COMBUSTION BEHAVIOR OF CHAR/CARBON PARTICLES

K. ANNAMALAI
Division of Engineering, Brown University, Providence, RI

AND

P. DURBETAKI
Fire Hazard and Combustion Research Laboratory, School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, GA

An observed phenomenon in the burning of char/carbon is the occurrence of a maximum erosion rate at a particular particle temperature. A hypothesis is made that the relative chemical kinetics of CO production and its subsequent oxidation in the gas phase could be responsible for the occurrence of a maximum burning rate. Numerical solutions for the burning rate of char/carbon/graphite particles undergoing two step oxidation processes and one reduction process, are obtained as a function of the particle temperature. Peak burning occurs, confirming the present hypothesis. However, such peak burning requires a combination of heterogeneous and homogenous kinetic schemes. A parametric study is carried out for the variation of the peak burning particle temperature with the particle size and pressure of the system. An approximate solution shows that the peak burning temperature is a logarithmic function of (particle size)^3/4 x (pressure)^7.

1. Introduction

With coal as a fuel in conventional and future power systems, the prediction of ignition and combustion behavior of coal/char particles becomes increasingly important. Particularly, the research on high temperature oxidation of char/carbon assumes a special significance in view of recent activities in the development of MHD power generation. Unlike the combustion of liquid droplets where the rate governing process is essentially diffusion, for the case of small particles (less than about 200 μm) the rate controlling process, to a significant level, is the chemical kinetics. A liquid droplet remains cooler than the surroundings because of the endothermicity of evaporation. The coal particle remains hotter due to heterogeneous exothermic gasification process (if oxidation reaction is dominant over reduction). A heterogeneous reaction is dependent on available reaction surface area which in turn is influenced by many parameters including reaction depth, intraparticle diffusion, external diffusion, pressure, and temperatures. The order of reaction is oxygen concentration dependent and the product of surface oxidation is temperature dependent.

Most of the earlier theoretical analyses and subsequent experimental comparisons have been carried out on char or graphite particles. Experiments conducted on heated graphite rods and filaments in low pressure oxidant atmospheres and carbon reduction with carbon dioxide have shown the existence of a peak reaction rate at some temperature. The existence of this peak reaction rate may be possible to explain in terms of (i) chemical processes, (ii) physical processes (transport of mass and heat), and (iii) particle surface and ambient conditions (i.e. experimental conditions).

Strickland-Constable used the chemical kinetics approach and thus proposed a "site theory" which also assumes overall variable activation energy for surface oxidation. Blyholder et al. developed a similar site theory. The variation in overall activation energy has been confirmed experimentally at very low pressures. On the other hand, Yang and Steinberg postulated that the peak reaction behavior may be due to varying reaction depth while the activation energy remains constant. For char particles burning in normal atmospheres, the gas phase oxidation is significant and mass transport processes to the particle surface assume a special significance.

169
Coupled with the experimental result that the peak burning behavior occurs even at normal pressures and that the peak burning rate is sandwiched between the limiting diffusion rates of CO and CO₂ production at the surface, the following hypothesis (based on external processes) is made. (i) Given a particle which produces only CO at the surface and gas phase oxidation of CO is negligible. Then for every mole of oxidant diffusing, there are two carbon atoms removed from the surface. This is called a CO-dominated case (CO-DC). (ii) Given that the gas phase oxidation is also equally fast, at higher temperatures, it appears as though all CO₂ is produced near the surface. Then for every mole of oxidant diffusing, only one-half of the mole is filtered through the gas oxidation zone to the surface and hence one carbon atom is removed from the surface. This is called a CO₂-dominated case (CO₂-DC). (iii) A peak burning rate may occur depending upon the relative chemical kinetics of heterogeneous and gas phase oxidations. The kinetics of coal/char may vary depending upon the particle size, pore size and structure, coal rank, surface activity (adsorption/desorption), composition of basic constituents, etc. Thus, a relatively fast heterogeneous reaction followed by a slow gas phase oxidation (CO burn up) can lead to a peak burning rate. The simplest problem is initially to treat the burning process with constant activation energy both for the heterogeneous and the gas phase reactions.

