The Oxidation of Carbonaceous Residue Dispersed in Porous Retorted Oil Shale

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The oxidation of carbonaceous material dispersed in a porous matrix of an inert solid is important in various processes, including the regeneration of coked catalysts, the firing of ceramics, the combustion retorting of oil shale, and the combustion of ashy coal. This work was mainly concerned with the oxidation of carbonaceous residue taking place in retorted oil shale. During the retorting of oil shale, kerogen is thermally decomposed to produce oil vapor, hydrocarbon gases, and carbonaceous residue. In various aboveground and in situ retorting processes this carbonaceous residue (char) is burned to produce energy for heating the raw shale. The efficient combustion of the carbonaceous residue is an important factor in increasing the oil yield because oil vapor or other supplemental fuels must otherwise be burned to obtain the required energy for retorting. Furthermore, the uniform and rapid combustion of oil shale char is also important in preventing oxygen from reaching the zone of kerogen decomposition where it can burn the valuable oil product.

The combustion of oil shale char in large samples of retorted shale has been studied by a number of invetigators (Dockter, 1976; Dockter and Turner, 1978; Mallon and Braun, 1976). Most of the previous work has been concerned with the combustion of oil shale char at high temperatures. Under these conditions the overall rate is controlled by the diffusion of oxygen through the ash layer. The rate expression for a diffusion-controlled reaction, however, is not capable of predicting the point at which the controlling mechanism shifts from chemical kinetics to diffusion, or vice versa, under different temperatures.

In this paper we report the results of an investigation in which the oxidation of oil shale char was studied experimentally and theoretically. The experiments were carried out under linearly increasing ambient temperature. The maximum temperature was below 1,000 K and thus the carbon dioxide–carbon reaction was unimportant in all the runs.

A mathematical model was formulated to analyze the experimental data. The model incorporates the chemical kinetics, diffusion parallel and perpendicular to the bedding plane, and the heat effects of the oxidation reaction. Chemical kinetics are represented by a global first-order expression for both the oxygen concentration and the amount of char remaining unreacted. Such an expression has been shown to represent satisfactorily the oxidation kinetics of oil shale char (Soni and Thomson, 1978; Sohn and Kim, 1980). The values of diffusivity and thermal conductivity were obtained using correlations proposed by previous investigators, as will be discussed in the text.

MATHEMATICAL FORMULATION

Since oil shale was formed by a sedimentary process and thus has a laminated structure, transport properties are quite different in the directions parallel and perpendicular to the bedding plane. Cylindrical samples with the axes placed perpendicular to the bedding plane were used. In the formulation of the governing equations, the chemical reaction was simplified to

$$C + O_2 = CO_2 \tag{1}$$

at the relatively low temperature studied in this work. Because of this simplification of oxidation reaction, the mathematical model presented here will be applicable to an oil shale piece that is completely retorted without much hydrogen-containing species. Effective diffusivities and thermal conductivities in the radial and axial directions and porosity were assumed constant.

Within the framework of the above assumptions, the problem may be stated by combining the mass balance equation for oxygen, the energy balance equation, and the mass balance equation for the solid reactant.

The mass balance equation for oxygen is as follows:

$$D_{er}\frac{\partial^2 x_A}{\partial r^2} + \frac{D_{er}}{r}\frac{\partial x_A}{\partial r} + D_{ez}\frac{\partial^2 x_A}{\partial z^2} - v_A\frac{RT}{P} = \epsilon\frac{\partial x_A}{\partial t} \tag{2}$$

Here we assumed that CD_{er} and CD_{ez} and, therefore, PD_{er}/RT and PD_{ez}/RT are constant.

