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Effects of Catalytic Mineral Matter on CO/CO₂
Temperature and Burning Time for Char Combustion

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Introduction

The high temperature oxidation of char is of interest in a number of applications in which coal must be burned in confined spaces. These include: the conversion of oil-fired boilers to coal using coal-water slurries, the development of a new generation of pulverized-coal-fired cyclone burners, the injection of coal into the tuyeres of blast furnaces, the use of coal as a fuel in direct-fired gas turbines and in large-bore low-speed diesels, and entrained flow gasifiers. In addition, there is a need to understand the temperature history of char particles in conventional pulverized-coal-fired boilers to better explain the processes governing the formation of pollutants and the transformation of mineral matter.

The temperature of char particle burning is the product of a strongly coupled balance between particle size and physical properties, heat transfer, surface reactivity, CO/CO₂ ratio and gas phase diffusion in the surrounding boundary layer and within the particle. In addition to the effects of particle temperature on burning rate, it has major effects on ash properties and mineral matter vaporization. Measurements of the temperature of individual burning char particles have become available in recent years and have clearly demonstrated large particle-to-particle temperature variations which depend strongly on particle size and on particle composition. These studies, done with pulverized coal, can not determine the CO/CO₂ ratio produced at the char surface or the catalytic effects of mineral matter in the individual char particles. Consequently, it has generally been assumed that CO is the only product of the carbon-oxygen reaction and that CO₂ is formed by subsequent gas phase reaction. More recent work, however, has pointed out the need to take CO₂ production into consideration in order to account for observed particle temperatures.

The importance of the CO/CO₂ ratio of carbon oxidation products is illustrated by examination of the heats of reaction for formation of these two products:

The heat released by formation of CO₂ is a factor of 3.5 higher than for CO so the temperature of a particle will depend strongly on the CO/CO₂ ratio produced. If gas diffusion through the boundary layer is fast, increased direct production of CO₂ produces a higher temperature and a higher burning rate. If the supply of oxygen to the surface is limited by diffusion through the boundary layer, production of CO₂ consumes half as much carbon as production of CO so carbon consumption rate is reduced even though temperature may be somewhat higher.

A energy balance model for predicting temperature history has been reported earlier. In this report, further refinement of this model by adopting advanced heat and mass transfer model is reported. Also, comparisons with the results from fluidized bed experiments are made to derive proper reaction kinetics parameters.

Experiment

The experiment were performed in a small fluidized bed quartz reactor. The procedures of experiment have been published (C.J. Tullin et. al). A bed of SiO₂ sand was fluidized with He/O₂ mixtures. Batches of four 4 mm size coal particles were reacted, and off-gas composition was monitored as a function of time. Different oxygen pressures (4-20%) and gas temperatures (1023-1123K) were examined.

The experimental conditions used are following.

- * $V_{mf} = 2.5 \text{ l/min}$ (minimum fluidizing volume flow rate)
- * $U_o = 2.5 U_{mf}$ (superficial velocity)
- * $z_o = 5 \text{ cm}$ (fixed bed height)
- * $d_p = 180 \text{ }\mu\text{m}$ (bed particle diameter)

Modeling

Our objective is to develop a model to reproduce the major features in the experiments. The assumptions made in the model are: (1) Uniform temperature inside the particle. (2) Constant bed gas temperature. (3) A power law relationship between density, diameter, and conversion.

These assumptions enable us to use a simple lumped parameter model. The main energy balance can be set up as in the following equation:

$$mC_p \frac{dT}{dt} = r_c(-\Delta H)A - hA(T-T_g) - \sigma \epsilon A(T^4 - T_g^4) \quad (1)$$

The following sections include the theories and the equations for each parameters and variables.