2. Problem Formulation

A carbon particle, uniformly heated by some external source to different surface temperatures is considered. (This assumption of uniform temperature limits the particle size.) Two oxidation regimes exist, one at the surface where the carbon oxidizes to CO and one in the gas phase where the CO oxidizes the CO₂. Oxygen diffuses to both oxidation zones. Carbon dioxide from the gaseous oxidation regime diffuses both towards the solid surface and away into the oxidizing atmosphere. The governing equations are reduced subject to the following assumptions.

(i) Spherical symmetry exists.
(ii) The heterogeneous oxidations are lumped on the external surface with an overall kinetics. All surface reactions including the reduction of solid carbon produce only CO at high temperatures. This assumption is consistent with the relative production rates of CO and CO₂. The production of CO follows a first order law with respect to oxygen and CO₂ concentrations (pressure less than 15 atm) in the temperature range considered here. The oxidation reaction in the gas phase appears to follow a second order when Y₂ < 5% and a first order when Y₂ > 5%. (v)
(iv) No sublimation occurs within the temperature of interest.
(v) The particle is heated (i.e., inductively) at constant pressure to a specified temperature in a cold gas. The motivation behind this assumption is that the earlier studies were carried out on cylindrical graphite rods heated to specified temperatures in cold surroundings.
(vi) All reaction rates are described by Arrhenius law. A monotonic linearly varying activation energy can be accommodated in the general expressions.
(vii) Lewis number is unity.

3. Governing Equations

Conservation Equations:

Mass

\[ \dot{m} = 4\pi r^2 \dot{v} = \text{constant} \quad (1) \]

Species

\[ \rho \nu \frac{dY_i}{dr} = \frac{1}{r^2} \frac{d}{dr} \left( r^2 \rho D \frac{dY_i}{dr} \right) + \dot{m}_i''', \quad i = \text{CO}, \text{CO}_2, \text{O}_2 \quad (2) \]

Energy

\[ \rho \nu \frac{dh_i}{dr} = \frac{1}{r^2} \frac{d}{dr} \left( r^2 \rho D \frac{dh_i}{dr} \right) - \dot{m}_i'' \omega_{i} \quad (3) \]

Reaction Kinetics:

At the particle surface due to oxidation reaction C(s) + 1/2 O₂ → CO

\[ \dot{m}_{c(s)} = \Lambda_{c(s)} (1 + v) e^{-\nu_{i} + \nu_{f} / RT} C_{c(s)} \quad (4) \]

At the particle surface due to reduction C(s) + CO₂ → 2CO

\[ \dot{m}_{c(s)} = \Lambda_{c(s)} (1 + v) e^{-\nu_{i} + \nu_{f} / RT} C_{c(s)} \quad (5) \]

In the gas phase CO + 1/2 O₂ → CO₂

\[ \dot{m}_{c(g)} = \Lambda_{c(g)} e^{-\nu_{i} + \nu_{f} / RT} C_{c(g)} C_{O_2} C_{CO_2} \quad (6) \]

Also

\[ \dot{m} = \dot{m}_{c(s)} + \dot{m}_{s(s)} + \dot{m}_{c(g)} \quad (7) \]

†Numerical calculations account only for external surface reaction. The approximate method given in later sections can account for volume reaction if surface area of reaction per unit volume is known as a function of temperature from experimental data.
The boundary conditions for solving Eqs. (2) and (3) are given by Eqs. (4) and (5) with known \( T_\infty \) and

\[
\text{as } r \to \infty: \quad T \to T_\infty, \quad Y_O \to Y_{O,in}, \quad Y_CO \to 0, \quad Y_{CO_2} \to 0
\] (8)

Using normalized parameters\[^{22,23}\] Eqs. (1)–(3) are transformed to yield

\[
\frac{d^2 \phi}{d \eta^2} + \xi_w \frac{d \phi}{d \eta} = 0
\] (9)

and

\[
\frac{d^2 Y_{CO}}{d \eta^2} + \xi_w \frac{d Y_{CO}}{d \eta} = \frac{D_{\text{eff}} e^{-1/4} Y_O Y_{CO} Y_{H} / \eta^{3/2}}{\eta^{3/2}}
\] (10)

