Distinctive Burning Characteristics of Carbon Particles

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Several reaction mechanisms exist in the literature for the gasification of char/carbon particles. The general procedure for modeling particle gasification is to assume a mechanism of combustion, obtain the theoretical burning rate and particle temperature, and then validate the mechanism by comparing the results with experimental data. The present work shows that the burning rate and particle temperature are independent of heterogeneous and homogeneous reaction mechanisms and their rate kinetics as long as the oxygen (O₂) and carbon dioxide (CO₂) concentrations at the burning surface are low compared to carbon monoxide (CO) concentration. Experimental data are cited which are in agreement with the model's predictions for both particle temperatures and burning times. The relevance of the results to industrial combustors is discussed.

On trouve dans la littérature plusieurs mécanismes de réaction pour la gazéification de particules de carbone ou de produit de carbonisation. La procédure générale employée pour modéliser la gazéification des particules consiste d'abord à supposer un mécanisme de combustion, puis à obtenir la vitesse de combustion théorique et la température des particules, et enfin, à valider ce mécanisme en comparant les résultats avec des données expérimentales. On montre dans ce travail que la vitesse de combustion et la température des particules sont indépendantes des mécanismes de réaction homogène et hétérogène et de leur cinétique tant que les concentrations en oxygène (O₂) et en dioxyde de carbone (CO₂) à la surface de combustion sont faibles en comparaison à la concentration en monoxyde de carbone (CO). Les données expérimentales fournies sont en accord avec les prédicitions de température des particules et de temps de combustion du modèle. On évalue l'importance des résultats pour les chaudières industriels.

Keywords: coal combustion, reaction mechanisms of carbon, carbon combustion, char gasification.

Successful design and maintenance of coal fired combustion equipment demands a knowledge of the combustion mechanism and the temperature field. Extensive literature exists for the mechanisms of carbon combustion. Carbon combustion/gasification is generally believed to proceed with one or more of the following reaction mechanisms:

**Heterogeneous reactions**

\[ \text{C(Solid)} + (1/2) \text{O}_2 \rightarrow \text{CO} \]  

(I)

\[ \text{C(Solid)} + \text{O}_2 \rightarrow \text{CO}_2 \]  

(II)

\[ \text{C(Solid)} + \text{CO}_2 \rightarrow 2\text{CO}, \text{Boudouard Reaction} \]  

(III)

**Homogeneous Reaction**

\[ \text{CO} + (1/2) \text{O}_2 \rightarrow \text{CO}_2 \]  

(IV)

If the gas phase is frozen and the heterogeneous reactions are fast, then the combustion model is called the single film model. When the Boudouard reaction (III) and gas phase oxidation rates are infinite, the combustion model is called the double film model. Earlier works obtained theoretical results for the burning rate with the single film and double film models, compared the results with experimental data and then validated the assumed mechanism(s) (Avedesian and Davidson, 1975; Basu, 1977; Ross et al., 1981). The performance of fluidized bed combustors, for example, has been successfully predicted by using double film models (Campbell and Davidson, 1975; Gibbs, 1975). According to Arthur (1951), reaction (I) was the significant mechanism for char combustion. However, Avedesian and Davidson's (1975) double film model still yielded results for the burning time close to experimental data.

The objectives of the present work are (i) to show that the burning rate and the particle temperature remain independent of the heterogeneous reaction mechanisms and their kinetics as long as the concentration of oxygen \( \gamma_{\text{O}_2} \) and carbon dioxide \( \gamma_{\text{CO}_2} \) at the partial surface are low compared to the carbon monoxide concentrations \( \gamma_{\text{CO}} \), (ii) to show that this result is independent of CO kinetics (homogeneous reaction), (iii) to consider a specific reaction scheme and to determine the conditions at which the assumptions that \( \gamma_{\text{O}_2} \), \( \gamma_{\text{O}_2} \gamma_{\text{CO}} \), and \( \gamma_{\text{CO}} \) are valid, and (iv) to compare the theoretical results for the particle temperature and burning times with experimental data. Furthermore, the results suggest that even if a carbon surface is subjected to forced convection, similar conclusions regarding the mechanisms are valid.

