lambda^5} \frac{d\lambda}{(e^{hc/\lambda kT} - 1)} \quad \text{erg cm}^{-2}$$

where λ is the wavelength of the emitted radiation, $h = 6.626 \times 10^{-27}$ erg s, $c = 2.98 \times 10^{10}$ cm s⁻¹ and $k = 1.38 \times 10^{-16}$ erg K⁻¹. For surface temperatures at two locations on the screen of T_1 and T_2 , where $T_1 > T_2$, the ratio of the emitted radiation from these two locations is given by

$$\frac{(R_{\lambda}^0 d\lambda)_1}{(R_{\lambda}^0 d\lambda)_2} = \frac{\exp\left(\frac{hc}{\lambda kT_2}\right) - 1}{\exp\left(\frac{hc}{\lambda kT_1}\right) - 1} = \frac{E_1}{E_2}$$

where E_1 and E_2 are the measured photodiode outputs. For $T \sim 1000$ K and $\lambda = 6665$ Å, $e^{hc/\lambda kT} \gg 1$, and it is easily shown that

$$\ln \frac{E_1}{E_2} = - \frac{hc}{\lambda k} \frac{\Delta T}{T_1^2}$$

where $\Delta T = T_1 - T_2$ and $\Delta T \ll T_1$. Thus, by measuring E_1 , E_2 and T_1 , one can obtain ΔT .

The experiments on the stainless steel screen showed that the monitored photodiode output varied from 1.22 to 0.48 mV. The average temperature of the screen as measured by the chromel-alumel thermocouple was 1260 K. Substituting $E_1 = 1.22$, $E_2 = 0.48$, $T_1 = 1260$ K and $\lambda = 6665 \times 10^{-8}$ cm, we calculate $\Delta T = 68$ K. Thus the mean deviation of the temperature is ± 34 K.

In another experiment a series of thermocouples were spot welded at different locations on the screen and the temperatures monitored. The measured mean deviation of the temperature was ± 25 K. The agreement between the photodiode and the thermocouple experiments is good, considering the different techniques employed in measurement.

3.4 Pyrolysis Experiments at Low Heating Rates

While the pyrolysis apparatus was under construction, some coal samples were pyrolyzed at low, uncontrolled heating rates. The chars resulting from the pyrolysis of coal and the virgin coal were sent to Micromeritics for analyses. The results obtained for both coal and char were nitrogen adsorption data at 77 K, carbon dioxide adsorption data at 300 K, mercury intrusion data from 1.5 to 30,000 psia, and He and Hg densities. These data are interpreted to yield total porosities, total surface areas and pore distributions. A description of the experiment, the results and the interpretation are given in the rest of this section.

3.4.1 Description of the Experiment

Approximately one gram of pulverized coal was spread as-received in a tantalum (0.002") boat of dimensions 5 cm x 1 cm x 0.5 cm. A chromel-alumel thermocouple made of 250 μ diameter wire was spot welded to the tantalum boat. A stainless steel tube of 3.2 cm OD and 12.5 cm long wrapped with heating wires and a layer of insulation served as a furnace for heating the tantalum boat containing the coal sample. The electrical power to the heating wires was provided by a variac, the primary of which was connected to a 115 V AC source. The heater assembly was enclosed in a pyrex bell jar. The air inside the bell jar was displaced by Argon and a continuous flow

of Argon was maintained throughout the experiment. In a typical experiment, the variac was set to a pre-determined voltage and the current was turned on. The heating rate was strongly influenced by the heat losses of the heater assembly to the surroundings and therefore was not rigorously controlled. The temperature of the coal sample was measured by monitoring the output of the thermocouple on a chart recorder. The current was turned off soon after the desired final temperature was reached. The system was allowed to cool to room temperature, the tantalum boat was removed and the char was transferred to a storage vial. The chars were stored in a nitrogen atmosphere.

The samples were dried at 373 K in a vacuum oven for a minimum of one hour prior to any measurements. The helium densities were measured on an Autopycnometer. The CO₂ adsorption data at 300 K were taken using an Accusorb 2100 E Physical Adsorption Analyzer. The N₂ adsorption data at 77 K were obtained on a Digisorb 2500. The mercury intrusion measurements were made on a mercury porosimeter, Poresizer 9300.