The transformed boundary conditions are

at \( \eta = 1 \): \( \phi = 1, Y_{CO} = Y_{CO,in}(T_\infty, \xi_w), \xi_{CO} \)

\( = \epsilon_{CO,in}(T_\infty, \xi_w) \) (11a)

at \( \eta = 0 \): \( \phi = 0, Y_{CO} = Y_{CO,in} \) (11b)

Equation (9) is solved explicitly subject to the conditions given by Eqs. (11a,b) to give

\[
\phi = \frac{(1 - e^{-\gamma \tau})}{(1 - e^{-\xi \tau})}
\] (12)

From the definitions of \( \phi, \beta_{in}, \) and \( \beta_{in}, \) the parameters \( h_\gamma, Y_\infty, \) and \( Y_{CO,0} \) are known in terms of wall conditions, ambient conditions and burning rate. The wall mass fractions are found by matching the flux fractions and Eq. (12) with flux fractions given by finite kinetic reactions, Eqs. (4) and (5). Thus

\[
Y_{CO,0}(T_\infty, \xi_w) = \left[ \frac{1 + \nu_s}{\nu_s + \nu_e} \right] \left[ 1 + \nu_s + \nu_e \nu_s \right] - \frac{\epsilon_{CO,in}(T_\infty, \xi_w)}{\nu_e}
\] (13)

\[
\epsilon_{CO,0}(T_\infty, \xi_w) = \left[ \frac{1 + \nu_s}{\nu_s + \nu_e} \right] \left( \frac{1 + \nu_s + \nu_e \nu_s}{\nu_e} \right) - \frac{\epsilon_{CO,in}(T_\infty, \xi_w)}{\nu_e}
\]

4. Numerical Method of Solution

The method of solution is a modified initial value method for fast convergence, following the procedure of Nachstein and Swigert.\[^{44}\] For a prescribed \( \theta_w \), an eigenvalue \( \xi_w \) is assumed such that the wall mass fractions lie within the range of zero and unity. Using Adams-Moulton integration formula,\[^{45}\] and starting conditions as prescribed by Eqs. (11a), (13) and (14), the mass fraction \( Y_{CO} \) is obtained at \( \eta = 0 \). This value is then compared with the imposed condition as given by Eq. (11b). Also, the temperature \( \theta \) approaches \( \theta_w \) as \( \eta \to 0 \). Thus with a single unknown \( \xi_w \) there are two forcing conditions. Expansions of \( Y_{CO,0} \) and \( \theta_{in} \), using Taylor series, are carried out including the remainder terms. The quantity \( \xi_w \) is then obtained while the sum of the squares of the two remainder terms is minimized. To evaluate the derivatives, corresponding perturbation equations are established and integrated.

5. Results and Discussion

The quantitative kinetics of the three reactions presented in Eqs. (4)–(6) are required for the determination of combustion characteristics. The mechanisms of these reactions are well explained in the literature survey by Walker et al.\[^{21}\] and Howard et al.\[^{11}\] The chemical kinetics constants for the heterogeneous and gas phase oxidations are listed in Table I. The results presented follow with the combination of kinetic constants listed in Table II.

5.1. Variation of Burning Rates

Figure 1 presents results of the burning rate for char and carbon particles. For the burning of carbon particles, if \( CO_2 \) reduction is dominant and CO oxidation is slow, at high temperatures no peak may result. Figure 2 gives corresponding curves for brown coal particles. Although the analysis is doubtful for brown coals, the results are included for the reason that the kinetic constants of this coal give rise to a rather pronounced peak and one can obtain the results for a wide range of parameters
TABLE I
Chemical kinetics constants \((T_e = 300 \text{ K}, \rho D = 0.67 \times 10^3 \text{ g/cm}^3 \text{ s})\)

