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EFFECTS OF PREIGNITION ON PULVERIZED COAL COMBUSTION

First Quarterly Report for the Period September 19-December 31, 1980

By
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EFFECTS OF PREIGNITION ON PULVERIZED COAL COMBUSTION

FIRST QUARTERLY REPORT

FOR THE PERIOD

19 SEPTEMBER 1980 - 31 DECEMBER 1980

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1. INTRODUCTION

The current research program is directed to study the effects of pre-ignition on pulverized fuel 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 with the capability of assessing, from existing laboratory data, the dominant primary and secondary chemical reactions that occur during pyrolysis.

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 coupled theoretical description of pore structure evolution and porous species transport during pyrolysis;
- 4) utilization of the porous species transport model to assess the dominant primary and secondary pyrolysis chemistry from existing laboratory data.

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

2. OPTIMUM PORE STRUCTURE

2.1 Introduction

Theoretical studies have been conducted to maximize the reactivity of char to oxygen with respect to the porous structure of the char. These studies have utilized the pore tree model^{1,2} for species transport³ and char reactivity.^{4,5} The study is separated into 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. Results of the latter study are not available but an outline of the theoretical approach is given.

2.2 Optimization with Respect to Char Characteristics

The most difficult aspect of determining the "optimum structure" is that of studying the influence of one and only one variable at a time. For example, char from the same parent coal but with different pretreatment processes may have different porosities and surface areas (etc.). A parametric study must isolate the effect of porosity at fixed surface area and that of surface area at fixed porosity in order to determine which char is more reactive and why. Then and only then can this theory be used to determine, a priori, the optimum pore structure with respect to char reactivity.

Figures 1 through 3 illustrate the parametric dependence of char reactivities on total porosity as functions of temperature with particle size, internal surface area, gas pressure and flow velocity held fixed. The results indicate that in all situations, reactivity markedly increases with porosity. This conclusion is a consequence of the fact that combustion is limited by gaseous diffusion within the pores. Increased porosities reflect better diffusional properties and increased reactivities.

The influence of internal surface area is depicted in Figs. 4 and 5. The surface area is varied while the porosity and particle size is held constant. Above 800 K, the reactivity is limited by diffusion into the pores and the effect of increasing the internal surface area is minimal.

Fig. 1 Dependence of reactivity on porosity for 100 μ particles in 1 atm air.

Fig. 2 Dependence of reactivity on porosity for 100 μ particles in 100 atm air.

Fig. 3 Dependence of reactivity on porosity for 1mm particles in 1 atm air.

Fig. 4 Effect of surface area on reactivity at high temperatures.

Fig. 5 Effect of surface area on reactivity at low temperatures.

However, the influence of surface area increases with decreasing temperature. Below 500 K, the $C + O_2$ reaction is kinetically limited and the reactivity scales directly with internal surface area. Since commercial char combustion below 800 K is not of great interest, it is the conclusion of this study that internal surface area is not an important parameter in optimizing char combustion.

To study the influence of the pore aspect ratio on char reactivity, it is necessary to reexamine the pore tree model.¹ The constant K_0 was introduced to reflect the pore aspect ratio. Statistical arguments required that K_0 be less than 20, otherwise a pore would always connect two larger pores. The value of K_0 was determined by statistically relating the radius of the largest pore (r_{max}) to the particle radius. Data on r_{max} then inferred that the value of K_0 was approximately 5. Hence, K_0 is between unity and twenty, with a probable value of five.

Any variation of K_0 will not only change the pore aspect ratio, but it will also change r_{max} , thereby changing the pore size range. In addition, the parameter K_0 influences the basic structure of the pore tree.¹ Hence, variation of K_0 reflects the variation of three properties of the char and caution must be taken in interpreting the sensitivity of char reactivity to K_0 . Numerical results are illustrated in Fig. 6. Higher reactivity is a consequence of larger K_0 .