3.4.2 Results

1) Coal: The results described below are for a lignite (PSOC 789) from Titus County, Texas. The pulverized coal was obtained from Pennsylvania State University. The results of the proximate and ultimate analyses for this coal reported in the Penn State Coal Data Base are reproduced in Table 3.2. For the pyrolysis experiments, the coal was used as received. The sizes of particles ranged from 1000 μ to less than 50 μ , 75% being in the range 100 - 900 μ . Since the heat conduction times for 1000 μ coal particles are $\sim$ 0.1 s and the heating rates are $\sim$ 1 K/s, the variation in the particle sizes has little influence on the results of the present experiment.

2) Temperature History: Two sets of experiments were performed and final temperatures of 976 and 1134 K were attained. As described in Section 3.4.1 the heating rates obtained in these experiments were not rigorously controlled. The temperature history for the two final temperatures is shown in Fig. 8. The heating rate varied from $\sim$ 1 K/s to 0.2 K/s.

TABLE 3.2
Characteristics of PSOC-789 Coal as Reported by
Pennsylvania State University

Proximate Analysis	Wt% As-Received	Wt% Dry-Basis
Moisture	27.12	
Ash	16.80	23.05
Volatile Molten	33.71	46.26
Fixed Carbon	22.37	30.69
Ultimate Analysis	Wt% As-Received	Wt% Dry-Basis
Ash	16.8	23.05
Carbon	39.86	54.69
Hydrogen	3.11	4.27
Nitrogen	7.22	9.90
Sulfur	0.62	0.85
Chlorine	0.01	0.01
Oxygen (By diff)	5.26	7.23

Fig. 8 Temperature histories for the slow pyrolysis of PSOC 789 coal.

3) Helium and Mercury Densities: Helium is not adsorbed and can penetrate almost all pores. Hence, the helium density represents the true density of the material. Mercury, being a nonwetting liquid does not penetrate the pores. Hence, mercury density represents the apparent density of the sample. The helium and mercury densities obtained for the PSOC 789 coal and the two chars prepared as described earlier are listed in Table 3.3. The porosity and total surface area, also given in Table 3.3, are discussed below.

4) Carbon Dioxide and Nitrogen Adsorption Data: The carbon dioxide adsorption data were taken at 298 K for the PSOC 789 coal and the two chars in the pressure range 0.1 to 760 torr. The volumes of CO₂ adsorbed as a function of pressure for the coal and the two chars are shown in Fig. 9.

The nitrogen adsorption data were taken at 77 K for the PSOC 789 coal and the two chars in the pressure range 50 to 760 torr. The volume of nitrogen adsorbed by the coal as a function of p/p_0 is plotted in Fig. 10. Here p is the pressure at which adsorbed volume is measured and p_0 is the saturation pressure of nitrogen at 77 K. The data for the two chars are shown in Fig. 11. The mercury intrusion data are presented below.

5) Mercury Intrusion Data: The mercury intrusion data were obtained for the PSOC 789 coal and the two chars in the pressure range 1 to 30,000 psia. The diameters of the pores filled at a pressure P were calculated using the Washburn equation¹¹

$$d = - \frac{4\gamma \cos\alpha}{P}$$

where γ is the surface tension and α , the contact angle of mercury, respectively. The surface tension and the contact angle were 485 dynes/cm and 130°, respectively. The cumulative intrusion volumes obtained as a function of pore diameter for PSOC 789 coal and the two chars are displayed in Fig. 12.

3.4.3 Interpretation

1) Total Porosity: The total porosity of a given sample can be deduced from the helium and mercury densities. This is given by

TABLE 3.3

Densities, Porosities and Surface Areas
 (Dry Basis) of PSOC 789 Coal and The Chars

	PSOC 789 Coal	Char 974 K	Char 1134 K	Units
Helium Density	1.71	1.88	2.30	g cm^{-3}
Mercury Density	0.923	0.864	0.848	g cm^{-3}
Porosity	0.46	0.54	0.64	
Total Surface Area (CO_2)	135	327	356	$\text{m}^2 \text{g}^{-1}$

Fig. 9 The adsorption isotherms of CO₂ at 300 K.

Fig. 10 Nitrogen Adsorption isotherm at 77 K for PSOC 789 coal.

Fig. 11 Nitrogen adsorption isotherms at 77 K for PSOC 789 chars.