<table>
<thead>
<tr>
<th>No.</th>
<th>Reactant</th>
<th>Rate Equation</th>
<th>(k^{(2)})</th>
<th>(E\text{, kJ/g-mole})</th>
<th>(D_{HI}^{(2)}) (100 (\mu m) &amp; 1 atm)</th>
<th>Part. Size, (\mu m)</th>
<th>Temp., K</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Brown Coal (\rho_0, \text{ atm})</td>
<td>37.8</td>
<td>56.5</td>
<td>47</td>
<td>200 — [24]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Coal Char (\rho_0)</td>
<td>8710</td>
<td>150</td>
<td>4720</td>
<td>25–100 1000–2000 [19]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Brush Carbon (\rho_0)</td>
<td>24720</td>
<td>184</td>
<td>12510</td>
<td>— — [4]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Carbon (\rho_0, \text{ K/cm}^3)</td>
<td>(1.9 \times 10^8)</td>
<td>198</td>
<td>173000</td>
<td>plate, stag. 900–1200 [18]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Bituminous Char (\rho_0)</td>
<td>8.0</td>
<td>67</td>
<td>10</td>
<td>34–60 1200–2300 [16]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Anthracite Char (\rho_0)</td>
<td>10.0</td>
<td>69.9</td>
<td>12</td>
<td>42–72 1200–2300 [16]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Petroleum Coke (\rho_0)</td>
<td>20.0</td>
<td>76.2</td>
<td>21</td>
<td>4–77 1200–2300 [16]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Carbon (\rho_0)</td>
<td>4.1 \times 10^{11}</td>
<td>247.9</td>
<td>(1.3 \times 10^7)</td>
<td>— — [19]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Char (\rho_0)</td>
<td>3.2 \times 10^{10}</td>
<td>248.0</td>
<td>85100</td>
<td>— — [19]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10a</td>
<td>Pitch Coke (\rho_0)</td>
<td>63.4</td>
<td>168.3</td>
<td>35</td>
<td>1040 1300–1600 [17]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10b</td>
<td>Pitch Coke (\rho_0)</td>
<td>63.4</td>
<td>168.3</td>
<td>0.6 est.</td>
<td>1040 1300–1600 [17]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>CO (\rho_0)</td>
<td>9.5 \times 10^{7}</td>
<td>125.6</td>
<td>68</td>
<td>— — [20]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>CO (with H2O, O2) (\rho_0)</td>
<td>1.3 \times 10^{-4}</td>
<td>125.6</td>
<td>3800 est.</td>
<td>— 840–2400 [21]</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^{(1)}\) No. 1–7: Heterogeneous Oxidation, No. 8–10a: Heterogeneous Reduction, No. 11–12: CO Oxidation.

\(^{(2)}\) Rate equations are as used in the quoted references; \(m^2/\text{ke} / \text{RT}\) for heterogeneous reactions, \(m^2/\text{ke} / \text{RT}\) for gas phase oxidation.

\(^{(3)}\) Units of \(k\) are \(g/(cm^2 \cdot s \cdot \text{atm})\) for No. 1–3, 5–7, 10a, 10b; \(\text{cm}^3/\text{s}\) for No. 4, 8, 9; \(1/\text{s}\) for No. 11; \(\text{cm}^3/(\text{mole s})\) for No. 12.

\(^{(4)}\) Damköhler numbers computed after rate equations were converted into the form given by Eqs. (5)–(7).

TABLE II
Combination of kinetic constants used in the numerical calculations

<table>
<thead>
<tr>
<th>Scheme</th>
<th>Numbers from Table I</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>4 + 10b + 12</td>
</tr>
<tr>
<td>II</td>
<td>4 + 9 + 12</td>
</tr>
<tr>
<td>III</td>
<td>7 + 10b + 11</td>
</tr>
<tr>
<td>IV</td>
<td>6 + 10b + 11</td>
</tr>
<tr>
<td>V</td>
<td>5 + 10b + 11</td>
</tr>
<tr>
<td>VI</td>
<td>1 + 10b + 11</td>
</tr>
<tr>
<td>VII</td>
<td>4 + 10a + 12</td>
</tr>
<tr>
<td>VIII</td>
<td>1 + 10a + 11</td>
</tr>
</tbody>
</table>

which then lead to the prediction of burning characteristics for any char particle with a similar behavior.