Before the detailed analysis is presented, a brief qualitative description of the problem is described. If a char particle is placed in a hot ambience, the particle temperature...
Figure 1 — Combustion regimes of char/carbon particles; a) negligible CO oxidation; b) significant CO oxidation; c) infinitely fast CO oxidation and Boudouard reaction.

Figure 2 — Surface mass fractions of CO and O₂ vs. T_s for spherical particles of radii 500 μm and 50 μm.

Figure 1c, where CO₂ and O₂ concentration at the surface are low compared to CO at the surface. The analysis does not imply that there is no CO₂ within the film region around the particle. The CO oxidation in the gas phase may be finite or may be infinitely fast. The model given below is valid even for Figure 1a (where CO oxidation is almost negligible) as long as the CO concentration is significantly higher at the surface compared to O₂. The analysis of this problem has been completed by two methods:

(i) species conservation (Annamalai, 1984)
(ii) atom balance (the present paper).

Both methods yield identical results for the mass burning rate and particle temperature. While the method of species conservation assumes a specific reaction mechanism at the particle surface

\[ C + \frac{1}{2} O₂ \rightarrow CO \]
\[ C + O₂ \rightarrow CO₂ \]

and a global reaction mechanism for oxidation of CO

\[ CO + \frac{1}{2} O₂ \rightarrow CO₂ \] (kinetics controlled),

the atom balance method does not need such a reaction scheme except for the restriction that \( Y_{CO} \) must be higher compared to \( Y_{CO₂} \) and \( Y_{O₂} \) at the surface. We know that at low temperatures and for small particles such a condition is not satisfied. Thus, one should use a kinetic controlled burning of C with \( O₂ \), calculate \( Y_{CO} \) and \( Y_{CO₂} \) at the surface, and determine the temperature at which \( Y_{CO} \) at the surface is higher than \( Y_{O₂} \) at the surface (Figure 2 gives such a result). Note that no assumption is made regarding the concentrations at the surface in obtaining Figure 2. We find that such a condition is satisfied if \( T_{particle} \) (or \( T_s \)) > 1200 K for \( r_s > 500 \mu m \) (fluidized beds) and \( T > 1600 \) K for \( r_s < 50 \mu m \) (pulverized coal fired boilers). As a further check, we have estimated the particle temperatures and the burning times using the following relations derived in this paper and compared these estimates with experimental results. The agreement is good.

Analysis

The analysis uses interface and gas phase conservation equations for elements, "C" and "O", and total enthalpy,
The boundary conditions are:

\[ \phi_e = 1, \ y = 0 \]  \hspace{1cm} (5b)

\[ \phi_e = 0, \ y = \infty \]  \hspace{1cm} (5c)

Similarly one can define \( \phi_s \) and \( \phi_w \) for the energy and momentum equations. If it is assumed that \( \text{Pr} = \text{Sc} = 1.0 \), then the differential equations are similar for momentum, total enthalpy and elements and the boundary conditions are the same. Hence

\[ \phi_e = \phi_s = \phi_w = \phi \]  \hspace{1cm} (6a)

For spherical particles, \( \phi_e = \phi_w = \phi \). If \( \text{Pr} = \text{Sc} \) and the Prandtl number is not equal to 1, then

\[ \phi_e = \phi_w = \phi \]  \hspace{1cm} (6b)

The solutions for \( \phi \) can be readily obtained using similarity techniques for flow problems either with the exact or integral methods (Williams, 1969; Annamalai and Sibulkin, 1979). For a spherical particle burning in a quiescent atmosphere, solution for \( \phi \) is available (Williams, 1969).