Fig. 12 Mercury intrusion volume vs. pore diameter for PSOC 789 coal and the chars.

$$\theta = \rho_{\text{Hg}} \left(\frac{1}{\rho_{\text{Hg}}} - \frac{1}{\rho_{\text{He}}} \right)$$

where θ , ρ_{Hg} and ρ_{He} are the total porosity, mercury, and helium densities of the sample, respectively. From the measured helium and mercury densities of the coal and the chars, the porosities have been calculated and are presented in Table 3.3.

2) Surface Area: Marsh¹² and Walker and Kini¹³ have shown that for coals and chars the true surface areas are measured from CO₂ adsorption isotherms at room temperature rather than the conventional N₂ adsorption isotherms at 77 K. It is argued that N₂ molecules at 77 K cannot penetrate the small pores in coals and chars which have the majority of the surface area. However, CO₂ can diffuse into the small pores at room temperature due to activated diffusion. As shown by Marsh and Siemieniowska¹⁴ and later by Walker and Patel¹⁵ one can make CO₂ adsorption measurements at low pressures and use the Dubinin-Polanyi equation to obtain the surface area. The Dubinin-Polanyi plots for the PSOC 789 coal and char (976 K) are shown in Fig. 13. The Dubinin-Polanyi plot for the char (1134 K) is shown in Fig. 14. As predicted by the Dubinin-Polanyi theory, the plots are linear. The intercepts of these plots correspond to the volume of the CO₂ necessary to cover the entire surface with a monolayer. Using the value of 25.3 Å² for the area of cross-section of CO₂ molecule, the total surface areas have been calculated for the PSOC 789 coal and the two chars. These are listed in Table 3.3.

3) Pore Distribution from the Nitrogen Adsorption Data: The pore distribution in the diameter range 22.5 to 550 Å was computed from the adsorption branch of nitrogen adsorption isotherm.¹⁶ The basic principle is that capillary condensation occurs in pores because the vapor pressure over a concave meniscus formed by liquid in the pore is lower than that of the bulk liquid. This lowering is given by the Kelvin equation¹⁷

$$-RT \ln(p/p_o) = \frac{2\sigma V}{r_p}$$

Fig. 13 Dubinin-Polanyi plot for PSOC 789 coal and char, 976 K.
The line is a least squares fit to data.

Fig. 14 Dubinin-Polanyi plot for PSOC 789 char, 1134 K. Line is least squares fit to data.

where σ , V and p_0 are the surface tension, molar volume of the liquid and vapor pressure of the bulk liquid at temperature T , respectively. P is the pressure at which condensation occurs in a pore of radius, r_p . In calculating the pore distribution, a correction is made for the effect of multilayer adsorption.¹⁸ The pore size distribution was calculated from the nitrogen adsorption isotherms for the coal and the two chars. The results are shown in Fig. 15.

4) Pore Distribution from Mercury Intrusion Data: The volume of mercury intruded into a solid at a pressure P is the integrated volume of all pores of diameter equal to or greater than d calculated from the Washburn equation. The intruded volume of mercury as a function of pressure directly yields the variation of pore volume with diameter of pores. The interpretation of mercury intrusion data is straightforward for solid objects. However, the case of powders is complicated by the presence of interparticle voids. It is difficult to determine the minimum pressure at which the interparticle voids are filled with the limited data on hand. We are currently making measurements on glass particles, which will allow us to estimate the intrusion volume due to the interparticle voids. The intrusion data obtained for pores below 3μ diameter (60 psia) are, however, not influenced by interparticle voids. Thus, the discussion that follows is limited to pores of diameter below 3μ .

3.5 Discussion

The coal and the char formed in pyrolysis of coal are like molecular sieves. The size distribution of the pores in coals are dependent on the nature of the coal.⁸ The pyrolysis of coal influences this distribution. It is known that the porosities and surface areas of coals increase during pyrolysis.^{7,19-23} The porosities and surface areas of the PSOC 789 coal and the chars presented in Table 3.3 show an increase with pyrolysis temperature. The surface area increases by a factor of 2.5 during pyrolysis. The change in surface area due to increasing the final temperature of pyrolysis from 974 K to 1134 K is relatively small.

Fig. 15 Pore distribution curves for coal and the chars from N_2 adsorption data.