The regions in the burning rate behavior are shown in Fig. 2. Region X corresponds to a CO-DC. One can obtain the activation energy for the production of CO in this region since the plot exhibits almost a linear behavior. Here the oxidation of CO is negligible.

Region Y exhibits the influence of gas phase oxidation.
oxidation of CO on the burning rate. The reduction of \( Y_{\text{co},w} \) occurs both due to heterogeneous oxidation and the gas phase oxidation of CO. The increase in the rate due to heterogeneous production of CO almost equals the gas phase oxidation of CO.

Region 2 shows the dominance of gas phase oxidation of CO over the production of CO at the surface. The burning rate approached a value similar to the diffusion limit for the direct CO\(_2\) product at the surface. Thus the peak occurrence is an indication that the particle is still producing a significant amount of CO. Figure 2 also shows the consequence of the assumption of second order gas phase reaction with a corresponding reduction in the Damköhler number.

Since the CO oxidation becomes rapid at some temperature, one would expect that the wall mass fraction of CO would also show a peak. Figure 3 shows that such a peak is exhibited by CO. The temperature corresponding to the peak burning rate is always higher than the one corresponding to the peak wall mass fraction of CO. Such a behavior is expected since this is just a precursory event of impending occurrence of peak burning rate. Also,

![Diagram](image)

**Fig. 2.** Burning Rate as a Function of the Surface Temperature for Brown Coal, 100 \( \mu m \), 1 atm; \( n_{\text{co}} = 1.0, n_{\text{o}} = 0, D_{\text{diff}} = 68.0 \) (Scheme VI); \( n_{\text{co}} = 1.0, n_{\text{o}} = 1.0, D_{\text{diff}} = 6.0; \). \( n_{\text{co}} = 1.0, n_{\text{o}} = 1.0, D_{\text{diff}} = 1.0 \).

![Diagram](image)

**Fig. 3.** Wall Mass Fraction of Species as a Function of Particle Surface Temperature for Brown Coal: A: \( T_w \) corresponding to maximum \( Y_{\text{co},w} \). B: \( T_w \) corresponding to maximum burning rate. --- Kinetic Scheme VI; .... Kinetic Scheme I.
this is a point at which the intensive oxidation of CO is about to start. The dotted line in Fig. 3 shows the effect of increased reduction rate on $Y_{\text{CO}}$ and $Y_{\text{CO,CO}}$ (which corresponds to a non-peaking condition).

Figure 4 shows the effect of particle size on burning rate, for brown coal. As the particle size is increased, at the peak region the CO oxidation increases more rapidly than the corresponding increase in the CO production rate. The former chemical process has a lower activation energy and hence the peak burning point moves toward a lower surface temperature. This is due to the fact that the gas phase reaction rate is proportional to the square of particle size while the surface reaction rate is proportional to the particle size.

The pressure was varied from about 0.1 atm. to 10.0 atm. The burning rate profiles were found to be qualitatively similar to Fig. 4. The effect arises mainly from the order of reactions. The gas phase reaction and the surface reactions are proportional to the pressure. Since at higher pressures the approach to CO-DC will be faster (if activation energy for CO production is less), one should expect a lower peak burning temperature.

5.2 General Correlation of Peak Burning Particle Temperatures

A plot of the inverse of peak burning temperature versus the ln(particle size) has produced a linear relationship as shown in Fig. 5. The short vertical lines specify the order of fluctuation in fixing the point since the iterative procedure was not carried out for every degree interval of surface temperature.

In the same figure the temperatures corresponding to peak $Y_{\text{CO,CO}}$ are plotted for $p^* = 1$. The peak burning particle temperatures and temperatures corresponding to peak $Y_{\text{CO,CO}}$ are found to be logarithmic functions of particle size and pressure. When one is interested in finding a range of temperatures for a given size distribution of coal char or coal particles, beyond which a furnace with cold surroundings has to be operated for minimum production of CO, a general correlation or general plot is more desirable than parametric plots. Hence, the following simplified analysis is made.