**INTERFACE CONSERVATION EQUATIONS**

**Element**

\[ \dot{m}^* Y_{e,s} - \rho \mathcal{D} (\partial Y_e/\partial y)_s = \dot{m}_{e,p}^* \]  \hspace{1cm} (7a)

where

\[ \dot{m}_{e,p}^* = \dot{m}^* \]  \hspace{1cm} if \( e = C \)  \hspace{1cm} (7b)

\[ = 0 \]  \hspace{1cm} if \( e = O \)  \hspace{1cm} (7c)

\[ Y_{e,s} = \Sigma Y_{s,i} (M_e/M_i) \]  \hspace{1cm} (7d)

**Energy**

If the reference condition for the thermal enthalpy is selected at \( T = T_s \), then the interface energy balance in terms of total enthalpy, \( h \), leads to:

\[ -\rho \mathcal{D} (\partial h/\partial y)_s = \dot{m}^* (h_p - h_s) \]  \hspace{1cm} (8)

Equations (7) and (8) will then be used to obtain \( \dot{m}^* \) and \( T_s \) as a function of \( (\partial h/\partial y)_s \), \( y_{s,i} \), and \( Y_{s,i,\infty} \).

**Solutions**

1. **Burning Rate per Unit Area (\( \dot{m}^* \))**

Using Equation (7d) with \( e = C \) and \( O \)

\[ Y_{C,s} = Y_{CO_2,s} (M_C/M_{CO_2}) + Y_{CO,s} (M_C/M_{CO}) \]  \hspace{1cm} (9a)

\[ Y_{O,s} = Y_{CO_2,s} (M_O/M_{CO_2}) + Y_{CO,s} (M_O/M_{CO}) \]  \hspace{1cm} (9b)

Assuming that

\[ Y_{O_{s,i}} < Y_{CO_2,s} \]

Equations (9) simplify to:

\[ Y_{C,s} \sim Y_{CO_2,s} (M_C/M_{CO}) \]  \hspace{1cm} (10a)

\[ Y_{O,s} \sim Y_{CO_2,s} (M_O/M_{CO}) \]  \hspace{1cm} (10b)
The assumption that \( Y_{CO_2} \ll Y_{CO} \) precludes the formation of \( CO_2 \) at the surface in significant amounts. This is consistent with the findings of Arthur (1951).

Hence

\[
|Y_{CO_2}/Y_{CO}| = M_{CO}/M_O
\]

(10c)

Using Equation (4) in Equation (7),

\[
\dot{m}^* = -\rho \Delta (\partial \phi/\partial y) \left( Y_{CO} - Y_{CO_2} \right) / \left( (\dot{m}_p/\dot{m}^*) - Y_{CO_2} \right)
\]

(11)

With \( \phi = C \) and \( O \), respectively, in Equation (11) and using Equation (10c) to eliminate \( Y_{CO_2} \), then

\[
Y_{O_2,s}/(1 + (Y_{O_2,s}/\rho_2)(1 + \theta)) - Y_{CO_2,s}
\]

(12)

The element mass fractions of "O" and "C" atoms in the free stream can be written in terms of free stream species concentration. Further, irrespective of the free stream "CO" concentrations, the following equality holds:

\[
(Y_{O_2,s}/\rho_2) - Y_{CO_2,s} = B_\omega
\]

(13a)

where

\[
B_\omega = (Y_{CO_2,s}/\rho_3) + (Y_{O_2,s}/\rho_2)
\]

(13b)

Using Equations (13) in (12),

\[
Y_{O_2,s} = (Y_{O_2,s}/(1 + B_\omega)
\]

(14)

and with Equation (14) in Equation (10b),

\[
Y_{CO_2,s} = 1 - [Y_{O_2,s}/(1 + B_\omega)]
\]

(15)

Let \( \epsilon = 0 \) in Equation (11) and then use Equation (14) with \( \dot{m}^*_p = 0 \); thus

\[
\dot{m}^* = -\rho \Delta (\partial \phi/\partial y) B_\omega
\]

(16)

Note that no heterogeneous reaction mechanisms have been assumed in obtaining the results for \( \dot{m}^* \) and \( Y_{CO_2,s} \). For the particles burning in quiescent air and for burning under forced convection, the derivative at the surface \( (\partial \phi/\partial y) \), can be obtained without regard to any gas phase oxidation mechanisms.