To interpret the results of Fig. 6, the influence of the pore aspect ratio is first examined. Consider a solid sphere with two small pores, each 1 μ in diameter and 5 μ in length. If reaction in these pores is diffusion limited, reaction will occur in the "mouth" of the pores near the exterior surface. If these two pores are combined into one pore (10 μ in length), the reactivity will be cut in half as now the "mouth" of only one pore reaches the exterior surface. However, on a statistical basis, the longer pore is twice as apt to reach the exterior surface. Hence, on a statistical basis, the reactivity is independent of pore aspect ratio. This conclusion is supported by the fact that the equations for species transport in diffusion control are independent of K_0 .³

Fig. 6 Sensitivity of reactivity to model parameter K_0 .

The proper interpretation of the results of Fig. 6 lies in the relationship between $r_{\max}$, the basic structure of the pore tree and the parameter K_0 . Because of the structure of the pore tree, the largest trees tend to be diffusion limited.^{1,3} Increasing K_0 reduces $r_{\max}$ (thereby eliminating the largest pore trees) and shifts the surface area from the largest trees to the smaller trees.¹ Since the smaller trees are more apt to be kinetically limited, the reactivity increases with increasing K_0 . It should be emphasized that, while this is the mechanism whereby the reactivity increases with K_0 , it is not believed to be physically possible to change the structure of the pore tree in this manner. Hence, while it is useful to see the sensitivity of the reactivity to the choice of K_0 , it is not possible to optimize reactivity via this mechanism.

The present study on the optimization of char reactivity with respect to char characteristics indicates that the char porosity is the most important parameter, 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, the values which are known.¹

In developing the char oxidation theory³ it was noted that the smallest pore trees would tend to be kinetically limited while the larger trees would be diffusion limited. The diffusion limited pores will be controlled either by continuum diffusion ($r_p > \text{mean free path}$) or Knudsen diffusion ($r_p < \text{mean free path}$). Figure 7 illustrates the relative fraction of the

Fig. 7 Relative contribution from the limiting processes for a 100 μ diameter, 75% porous char particle in air @ 1 atm.

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. 7 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 $g(r_p)$ 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 $\bar{g}(r_p)$:

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

where a_1 , a_2 and a_3 are constant.

To examine the sensitivity of the reactivity to $\bar{g}(r_p)$, a perturbation to the $1/r_p^3$ distribution has been 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

$$\bar{g}_1(r_p) = \frac{-Q\bar{g}_0}{\beta} \left[\ln(r_p/r_{\min}) - \ln(r_{\max}/r_p) \right],$$

where Q is an adjustable constant. The function $\bar{g}_1(r_p)$ was chosen such that the distribution of porosity with pore size is altered but the total porous volume is invariant with $\bar{g}_1(r_p)$. This is demonstrated in Fig. 8 where the normalized porous volume between $r_{\min}$ and r_p is illustrated as a function of the parameter Q . The variation in integrated porosity between $Q = +1$ and $Q = -1$ is consistent with available mercury porosimetry data for coals⁶ and chars.⁷

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 postponed until a complete physical understanding of the calculations is obtained. At that time, the results and their general implication will be presented.

Fig. 8. Normalized pore volume distribution.

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 has been completed.

The details of the reactor design are discussed below. Past designs are enumerated in Sec. 3.2 and the design criteria are presented in Sec. 3.3. Power, current and voltage requirements for an electrically heated grid are described in Sec. 3.4 and, finally, a brief description of the apparatus is given in Sec. 3.5.

3.2 Background

There has been considerable interest in pyrolysis of coal at high heating rates in recent years and several articles have appeared in the literature on the design of the pyrolysis apparatus. Anthony et al.⁸ have described a device for pyrolysis consisting of an electrically heated metal screen strip capable of heating rates of 600-12000°C/s. Hamilton et al.⁹ have recently designed a similar unit which differs from that of Anthony et al. mainly in having a precisely uniform rate of heating. A commercial unit is available from Chemical Data Systems which has been used by Blair et al.¹⁰ While these devices can be used for high heating rates, only small quantities of samples (10-20 mg) can be heated. Although small quantities of coal are sufficient for measurements such as mass loss and volatile composition, we find relatively large samples (0.5 - 1g) are required for our measurements such as Hg porosimetry, surface area and helium density measurements. Hence, we have designed a unit, essentially a modification of the previous designs, for heating large quantities of coal.