The pore sizes that occur in coals and coal chars can be divided into three classes, namely

- (1) Ultra-micropores (4 - 12 Å)
- (2) Micropores (12 - 300 Å), and
- (3) Macropores (300 Å - 3μ).

The size distribution of pores in the 4-12 Å range cannot be determined with the currently available experimental techniques. However, an estimate of the pore volume in the ultramicropores can be made from the measured surface areas assuming a mean diameter for the pores and cylindrical geometry. Thus, assuming a mean diameter of 8 Å, the total surface areas for the PSOC 789 coal and the chars presented in Table 3.3 are converted to volumes in the ultra-micropores. These are listed in Table 3.4. It is seen from Table 3.4 that the pore volume in the ultra-micropores increases by a factor of 2.5 on pyrolysis. While this increase in the pore volume of the ultramicropores is of scientific interest, this is not a region of interest for optimizing char reactivity.

The size distribution in the micropores is obtained from the nitrogen adsorption isotherm. The integrated pore volume as a function of pore diameter in the range 12-300 Å is shown in Fig. 15. It is noted from Fig. 15 that the pores evolve continuously when coal is pyrolyzed. No sudden jumps in the pore distribution seem to occur when coal is pyrolyzed. The integrated pore volumes in the micropores for the PSOC 789 coal and the two chars as determined from Fig. 15 are presented in Table 3.4. The volume in the micropores is at least an order of magnitude smaller than that in macropores.

The pores in the range 300 Å to several microns are of utmost importance for optimizing char reactivity. The size distribution in this range is obtained from mercury intrusion data and shown in Fig. 12. The integrated volumes in the macropores for the PSOC 789 coal and the two chars are given in Table 3.4. The volume in the macropores is considerably higher than those in the micro and ultramicropores. The evolution of pores in this size range has again been gradual as seen from curves in

TABLE 3.4

SPECIFIC VOLUMES FOR DIFFERENT PORE SIZE RANGES
IN PSOC 789 COAL AND THE CHARS (DRY BASIS)

	PSOC 789 Coal	Char 974 K	Char 1134 K
Ultramicropores	.027 cc/g	.065	.071
Micropores	.006	.01	.017
Macropores	.07	.11	.12

Fig. 12. Since the char reactivity theory predicts that the dominant char oxidation reactions occur in the macropores, one can conclude that the mercury intrusion experiments will yield the most relevant data for the char reactivity optimization studies. In our future studies, only the pore evolution in the 300 Å to several micron range will be determined using the mercury porosimeter.

4. THEORETICAL DESCRIPTION OF PORE STRUCTURE EVOLUTION

4.1 Introduction

A theoretical description of the evolution of the pore structure requires, as a first step, a spatial description of the pore tree, i.e., a mathematical description of the pore tree depicting the number and size of the pores as a function of distance into the pore tree. Pore evolution may then be described as a time dependent growth of the branches of the tree due to pyrolysis of the material on the walls of the pores. However, a spatially dependent description of the pore tree cannot be calculated without first extending the statistical description of the pore tree. As such, the current effort has been directed towards this goal. The statistical description has been completed to the extent that the volume and surface area of a pore tree can be obtained for any distribution function $\bar{g}(r_p)$. Hence, the errors introduced in the $S_T(r_p)$ moment of $\bar{g}(r_p)$ (Section 2.3) can be assessed. The development of the spatial description of the pore tree from the statistical description will be carried out during the next quarter.

4.2 Statistical Description of the Pore Tree

The concept of the pore tree¹ depicts that every pore that reaches the exterior surface of the char particle is the trunk of a tree. In addition, every branch of every tree is itself the trunk of a smaller tree. Let $N_t dr_p$ be the number of pores of radius r_p (within size range dr_p) in a tree whose trunk radius is r_t . If $N dr_p$ represents the total number of pores of radius r_p (within size range dr_p) in a sphere of radius a , then the distribution function N can be determined by counting every pore of radius r_p in every tree in the char sample. Hence,

$$N = \int_{r_{\min}}^{r_{\max}} N_t \bar{g}(r_t) 4\pi a^2 dr_t$$

where $\bar{g}(r_t)$ is the number of tree trunks per unit external area of the char sample.¹