2. PARTICLE/SURFACE TEMPERATURE \( (T_s) \)

Writing Equation (8) in terms of \( \phi \) and then using Equation (16) to eliminate \( (\partial \phi/\partial y) \),

\[
(h_s - h_\omega) = (h_p - h_\omega) B_\omega
\]

(17)

Taking the reference condition at the surface temperature,

\[
h_\omega = h_s(1 + B_\omega)
\]

(18)

Expanding \( h_s \) and \( h_\omega \) in terms of mass fractions and enthalpy of species and using the result for \( Y_{CO_2,s} \) (Equation 15),

\[
(h_s/h_{CO}) = [(Y_{O_2,s}/\rho_2)/Y_{CO_2,s}] + (Y_{CO_2,s}/\rho_3) \times [2 - (h_{CO}/h_{CO}(MCO/MCO))] [1 + \gamma_1]
\]

(19)

In deriving Equation (19), the assumption that \( Y_{CO_2,s} \) is very small has been used. Defining \( Q_1 = -h_{CO}(1 + \gamma_2) \) and \( Q_3 = -(h_{CO}MCO - h_{CO}(MCO/MCO))/MCO \), Equation (19) can be rewritten as

\[
(-h_s/Q_1) = (Y_{O_2,s}/\rho_2) - (Y_{CO_2,s}/\rho_3)(Q_3/Q_1)
\]

(20a)

where

\[
\dot{h}_s = \int_{T}^{T_s} C_p dT
\]

(20b)

Radiation loss could be accounted for replacing \( Q_1 \) and \( Q_3 \) with \( Q_1 \) and \( Q_3 \), where

\[
Q_1 = Q_1 - q_p/\rho_2
\]

(20c)

\[
Q_3 = Q_3 + q_p/\rho_3
\]

(20d)

Further, if \( C_p \) is constant, the particle temperature relation is given as

\[
[(T_s - T_\omega)/Q_1] = (Y_{O_2,s}/\rho_2) - (Y_{CO_2,s}/\rho_3)
\times (Q_3/Q_1)
\]

(20e)

With Equations (20), the temperature of a burning carbon surface can be estimated.

Results and Discussion

The relations for the burning rate \( (\dot{m}^*) \), (Equation (16)), derived in the present study are exactly the same as those previously obtained using the species conservation equations and Schwab-Zeldovich formulation (Annamalai, 1984); but, with the species equations, specific heterogeneous and homogeneous reaction mechanisms were needed. The present approach suggests that even the knowledge of the reaction mechanism is unnecessary. For simplicity we will consider only a spherical particle. With \( y = r \), the general solution for \( \phi \) is given as

\[
\phi = [1 - \exp(-\dot{h}/4\pi r^3 d^3 r)]
\]

(21)

Evaluating \( (\partial \phi/\partial r) \), and using the result in Equation (16),

\[
\dot{m}^* = 4\pi r^2 \dot{h} \ln(1 + B_\omega)
\]

(22a)

The expression (22a) is valid irrespective of the extent of CO oxidation.

If the relative velocity between the particle and gas is significant (e.g., fluidized bed combustors), Equation (22a) could be modified as

\[
\dot{m} = 2\pi r^2 \dot{h} \ln(1 + B_\omega)
\]

(22b)

where

\[
Sh = (2h_\omega r^2)/\rho d\]

(22c)

and \( h_\omega \) is the mass transfer coefficient.

Consider the two extreme cases of carbon combustion: single film (frozen gas phase) and double film (infinite gas phase oxidation) models. Since no assumption has been made regarding the CO oxidation kinetics, Equations (22) are applicable for both cases. Further, for diffusion controlled combustion \( y_{CO_2,s} = y_{O_2,s} = 0 \); the result as given in Equation (22) is the exact solution for both cases. Hence, the burning rates and particle temperatures are identically the same. For the case where the kinetics may be finite with whatever assumed reaction mechanisms, Equations (22) and (20) are still valid as long as \( y_{CO_2,s} \), \( y_{O_2,s} \), \( y_{CO_2,s} \) is valid, we consider a case where the carbon particle burns with the heterogeneous reaction (solid) \( 1/2 O_2 + CO \) and the homogeneous gas phase reaction is assumed to be frozen. For a first order
reaction and the surface kinetics constants given by Mulcahy and Smith (1969) for bituminous coal chars, Figure 2 shows the surface mass fractions of oxygen and carbon monoxide as a function of the surface temperature \( T_s \) for two particles sizes. The mass fraction of CO at the surface is greater than about three times the mass fraction of O\(_2\) at the surface for \( T_s > 1000 \) K for \( r_s = 500 \) \( \mu \)m, and for \( T_s = 1800 \) K for \( r_s = 50 \) \( \mu \)m. If CO oxidation takes place in the gas film surrounding the particles, then it was shown earlier (Annamalai and Dubertak, 1978) that \( Y_{CO,1} > Y_{O_2,1} \) and \( Y_{CO,1} > Y_{O_2,1} \) as long as \( 1600 < T_s < 2200 \) K.