I. Heat of reaction

We can calculate the heat of reaction as a function of the fraction X_{CO} of the products appearing as CO. The temperature dependence can be calculated from C_p data. Based on experimental results, X_{co} (CO reaction fraction) was set as 0.01 (almost all CO oxidized to CO_2 in the gas phase until the end of the reaction).

$$-\Delta H = [(-\Delta H_{CO}) X_{CO} + (-\Delta H_{CO_2})(1-X_{CO})] 4.184/M_c \quad [\text{J/g}] \quad (2)$$

II. Density and diameter

The relationship between normalized apparent density and normalized particle density can be represented as a power law (Waters,1988). For the carbon used in this fluidized bed experiment, the values of a , b are approximated to be 0.25.

$$\frac{\rho}{\rho_o} = \left(\frac{m}{m_o}\right)^a \quad (3)$$

$$\frac{d}{d_o} = \left(\frac{m}{m_o}\right)^b \quad (4)$$

III. Surface area

The surface area [cm^2/gC] which is responsible for the reaction is not yet clear. But it has been generally accepted using micropore surface area measured by CO_2 adsorption (Dudek,1989) or BET N_2 method. The measurement of surface area variation during the reaction is available from Dudek and also from Waters. Usually pore surface area has a maximum around conversion of 0.1 and decreases monotonically. We used the normalized distribution for spherocarb and multiplied it by $500 \text{ m}^2/\text{g}$ for this case.

$$S_g = 500.0 \cdot 10^4 \cdot (1.0 + 2.89 \cdot x - 29.62 \cdot x^2 + 122.67 \cdot x^3 - 275.08 \cdot x^4 + 339.27 \cdot x^5 - 1216.26 \cdot x^6 + 555.65 \cdot x^7) \quad [\text{cm}^2/\text{g}] \quad (5)$$

IV. Heat and mass transfer

To calculate heat and mass transfer coefficients, we used non-steady state theory which is based on the frequency of the renewal of oxygen at the surface of the particle (La Nauze). This term is composed of two factors; one is from gas convective component and the other is from particle convective component. The gas convective renewal frequency can be easily understood. The particle convective component proposes more refinement. It is, however, appropriate for the vigorous fluidized bed with much bigger particles comparing to bed particles.

$$f = f_g + f_p = \frac{U_{mf}}{\varepsilon_{mf} d} + \frac{u_b}{d} \quad (6)$$

$$k_g = 2 \frac{D_g \epsilon_{mf}}{d} + \left(\frac{4 D_g \epsilon_{mf} f}{\pi} \right)^{1/2} \quad (7)$$

$$h = 2 \frac{k}{d} + \left(\frac{4 k^2 f}{\pi \alpha} \right)^{1/2} \quad (8)$$

Bubble diameter and bubble rising velocity can be calculated from following equations.

$$d_b = \frac{0.54}{g^{1/5}} (U_s - U_{mf})^{2/5} (z + 4 \sqrt{A_o})^{4/5} \quad (9)$$

$$U_b = U_o - U_{mf} + 0.711 (g d_b)^{1/2} \quad (10)$$

IV. Effectiveness factor

In order to calculate the effectiveness factor, we need to know the tortuosity and porosity as a function of conversion. Here we assume tortuosity to have a constant value of 3 during the reaction. Porosity as a function of conversion can be calculated from the power law relationship of density to the mass. The Thiele modulus for first order intrinsic reaction is

$$\phi = \frac{d}{6} \sqrt{\frac{\rho S_g k_s R T}{D_e \chi}} \quad (11)$$

For the zero order intrinsic reaction it is

$$\phi = \frac{d}{6} \sqrt{\frac{\rho S_g k_s}{D_e C_s \chi}} \quad (12)$$

and for the half order intrinsic reaction it is

$$\phi = \frac{d}{6} \sqrt{\frac{\rho S_g k_s}{D_e C_s^{1/2} \chi}} \quad (13)$$

Where χ is gram of carbon reacted per one mole of oxygen. The mean diffusivity is calculated from bulk gas diffusivity and Knudsen diffusivity. Then effective diffusivity

can be calculated by multiplying the porosity to the mean diffusivity and dividing it by the tortuosity. The effectiveness factor is calculated from the following equation.

$$\eta = \frac{1}{\phi} \left(\frac{1}{\tanh(3\phi)} - \frac{1}{3\phi} \right) \quad (14)$$

Discussion

Fig.1 shows the general shape of the temperature and conversion curves during the reaction. This case is for an intrinsic reaction order of one and 8% oxygen partial pressure. The shape of the temperature curve depends on the diameter of the particle, the oxygen partial pressure, and the surrounding gas temperature. For the conditions used in the experiment, the temperature rises suddenly in a short time period (initial temperature rise), then decreases slowly with increasing conversion (pseudo steady state). After conversion reaches a value of about 0.9, the temperature falls steeply till total conversion (steep temperature drop). Conversion increases very steadily until 0.9 and, after that, the conversion slowly increases toward unity. Increasing oxygen partial pressure increases the initial temperature rise (or excess temperature, ΔT), so does increasing surrounding gas temperature. The effects of changing particle size on excess temperature are not clear. It seems that there exist an optimal size to get a maximum value of excess temperature. This will be investigated further. Depending on conditions, the temperature can increase after the initial temperature rise. The relative magnitudes of the heat generation and heat loss terms determine the shape of the carbon conversion curve.