The energy balance equation is as follows:

$$k_{er}\frac{\partial^2 T}{\partial r^2} + \frac{k_{er}}{r}\frac{\partial T}{\partial r} + k_{ez}\frac{\partial^2 T}{\partial z^2} + (-\Delta H)v_A = \rho c_p\frac{\partial T}{\partial t} \tag{3}$$

in which k_{er} and k_{ez} have been assumed constant. The mass balance for carbonaceous residue obtained from a Green River oil shale can be written as follows (Sohn and Kim, 1980):

$$\frac{\partial w}{\partial t} = Ae^{-E/RT}px_A(1-w) \tag{4}$$

The expression for v_A can be obtained by considering the stoichiometry and the apparent density of the retorted shale, as given below:

$$v_A = \alpha_B\rho_B\frac{\partial w}{\partial t} = \alpha_B\rho_B Ae^{-E/RT}px_A(1-w) \tag{5}$$

Equations 2 to 5 represent the complete statement of the problem. The boundary and initial conditions for these equations are as follows:

$$\text{at } r = R_P \quad x_A = 0.21, \quad T = T_b \tag{6}$$

$$\text{at } z = H \quad x_A = 0.21, \quad T = T_b \tag{7}$$

$$\text{at } r = 0 \quad \frac{\partial x_A}{\partial r} = 0, \quad \frac{\partial T}{\partial r} = 0 \tag{8}$$

$$\text{at } z = 0 \quad x_A = 0.21, \quad T = T_b \tag{9}$$

$$\text{at } t = 0 \qquad x_A = 0.21, w = 0 \qquad T = T_0 \tag{10}$$

A sufficiently large flow rate of air was used in the experiment to eliminate external mass and heat transfer effects as specified by Eqs. 6, 7, and 9.

The solution of Eqs. 2 to 5, together with the boundary and the initial conditions 6 to 10, yields x_A, T, and w as functions of r, z, and t. The overall conversion, which is of greater practical interest, may be obtained from the following relationship:

$$X = \frac{\int_0^H \int_0^{R_p} 2\pi r w dr dz}{\int_0^H \int_0^{R_p} 2\pi r dr dz} = \frac{\int_0^H \int_0^{R_p} 2\pi r w dr dz}{\pi R_p^2 H} \tag{11}$$

EXPERIMENTAL APPARATUS AND PROCEDURE

The oxidation of char in retorted shale was followed using a typical thermogravimetric analysis apparatus (Szekely et al., 1973, 1976). The sample holder was made of a thin nichrome wire. The temperature close to the sample was monitored by means of platinum/platinum-rhodium thermocouples. The reactor consisted of two coaxial cylinders. The reactant gas was preheated in the annular space before flowing past the sample. This minimized the temperature difference between the inner tube and the sample and thus the effect of radiation on temperature reading.

The oil shale used in this work came from the Anvil Points mine in Colorado, and its Fischer assay grade was 0.21 dm^3/kg. Specimens were obtained by coring the raw shale perpendicular to the bedding plane. The "core" was cut to cylinders of equal height and length and those whose heights were one-half the diameters. Retorted shale containing carbonaceous residue was prepared by completely retorting cylindrical samples of raw shale in nitrogen atmosphere under an increasing temperature (0.083 K/s) up to 773 K (Sohn and Kim, 1980). Samples containing 7 to 9% carbonaceous residue were obtained by this procedure. The samples were heated under flowing air at a constant heating rate and the oxidation reaction was followed by continuously recording the weight change.

PARAMETER VALUES USED IN THE MATHEMATICAL MODEL

The pre-exponential factor A and the activation energy E in Eq. 4 were obtained previously (Sohn and Kim, 1980) to be 2.47×10^3 (s·kPa)$^{-1}$ and 92,300 J/mol, respectively.

The effective diffusivity of oxygen in the r direction, D_{er}, was obtained using the correlation reported by Mallon and Braun (1976). Thus, for the 0.21 dm^3/kg grade shale used in this work, $D_{er} = 0.363$ cm^2/s. Mallon and Braun (1976) also reported that the effective diffusivity perpendicular to be bedding plane is about one-half that parallel to the bedding plane. Thus, $D_{ez} = D_{er}/2$.

The porosity of retorted shale was obtained using the relation reported by Dockter and Turner (1978), which gives $\epsilon = 0.56$ for $F = 0.21$ dm^3/kg.

Values of the thermal conductivities, k_{er} and k_{ez}, of retorted shale were obtained from the correlations by Tihen et al. (1968) as functions of raw shale grade and temperature. They presented k_{er} and k_{ez} for burnt shale (after char is burned away) and retorted shale (containing char), the former being approximately half that of the latter. Therefore, in this work k_{er} and k_{ez} were expressed in terms of the local concentration of char by interpolation (Kim, 1980).