These conditions bracket the temperatures experienced in several applications. For carbon particles burning in fluidized bed combustors, the measured \( T_s \) = 1200 to 1300 K and \( r_s < 500 \) \( \mu \)m (Ross et al., 1981) and for particles burning in a pf fired boilers, \( T_s = 1600 \) to 1800 K (assumed to be the same as the gas temperature) and \( r_s < 50 \) \( \mu \)m (Loisson and Kissell, 1962). Thus, for these practical cases, either the heterogeneous reaction or homogeneous CO oxidation mechanism is not a factor in the estimation of particle temperature or burning time.

**Comparisons to experimental data**

Particle temperatures and burning times of char particles in a fluidized bed were measured by Ross et al. (1981), Chakraborty and Howard (1981), Avedesian and Davidson (1975). These experimental data will now be compared with the theoretical results for the particle temperatures and burning times generated with the current approach. Figure 4 shows the comparison of measured particle temperature difference \( T_s - T_w = T_s - T_{bed} \) and theoretical results generated with Equations (20) and (22b). The following data were used in the calculations: \( Sh = 1.42 \) (Avedesian and Davidson, 1975), \( \rho D = 0.65 \times 10^{-4} \) kg/m \( \cdot \) s, \( C_p = 1.15 \) kJ/kg K, \( B_w = Y_{O_2,w}/Y_{C} \), \( Q_1 = 9242 \) kJ/kg, \( Q_3 = 14321 \) kJ/kg, \( T_w = 1173 \) K, \( Sh = 1.42 \). For fluidized beds, \( Y_{O_2,w} \) is equal to the oxygen concentration in the emulsion phase. Since the radiation loss is significant, an iterative procedure is used in obtaining the particle temperatures. Qualitatively the results show decreasing particle temperature with increasing particle size. While the burning rate \( m \) is proportional to \( r_s \) (Equation 22b), the radiation loss \( Q_R \) is proportional to \( r_s^2 \) and, hence \( (Q_R/m) \) is proportional to \( r_s \). Thus, according to Equation (20c) the effective heat (\( Q_{inf} \)) available for heating of the particle is decreased at increased particle size. Experimental data shown in Figure 4 confirm these findings. Further, the quantitative comparison appears to be reasonably good. Yates and Walker (1977) measured the particle temperature difference \( T_s - T_{bed} \) at 60°C for \( r_s = 3.75 \) mm and 140°C for \( r_s = 1.25 \) mm while the present calculation shows the corresponding results as 41°C and 122°C, respectively. It should be noted that the calculated temperatures are independent of CO kinetics.

As a further verification of the present results, the burning times were calculated using Equation (22b) and the \( d^2 \) law. Table 1 compares the predicted burning times and the experimental data. The theoretical results agree very well with the results of Avedesian and Davidson (1975). However, the agreement with the results of Chakraborty and Howard (1981) is not good except for \( r_s = 2.2 \) mm. Avedesian and Davidson (1975) compared their experimental data with the results from the double film model while the comparison here is made with CO being the surface product and with no assumption regarding the rate kinetics of CO. Thus the reaction scheme could be either the single film model with C + 1/2 O\(_2\) = CO or the model C + CO\(_2\) = 2CO, C + 1/2 O\(_2\) = CO, CO + 1/2 O\(_2\) = CO\(_2\) with CO oxidation finite. Thus it is shown that the experimental data could be equally validated with the present model where CO oxidation is finite. Thus, for the burning of char particles, the agreement of both the particle temperatures and burning times with the experimental results do not validate the appropriate reaction mechanism (i.e. single film, double film or burning with finite CO kinetics) since the results are independent of the reaction mechanisms. However, this conclusion does not apply in the regime where the surface mass fractions of O\(_2\) and CO\(_2\) are significantly higher than the surface mass fraction of CO. Then, for the ignition regime of char particles the temperature are low, one should use the appropriate model for the surface and homogeneous reactions in obtaining the results for the particle temperature and ignition times.