The quantity $f(r_p)dr_p$ is defined as the number of pores of radius r_p (within size range dr_p) per unit volume. The quantities $\bar{g}(r_p)$ and $f(r_p)$ were related by¹

$$f(r_p) = \frac{2\bar{g}(r_p)}{\ell_p}$$

where ℓ_p is the length of the pore

$$\ell_p = kr_p$$

and k is a known constant. Since N is related to f by

$$N = \left(\frac{4}{3} \pi a^3\right) f$$

it follows that

$$\int_{r_{\min}}^{r_{\max}} N_t \bar{g}(r_t) dr_t = \left(\frac{r_{\max}}{r_p}\right) \bar{g}(r_p) \quad (3)$$

where $r_{\max}$ has been related to the particle radius a by¹

$$r_{\max} = \frac{2a}{3k}$$

The branch distribution function N_t may be obtained from Eq. (3) for arbitrary $\bar{g}(r_p)$. The N_t corresponding to the $1/r_p^3$ distribution becomes

$$N_t = \frac{A(r_t)}{r_p^4} \quad (4)$$

where $A(r_t)$ is an unknown function of r_t . Defining ϵ such that there is one pore in the pore tree whose radius lies between ϵr_t and r_t ,

$$\int_{\epsilon r_t}^{r_t} N_t dr_p \equiv 1$$

it follows that

$$A = \left(\frac{3\varepsilon^3}{1-\varepsilon} \right) r_t^3 \quad (5)$$

Combining Eqs. (3) - (5), $N_t(r_t, r_p)$ for $g \sim 1/r_p^3$ becomes

$$N_t = r_t^3 / r_p^4 \quad (6)$$

Following the same procedure for $\bar{g}_0 + \bar{g}_1$ (Section 2.3), N_t becomes

$$N_t = \frac{r_t^3 \left[1 - \frac{Q}{\beta} \left\{ \ln(r_p/r_{\min}) - \ln(r_{\max}/r_p) \right\} \right]}{r_p^4 \left[1 - \frac{Q}{\beta} \left\{ \ln(r_t/r_{\min}) - \ln(r_{\max}/r_t) \right\} \right]} \quad (7)$$

where $Q = 0$ corresponds to $\bar{g} = \bar{g}_0$.

The internal surface area and porous volume associated with each pore tree are defined in terms of N_t :

$$S_T(r_t) = 2\pi r_t \ell_t + \int_{r_{\min}}^{r_t} 2\pi r_p \ell_p N_t dr_p \quad (8)$$

$$V_T(r_t) = \pi r_t^2 \ell_t + \int_{r_{\min}}^{r_t} \pi r_p^2 \ell_p N_t dr_p \quad (9)$$

Using N_t associated with the $1/r_p^3$ distribution, S_T and V_T become

$$S_T(r_t) = 2\pi r_t \ell_t \left(\frac{r_t}{r_{\min}} \right) \quad (10)$$

and

$$V_T(r_t) = \pi r_t^2 \ell_t \left(1 + \ln(r_t/r_{\min}) \right) \quad (11)$$

respectively. The above expression for $S_T(r_t)$ is identical to that derived¹ by an integral constraint, except for the influence of pore combination.² The surface area associated with the pore tree may be several orders of magnitude greater than the surface area of the trunk. However, the volume of the pore tree may, at most, be one order of magnitude greater than that of the trunk. This is consistent with one's observation of an ordinary tree or river system which depict the physical image of the pore tree. It should also be noted that the above expressions for S_T and V_T reduce to a single cylindrical pore in the limit of $r_t \rightarrow r_{\min}$ (the leaf of the tree).

The total surface area (S_p) and total porous volume (V_p) of a char sample can be expressed as integrals over all trees that reach the exterior surface of the particle.

$$S_p = \int_{r_{\min}}^{r_{\max}} S_T(r_t) \bar{g}(r_t) 4\pi a^2 dr_t \quad (10)$$

$$V_p = \int_{r_{\min}}^{r_{\max}} V_T(r_t) \bar{g}(r_t) 4\pi a^2 dr_t \quad (13)$$

Equations (12) and (13) are identically satisfied by Eqs. (10) and (11) for $S_T(r_t)$ and $V_T(r_t)$, respectively. This is a consequence of the rigorous development of N_t , S_T and V_T .