The heat capacity of retorted shale, compiled by Carley (1975), is

$$c_p = 0.828 + 9.2 \times 10^{-4}(T - 298) \text{ kJ/(kg·K)} \tag{12}$$

The density of retorted shale ρ is 1.9 kg/dm^3 and $(-\Delta H) = 393$ kJ/mol, assuming the heat of combustion of graphite. From the amount of char obtained $\alpha_B \rho_B = 12.7$ mol/dm^3.

COMPARISON OF EXPERIMENTAL RESULTS WITH MODEL PREDICTIONS

Experiments were carried out with cylindrical retorted shale samples of equal height and diameter of 1.588 cm and also with samples of 1.588 cm dia. and 0.794 cm height. Three different heating rates were used, starting at 553 K. The reaction rate is negligible below this temperature. A sufficiently large flow rate of air was used to eliminate external mass and heat transfer effects. The governing partial differential equations were solved by a finite-difference method detailed in Kim (1980).

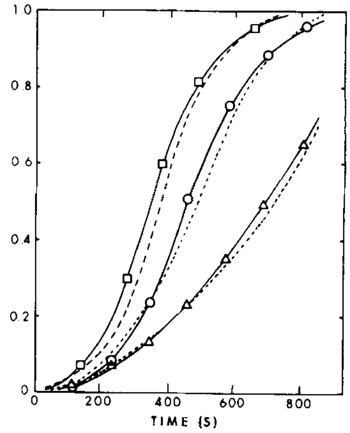

Figure 1. Comparison between the calculated and the measured results (-□- $R_p = 2H = 1.59$ cm, heating rate = 0.23 K/s; -O- $R_p = H = 1.59$ cm; heating rate = 0.28 K/s; -Δ- $R_p = H = 1.59$ cm, heating rate = 0.1 k/s; ---- model prediction).

Figure 1 shows the comparison between the calculated and the measured conversion vs. time relationships under different heating rates. In these experiments, conditions were so chosen that the controlling mechanism switched from chemical kinetics at low temepratures to diffusion at higher temperatures. This assured the severest test of the validity of the model. The good agreement indicates that the model is valid regardless of the controlling mechanism. Shown in Figure 2 is the comparison between the calculated and measured temperatures at the center and at one-half the radius from the center of the pellet. As can be seen, there is a significant temperature gradient inside the sample. From the good agreement seen in these figures, we can conclude that the mathematical model gives a good representation of the oxidation process over the entire range of experimental conditions.

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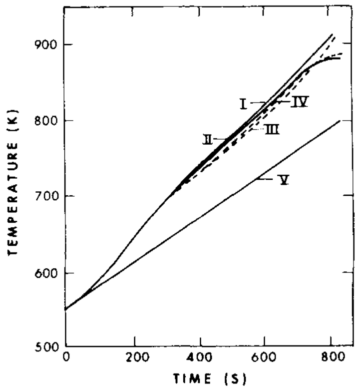

Figure 2. Comparison of the calculated and measured temperatures at the center and at one-half the radius from the center of the pellet ($R_p = H = 1.59$ cm; heating rate = 0.28 K/s; *I* measured—center; *II* measured—half radius; *III* model prediction—center; *IV* model prediction—half radius; *V* measured—bulk).

NOTATION

C = total concentration of gas
D_{er}, D_{ez} = effective diffusivity in the r and the z directions, respectively
E = activation energy
H = height of the cylindrical samples
$(-\Delta H)$ = heat of reaction
k_{er}, k_{ez} = effective thermal conductivity in the r and z directions, respectively
P = total pressure
r = radial coordinate
R_p = radius of the cylindrical sample
T_b = bulk-gas temperature
T_o = initial temperature of the solid
v_A = local consumption rate of oxygen per unit volume
w = local value of the fractional consumption of carbon
x_A = mole fraction of oxygen
X = overall conversion of solid reactant
z = axial coordinate
$\alpha_B \rho_B$ = apparent concentration of carbon
ϵ = porosity
ρ = density

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