**Summary and conclusions**

The burning rate and particle temperatures have been shown to be independent of CO kinetics and thus indepen-
ponent of the reaction mechanism. Increased CO oxidation results in decreased O₂ concentration and increased CO₂ concentration. The decrease of O₂ results in decreased char consumption rate while the increase of CO₂ concentration results in increased reduction rate thus maintaining the same char burning rate. Similarly the decreased oxidation of C to CO and the increased reduction rate tend to lower the particle temperature while the increased CO oxidation in the gas phase tends to raise the particle temperature. Thus, the particle temperature remains independent of CO kinetics. Similar results have been obtained for group combustion of char particles (Annamalai, 1987).

1. The heterogeneous and homogeneous reaction mechanisms, and their chemical kinetics, are not factors in estimating the burning rates and particle temperatures of carbon combustion/gasification as long as the surface mass fractions of CO₂ and O₂ are low compared to CO.

2. For a spherical particle burning in a quiescent atmosphere, the CO mass fractions are very high compared to CO₂ and O₂ at Tᵢ > 1000 K for rₑ > 500 μm and at Tᵢ > 1600 K for rₑ > 50 μm. These conditions are satisfied in fluidized bed combustors and pulverized coal-fired boilers, respectively.

3. Support for these conclusions was provided by comparisons to experimental data. Good agreement was obtained for both particle temperatures and burning times.

Nomenclature

- B = transfer number
- Cₑ = specific heat at constant pressure, kJ/(kg · K)
- Dₑ = diffusion coefficient, m²/s
- d = diameter of particle, m
- hₑ = total enthalpy, kJ/kg
- hₑₑ = enthalpy of formation, kJ/kg
- hₑₑₑ = mass transfer coefficient, kg/(m² · s)
- hₑₑₑₑ = thermal enthalpy, kJ/kg
- kₑₑₑₑ = thermal conductivity, kJ/(m · s · K)
- Le = Lewis number = Dₑ/αₑₑₑₑ
- Mₑₑₑₑ = atomic weight of element e
- Mₑₑₑₑₑ = molecular weight of species i
- mₑ = mass burning rate, kg/s
- mₑₑₑₑ = mass burning rate per unit area, kg/(m² · s)
- Pr = Prandtl number = ν/αₑₑₑₑ
- Qₑₑₑₑ = radiation heat loss, kJ/s
- Qₑₑₑₑₑ = hₑₑₑₑₑ Mₑₑₑₑₑ/ρₑₑₑₑ, kJ/kg
- Qₑₑₑₑₑₑ = (2hₑₑₑₑₑ Mₑₑₑₑₑ - hₑₑₑₑₑ Mₑₑₑₑₑ)/Mₑₑₑₑₑ, kJ/kg
- rₑ = radius, m
- Sc = Schmidt number = ν/Dₑ
- Sh = Sherwood number = (2hₑₑₑₑₑ rₑ/νDₑ)
- Tₑ = temperature, K
- t = time, s
- u = velocity, m/s
- Vₑₑₑₑ = mass fraction of element e
- yₑₑₑₑₑ = coordinate normal to surface
- αₑₑₑₑₑ = thermal diffusivity = kₑₑₑₑₑ/ρₑₑₑₑₑ, m²/s
- νₑₑₑₑₑ = kinematic viscosity, m²/s
- ρₑₑₑₑₑ = density, kg/m³
- ϕₑₑₑₑₑ = ratio of a quantity (element, enthalpy, or momentum) and its surface value relative to its free stream value (see, e.g., Equation 4)

Subscripts

- bed = fluidized bed conditions
- C = carbon
- ch = char
- e = element
- h = relates to energy (enthalpy) equation
- l = inert
- i = species
- O = oxygen
- p = solid (particle)
- s = surface
- T = temperature
- u = relates to momentum (velocity) equation
- αₑₑₑₑₑ = free stream

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