Since the particle is surface heated, it is expected that most of the CO oxidation occurs near the surface. The peak occurs when reduction is not dominant, consequently the situation where the reduction rate is considerably smaller than the oxidation rate is considered. To account for the total surface area of the porous char the surface Dukhölp number ($D_{\text{char}}$) and $\Gamma_i$ can be modified to be defined in terms of the surface area $S_i$ and $S_i = S(\theta_i)$, a function of the temperature. However, the calculations for the numerical results presented here were carried out assuming an overall surface reaction. Then imposing such assumptions, the following set of equations are derived:

$$
\tag{15}
\epsilon_{\text{CO,CO}} - \epsilon_{\text{CO,CO}} = \theta_i \Gamma_i Y_{\text{CO,CO}} / \epsilon_{\text{CO,CO}}
$$
The flux fraction in the far stream is obtained from defining equations and Eq. (12). Thus

\[ \epsilon_{CO,w} = Y_{CO,w}/(1 - e^{-\epsilon_w}) \]  

(16)

From Eqs. (13) and (14), for the case of \( \Gamma_\epsilon \ll \Gamma_i \) and with the assumption that \( \epsilon_w \) is small, then

\[ \frac{Y_{CO,w}}{\epsilon_w} = (1 + \nu_3) + \left( \frac{Y_{O_2,w}}{\nu_3} + \frac{1}{\nu_3} \Gamma_i \right) \]

(17a)

\[ \epsilon_{CO,w} = \left( 1 + \nu_i \right) - \left( 1 + \nu_3 \right)(1 + \nu_2)\nu_3/\nu_3 \Gamma_i \]

(17b)

Using Eqs. (16) and (17) in (15) and solving for \( \epsilon_w \), yields

\[ \epsilon_w = \frac{Y_{O_2,w}}{v_3} \left\{ \frac{Y_{O_2,w}}{v_3} + \frac{1}{\Gamma_i v_3} + \frac{1 + \nu_3}{1 + \nu_3} \frac{1 + \nu_i}{1 + \Gamma_i \theta_w} \right\} \]

(18)

Maximizing \( \epsilon_w \) with respect to \( \theta_w \), considering only dominant exponential terms at the peak burning point and expanding \( D_{III,a} \) and \( (D_{III,a})_1 \), the result is achieved is

\[ 1/T_{w,p} = \frac{[R \ln(d_w^3 p^{-2})]}{(E_{w,i} + E_p)} + \text{constant} \]

(19)

All the results obtained for particle temperatures at peak burning conditions are plotted against \((d_w)^3\) \((p^{-2})^2\) on a semilog plot. Such a correlation appears to fit this example very well as seen in Fig. 6, for pressures varying from 0.1 atm to 10 atm. Also, a comparison is made for the theoretical slope as obtained in Eq. (19) with the slope obtained from the least squares fit of the points in Fig. 6. This derived relation is very useful since with a single point for the peak burning temperature for any selected char (such as given in Fig. 1) a wide range of characteristics for different conditions can be predicted.

6. Summary of Results

(1) In the absence of reduction, a low activation energy for the heterogeneous production of CO and a relatively high activation energy for the gas phase oxidation of CO results in a peak for the surface temperature dependent burning rate. Under relatively strong reductions at lower temperatures, the peak burning behavior may not occur.

Fig. 6. Peak Burning Temperatures versus \( p^{-2} d_w^3 \); ——— Approximate Theory; Numerical Results: \( \square 200 \mu m, \bigcirc 100 \mu m, \triangle 50 \mu m, \bigotimes 25 \mu m; \ 1/T_{w,p} = \ -0.151425 \times 10^{-3} + 0.109985 \times 10^{-3} \log d_w, p^{-2}; \) Slope (fit) = 0.10999 $\times 10^{-3}$, Slope (theory) = 0.105 $\times 10^{-3}$ (Numerical Results for Scheme VI).
(ii) Large particles and high pressures can give rise to the peak burning rate at lower surface temperatures. The inverse of peak burning surface temperature was found to be proportional to the logarithm of \((\text{particle size})^n \times \text{(pressure)}^n\) for the systems considered here. However, this relation is generally applicable to other chars and graphite particles. Varying internal reaction area can be accounted for in the approximate model.