TABLE 3.1

Range of Experimental Conditions

<u>Parameter</u>	<u>Range</u>
Coal type	Lignite to bituminous
Particle size	100 to 1000 μ
Final temperaturc	800 to 2000 K
Heating rate	1 to 10000 K/s
Pressure	1 to 20 atm
Atmosphere	He and O ₂

3.3 Design Criteria

The heat capacity of coal is given approximately by $C_p = 2 \times 10^{-3} T$ J/g K where T is the absolute temperature. One requires 3910 joules of energy to raise the temperature of 1 g of coal from room temperature to 2000 K. At a heating rate of 10^4 K/s, a power of 23 kW must be supplied for 0.17 s. Pulsed/CW lasers and flash lamps are not favorable because of the combination of large total energy and long duration of pulse requirements. An electrically heated grid would be a good choice provided the design of the grid satisfies the following criteria: (i) the conduction times within the grid are short compared to that of the coal particles of the size considered, i.e., the grid surface remains uniform in temperature, (ii) the grid acts as a thermal bath as far as possible, i.e., the thermal mass of the coal particles is small compared to the grid, and (iii) the coal must remain in physical contact with the grid. The cost and availability of the grid material are further concerns. We have chosen 325 mesh SS304 screen for temperatures to 1400 K and tungsten for higher temperatures. In the rest of this section, it is shown that the above screens meet the criteria mentioned above.

The properties of SS304, tungsten and coal are given in Table 3.2. For a single coal particle of diameter D, placed in a bath of temperature T_f , the transient time for heating by conduction is given by¹¹

$$\tau_{\text{thermal}} = D^2/8K$$

where K is the thermal diffusivity of the material

$$K = \frac{\lambda}{\rho C_p}$$

and λ , ρ and C_p are the thermal conductivity, density and heat capacity, respectively. The thermal transient times for coal, SS304 and tungsten are illustrated in Fig. 9 as a function of particle size. The transient time for 100 μ coal particles vary from 2 ms at 300 K to 0.5 ms at 1500 K, indicating the particles can keep up with a grid heating rate as high as 6×10^5 K/s.

TABLE 3.2

Physical Properties of Materials

Property	SS304	Tungsten	Coal	Units
Melting point	1430	3410	--	$^{\circ}\text{C}$
Density ρ	7.9	19.3	1.0	g cm^{-3}
Heat capacity C_p				
at 300 K	0.50	0.134	0.6	$\text{J g}^{-1} \text{K}^{-1}$
at 1500 K	0.63	0.159	3.0	$\text{J g}^{-1} \text{K}^{-1}$
Thermal conductivity, λ				
at 300 K	0.15	1.7	.0028	$\text{W cm}^{-1} \text{K}^{-1}$
at 1500 K	0.33	0.8	.069	$\text{W cm}^{-1} \text{K}^{-1}$
Resistivity, P_r				
at 300 K	72	5.7	--	$\mu\Omega - \text{cm}$
at 1500 K	90*	40.4	--	$\mu\Omega - \text{cm}$

*Based on an alloy of composition similar to SS304

Fig. 9 Thermal transient times for coal, tungsten and SS304.

For SS304 and tungsten grids, temperature non-uniformities occur in the lateral direction over a distance equal to the particle size. Fig. 9 illustrates that the transient times associated with these non-uniformities are at least a factor of three shorter than that of coal. Hence, if we use a 325 mesh screen (.0014" diameter wire) for heating 100 μ particles, the transient times are short enough to ensure uniformity of the temperature of the grid.