The surface area contained in the pore trees whose trunk radii lie between $r_{\min}$ and r_1 is defined as S_{partial} .

$$S_{\text{partial}} = \int_{r_{\min}}^{r_1} S_T(r_t) \bar{g}(r_t) 4\pi a^2 dr_t \quad (14)$$

Comparison of Eqs. (12) and (14) illustrates that $S_{\text{partial}} \rightarrow S_p$ when $r_1 \rightarrow r_{\text{max}}$, i.e., when all pores are included in the integral. The significance of S_{partial} is seen in the first term of Eq. (1), Section 2.3. It represents the contribution to the carbon removal rate by the pore trees that are kinetically limited. In Section 2.3, S_{partial} was evaluated for $Q = 0$ only. The errors introduced through this approximation may be evaluated from Eqs. (7), (8) and (14) for arbitrary Q . After some lengthy algebra, it can be shown that

$$S_{\text{partial}} = \frac{2\theta V}{\beta r_{\text{min}}} \left[\left(\frac{r_1 - r_{\text{min}}}{r_{\text{max}}} \right) \left(1 + \frac{Q(\beta - 2)}{\beta} \right) + \frac{2Q}{\beta} \frac{r_{\text{min}}}{r_{\text{max}}} \ln(r_1/r_{\text{min}}) \right]$$

where V is the bulk volume of the char sample and all other variables were defined in Section 2.3.

The error in the value of S_{partial} obtained in Section 2.3 can be determined from

$$\frac{\left(S_{\text{partial}}/S_p \right) \Big|_{Q \neq 0}}{\left(S_{\text{partial}}/S_p \right) \Big|_{Q=0}} = 1 + \delta$$

where

$$\delta = \frac{2Q r_{\text{min}} \ln(r_1/r_{\text{min}})}{(r_1 - r_{\text{min}})(\beta + Q(\beta - 2))}$$

The quantity δ represents the error in S_{partial} , not the error in the carbon removal rate due to inaccuracies in S_{partial} . For $Q = -1$, $\delta \rightarrow -1$ as $r_1 \rightarrow r_{\text{min}}$. Thus, 100% errors occur in S_{partial} in the limit of $S_{\text{partial}} \rightarrow 0$. It is this limit in which the carbon removal rate is unaffected by S_{partial} . The error in the carbon removal rate is δ times the fraction of the carbon removal rate controlled by S_{partial} . This is approximated by $\delta S_{\text{partial}}/S_p$. Therefore,

the error in carbon removal rate $\approx \frac{2r_{\min} Q \ln(r_1/r_{\min})}{r_{\max} [\beta + Q(\beta-2)]}$,

which is, at most, a 1% effect. Hence, the approximation made in Section 2.3 in determining S_T and S_{partial} will not influence the predicted oxidation rates.

The primary significance of the statistical description of the pore tree developed above is not its influence on the calculations of Section 2.3, but that it is the first step in developing a spatially dependent description of the pore tree. Such a description of the pore tree will be carried out during the next quarter.

5. SUMMARY

The technical effort on Task 1, pore structure optimization, is complete. Only the documentation of the computer code and the writing of a detailed technical paper remains. The basic conclusion reported in Section 2 is that the particle size and porosity are the most important physical properties of char when considering char oxidation above 800 K. The distribution of porosity with pore size is of secondary importance and introduces factor of two changes in oxidation rates. The internal surface area and pore aspect ratio have no significant influence on char oxidation above 800 K.

Under Task 2, the apparatus for the bench scale pore evolution experiments has been constructed. Coal samples will be heated at various rates to various final temperatures and the pore structure of the remaining char will be measured. Preliminary data have been analyzed using N_2 and CO_2 adsorption, Hg porosimetry and Hg and He densities. Details are reported in Section 3. In future studies, the CO_2 and N_2 adsorption will be omitted as they have not yielded any surprising empirical results and they do not offer any information which is useful to the theory of a tailored pore structure for enhanced char reactivity. The Hg and He densities are important as they yield the char porosity and the Hg porosimetry is important as it yields the size distribution of the large pores which control char oxidation. Both the He pycnometer and Hg porosimeter have been purchased. All future experiments and char analyses will be performed in-house.

The theory of pore evolution, Task 3, has been initiated. A statistical description of the pore tree has been developed and is reported in Section 4. A spatial description of the pore tree and the pore evolution theory will be developed in the coming months of the program.

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