(iii) Along with the occurrence of a peak burning rate, there is always associated a peak wall mass fraction for CO gas. The characteristics of the corresponding temperatures are similar to the ones given in (i) and (ii). Although the CO oxidation near the surface is sufficient enough to cause a peak burning rate, it is not high enough to complete the combustion process near the particle surface. A peak in mass fraction of CO near the surface signifies a strong reduction condition.

(iv) Peak burning rates are sandwiched between two limiting diffusion rates corresponding to CO and CO₂ production from the carbon surface, confirming the experimental results of Kimber and Gray.²⁵

(v) The present analysis is useful in understanding the complexities in the evaluation of kinetic constants based on the erosion rate of carbon under CO burn up conditions. Thus “apparent activation energy” may vary from a high value at low temperatures to almost a null value near high temperature regions.

Nomenclature

A preexponential factor
D mean binary diffusion coefficient
\(D_{\text{m,}\alpha}\) = \(A_{\alpha}r_{\alpha}^n (p/E_{\alpha})^{n/\rho D}\), third Damköhler number, gas phase
\(D_{\text{m,}\omega}\) = \(A_{\omega}r_{\omega}^n (p/E_{\omega})^{n/\rho D}\), third Damköhler number, surface
\(c_p\) specific heat
\(d\) particle diameter
\(E_{\alpha}^*\) activation energy, \(E_{\omega}^* = E_{\omega}/E_{\omega}\)
\(h_T\) = \(\frac{1}{2}c_p\) \(\Delta T\), enthalpy
\(m\) burning rate
\(m_{\beta}\) = \(4\pi r^{n+1}[pY_{\beta} - pD(Y_{\beta}/Dr)]\), mass rate
\(n\) = \(n_{\text{ro}} + n_{\text{o}} + n_{\text{H2O}}\), overall order of reaction
\(p\) pressure
\(p^*\) = \(p/p_{\text{amb}}\)
\(q\) heat of reaction
\(R\) gas constant
\(r\) radius
\(S\) total reaction area per unit mass at any temperature
\(T\) temperature
\(W\) molecular weight
\(Y\) mass fraction

\(\beta_{\omega}\) = \(Y_{\omega}/v_\alpha W_\alpha\) - \(Y_{\omega}/v_\omega W_\omega\), species coupling function
\(\beta_{\omega}\) = \(h_{\omega}/\rho_{\omega}\) - \(Y_{\omega}/v_\omega W_\omega\), thermal coupling function
\(\Gamma_{\beta}\) = \([E_{\omega}^*/(D_{\text{m,}\alpha})_\alpha \exp(-E_{\omega}^*/\theta_{\beta})\] / \(\theta_{\beta}\), gamma function
\(e_{\omega}\) = \(m_{\omega}/m\), flux fraction
\(\eta\) = \(r_{\omega}/r\), normalized distance
\(\theta\) = \(T/\theta_{\omega}\), normalized temperature
\(\nu\) = \(T_{\text{iso}}/T_{\text{crit}}\), normalized temperature
\(\omega\) = \(W_{\text{iso}}/W_{\text{crit}}\), normalized temperature
\(\xi\) = \(m/4\pi rDr_{\omega}\), normalized burning rate density
\(\phi\) = \((\beta_{\omega} - \beta_{\omega,\beta})/(\beta_{\omega,\beta} - \beta_{\omega})\), normalized coupling function

Subscripts
\(\text{amb}\) ambient condition
\(C\) carbon or coal
\(CO\) carbon monoxide
\(CO_2\) carbon dioxide
\(g\) gas phase reaction, Eq. (6)
\(H_2O\) steam
\(i\) = 1, 2
\(j\) = T, O, CO₂
\(o\) initial
\(O\) oxygen
\(p\) = CO, principal species; peak condition in the burning process
\(T\) thermal
\(w\) wall
\(l\) surface oxidation, reaction Eq. (4)
\(2\) surface reduction, reaction Eq. (5)
\(\infty\) far stream condition

Superscripts
\(i\) result in the ith iteration
\(\dagger\) nondimensional quantity

Acknowledgments

One of the authors gratefully acknowledges with thanks Professor Merwin Sibulkin of Brown University for helpful discussions and assistance in the preparation of this manuscript.