In addition to ensuring temperature uniformity of the grid, it is necessary to insure that the thermal mass of the grid is large compared to that of the coal. The mass of SS screen is calculated to be .019 g/cm². A monolayer of coal particles of uniform spheres of 100 μ diameter covering 1 cm² is .005 g. Using an average value of heat capacity of 0.56 J/g K, we see that the heat content of the screen is .01 J/cm² K. The heat content of coal covering 1 cm² surface varies from .003 J/K, at 300 K to 0.015 J/K at 1500 K. Since it is planned to use two screens to sandwich the coal, we note that the heat content of the screen is 1.5 times that of coal at high temperatures. However, for low rank coals at these temperatures, one expects a mass loss of 40-60%. Hence, the heat content of the screen will always be at least 3 times that of the heated coal.

The third design requirement is to ensure that the coal particles are in contact with the screen. A ceramic baffle will be placed on the top and bottom of the screen. The weight of the ceramic baffle will serve to press the screen and coal together insuring thermal contact with the grid. The baffles in the ceramic will allow the pyrolysis gases to escape.

3.4 Power, Current and Voltage Requirements

The power required to heat the screen is given by

$$P = mC_p \left(\frac{dT}{dt} \right)$$

where m , C_p and $\left(\frac{dT}{dt} \right)$ are mass, heat capacity and heating rate, respectively. Fig. 10 illustrates the power required to heat two SS screens as a function of mass of coal for two different heating rates. In this and subsequent calculations, only the thermal mass of the screens was considered. However, the mass of coal is the parameter since the area of the screen occupied by the

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Fig. 10 Power required to heat two 325 mesh SS screens containing mass m of coal.

closely packed monolayer of coal particles is directly proportional to the mass of coal, e.g., 1 g of 100 μ coal particles will require 200 cm² of surface area. The current and voltage requirements depend on the ratio w/l where w and l are the width and length of the screen respectively. The current is assumed to flow along the direction of l . Figs. 11 and 12 illustrate the current and voltage requirements of the screen.

Consider the case of heating 1 g of coal to 2000 K at a heating rate of 10^4 K/s. From Fig. 10, it is noted that a power of 37.5 kW is to be supplied for 0.17 seconds. The current and voltage requirements depend on the dimensions of the screen. Thus, a screen of 6.3 x 32 cm will require 500 amps and 75 volts whereas a screen of 12.5 x 16 cm will require 1000 amp and 37.5 volts. The voltage and current requirements for W screen are similar to SS304 and are not shown here.

3.5 Description of Apparatus

A convenient source of low voltage and high current is a bank of automobile batteries. A battery bank, a variable resistor and two solenoids in series will be used to control the power input to the screen. One of the solenoids will be normally open and the other normally closed. A delay generator will control the two solenoids and thus the time for which the voltage is applied to the screen.

The screen holder is designed such that the dimensions of the screen can be varied. A chromel-alumel thermocouple spot-welded to the screen will monitor the temperature of the screen. In addition, voltage and current will be monitored on an oscilloscope. The screen assembly is enclosed in a pressure vessel equipped with electrical feed-throughs and several ports for diagnostics. The vessel is connected to a vacuum pump and a gas feed line which enables one to evacuate the vessel and charge with an inert gas such as helium. A schematic of the apparatus is shown in Fig. 13.

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Fig. 11. Current requirements for heating two 325 mesh SS screens containing mass m of coal.

Fig. 12 Voltage requirements for heating two 325 mesh SS screens containing mass m of coal.

Fig. 13 Schematic of the pyrolysis apparatus.

4. SUMMARY

The theoretical task to optimize pore structure with respect to char reactivity has indicated that the total porosity and the distribution of porosity are the most important char characteristics to consider when trying to optimize char oxidation above 800 K. The bench scale experiment designed to achieve the optimum char structure has been designed and will be constructed during the next quarter.

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