We can compare the calculated conversion curves with measured values at different oxygen partial pressure to find out the actual intrinsic reaction order. The order of the intrinsic reaction is between zero and one. Fig. 2 shows that the use of first order in the model predicts a broader spectrum of conversion curves than the measured values

as oxygen partial pressure changes. We used Smith's reaction rate of $305\exp(-42/RT)$ as a first order reaction coefficient. Fig.3 shows the comparison for the zero intrinsic order case at $T_g=1023K$. The apparent reaction order for oxygen should be a little above 0.5. The best fit of the experimental results using zero order at 1023K was obtained with a rate coefficient of $5.4 \cdot 10^{-4}\exp(-20/RT)$.

However, the results are not as sensitive to changes in activation energy as to changes in the order of reaction. Fitting the results with a rate of $1.06\exp(-36/RT)$ also shows a fair fit. Because there are particle-to-particle variations in reactivity and experimental error, we need a large database to determine the exact reaction rate coefficient and reaction order. For the experimental conditions (1023-1123K, 4-12% O_2), a rate coefficient of $4.5-5.4 \cdot 10^{-4}\exp(-20/RT)$, for a zero order, is not a bad choice. We need to use lower pre-exponential factor ($4.5 \cdot 10^{-4}$ at 1123K) for high surrounding gas temperature. This may be due to the loss of reactivity by graphitization (R.H. Hurt). The loss of reactivity seems to be proportional to the gas temperature rise and the length of time the particle stays in the reactor.

Fig.4 shows the results of experiment and modeling for oxygen partial pressures ranging from 2% to 20% at 1073K. Using a zero order does not fit the data well at 1073K. The discrepancy between the modeling and experimental results may be due to the wrong choice of activation energy and intrinsic reaction order. Another possibility, however, is that the reactivity decreased during the reaction. Because the total conversion time for 2% oxygen is about 2500 sec (more than 40 min), the carbon particle may have enough time to suffer physical structural changes losing its reactivity. Further studies are needed to assess this effect.

Overall, using a half order for the intrinsic reaction fits the experimental results best. Using a pre-exponential factor of 0.35 and an activation energy of 20 kcal/mol gives an excellent fit of the experimental results at 1073K for the oxygen partial pressure ranging from 2% to 20%. These constants fit the data obtained at other temperatures quite

well. However, the 4% oxygen data at 1023K are not fitted as well, possibly due to experimental error in controlling the surrounding gas temperature or oxygen partial pressure.

Future work

Further refinement of model by adopting mechanical heat and mass transfer model developed by Linjewile and Agarwal will be made and comparisons with experimental results will be reported. Once the char oxidation model is optimized, the associated data on CO/CO₂ ratios will be analyzed.

Particle temperature and Conversion

($P_{O_2} = 0.08$)

Fig.1 Temperature and conversion curves during the reaction

Conversion at different O_2 partial pressure
($T_g=1023\text{ K}$, $d_o=4\text{ mm}$)

Fig.2 Comparison of modeling and experimental results
(1st order, Smith's kinetics)

Conversion at different O₂ partial pressure

(Zero order, $A_o = 5.4 \times 10^{-4}$, $E_a = 20 \text{ kcal}$, $T_g = 1023 \text{ K}$)

Fig.3 Comparison of modeling and experimental results

Conversion at different O_2 partial pressure

(Zero order, $T_g = 1073K$, $A_o = 4.8 \times 10^{-4}$, $E_a = 20kcal$)

Fig.4 Effect of oxygen partial pressure ($T_g = 1073K$)

Conversion at different O_2 partial pressure

(Half order, $A_o = 0.35$, $E_a = 20\text{kcal}$, $T_g = 1073\text{K}$)

Fig.5 Effects of oxygen partial pressure (half order intrinsic reaction)

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