REFERENCES

COMMENTS

R. F. Chaiken, U.S. Bureau of Mines, USA. Other than graphite, I do not know of any chars or coals to which your model would apply. Hence I do not see what information related to char/coal burning you could derive from your analysis.

J. Lahaye, C.N.R.S., France. The model you proposed for the combustion of char, coke and coal particles has been established mainly from literature results.

A significant amount of work has been published on carbon oxidation and a great number emphasize the role of porosity in the oxidation of carbon. In assuming only external surfaces of particles to participate to oxidation, do you not believe that you oversimplify your model?

Authors’ Reply. Both of these comments pertain to the effect of internal reaction area on the present results. The kinetics utilized in our present model was taken from systems (such as porous chars) where internal reaction exists. Indirectly this is accounted for through global pre-exponential factors and activation energies for the heterogeneous reactions. We have used a global scheme for the following reasons: i) the method is simple and avoids complex internal transport processes, ii) some of the previously published kinetics for the rates of burning are based upon the external area and hence a similar procedure must be adopted for the numerical results; iii) the method can account for lineally varying activation energy; iv) If the internal reaction area S of a porous char/coal particle is known as a function of particle temperature Θ, for a given heterogeneous reaction, the frequency factor Λw and activation energy Ew can be suitably modified. A simple case is when S = S0 exp(±E0/Θ) for the reaction C+1/2 O2 → CO. Then the modified pre exponential factor Λw′ = Λw S0 and the modified activation energy Ew′ = E0/E0′ where E0′ = E0/E0′. Using approximate procedure given by eqs (15) to (19), for any generalized function S = S(Θ), the particle temperature Tw at the peak burning condition is solved from the following relation:

\[ S \frac{\Theta_w^2}{\Theta_w} \frac{dS}{d\Theta_w} + E_w + \Theta_w = \Theta_w (1 + v_w) \ln (1 - \Theta_w) \]

We feel that our simple procedure is justified in view of the uncertainties regarding: i) what fraction of internal area constitutes reaction area, ii) how the internal reaction area varies with respect to reacting gaseous species like O2, CO2, etc. (see Kimber et al.) and with respect to particle temperature, and iii) what is the realistic modeling of pore
spaces and associated macroscopic and/or microscopic transport processes through the pores.

REFERENCES


Authors' Reply. Prof. Glassman raises an interesting question. Mathematically the governing equations derived for the system include both diffusion and kinetics terms. Thus the solution will automatically lead to the diffusion limit (see reaction scheme II, Fig. 1) corresponding to CO production when the CO production rate is fast compared to the CO oxidation rate. On the other hand if the CO oxidation rate is fast compared to the CO production rate then the burning rate approaches the diffusion limit corresponding to CO₂ production at the surface (see dark line in Fig 2). The question of what particle size or temperature will lead to the diffusion limit depends upon the reactivity for the chemical reaction of the given coal/char particle. Caution must be exercised in using the results of liquid droplets for the coal particles. In the burning of liquid droplets the temperature of the droplet is such that the evaporation kinetics (purely physical) are infinitely fast, whereas, the gasification of char/graphite particles is controlled by the finite chemical kinetics of adsorption and desorption processes. Thus the gasification rate at the surface depends upon the availability of oxygen which decreases as the rate of gas phase oxidation of CO increases. Even at moderately higher temperatures the burning rates may be controlled by the kinetics of the coupled processes of CO production, CO oxidation, and reduction of carbon by CO₂.

1. Glassman, Princeton University, USA. The range of temperature and particle sizes covered would indicate that the burning rate was diffusion controlled and therefore the kinetics could not affect the burning rate. As has been shown in the burning of a liquid droplet, as one increases the activation energy from zero (infinite rate) activation upwards, the temperature peaks at zero activation energy and lowers and broadens as the activation energy increases. The broadened temperature profile moves closer to the surface since the burning rate is constant and thus the temperature gradient of the surface must be constant (as function of activation energy). I believe if you check the characteristic times for chemical reaction and diffusion for your conditions, you would find this so.