$\phi_2 P_{c_1}$, insight can be gained regarding the extrapolation of solubilities to high temperatures. Although Henry's law does not apply to the less volatile component, the final results: $f_2/x_2 = \phi_2 P_{c_1}$ and Eq. 34 can be applied. Most of the equations, derived in this study, should not be used away from T_{c_1}. Sharp changes in slope near T_{c_1} can alter some of the derivatives drastically.

NOTATION

c = Poynting correction
f = fugacity
h = enthalpy
$\bar{h}$ = partial molar enthalpy
h^0 = molar enthalpy in ideal gas state
H_2 = Henry's law constant of solute
P = pressure
P_1^0 = vapor pressure of pure solvent
P_{c_1} = critical pressure of solvent
R = gas constant
T = absolute temperature
u = molar internal energy
v = molar volume
$\bar{v}$ = partial molar volume
x = mole fraction in the liquid
y = mole fraction in the vapor

Greek Letters

γ = activity coefficient
γ^* = normalized activity coefficient of solute
μ = chemical potential
ϕ = fugacity coefficient (ϕ^0 for pure component)

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Effect of Pore Structure on Particle Ignition During Exothermic Gasification Reactions

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One distinctive feature of a char gasification reaction is the change in pore structure of the solid reactant that occurs continuously as reaction proceeds. Earlier models were proposed by Petersen (1957) and by Hashimoto and Silveston (1973) to study the effect of solid pore structure on gasification kinetics. More recent development of a random pore model (Bhatia and Perlmutter, 1980; Gavalas, 1980) assumed that the reaction rate in the kinetic control regime is proportional to the surface area of the solid and showed that the change of reaction rate with conversion can be characterized by a pore structure parameter ψ in the form:

$$\frac{dX}{d\tau} = \frac{S}{S_o} = (1 - X)\sqrt{1 - \psi ln\,(1 - X)} \qquad (1)$$

or in terms of the dimensional time scale as

$$\frac{dX}{dt} = \frac{k_s C_o^n S_o}{1 - \epsilon_o}(1 - X)\sqrt{1 - \psi ln\,(1 - X)} \qquad (2)$$

The parameter ψ contains the initial porosity, surface area, and total pore length, all obtainable from the pore volume distribution of the solid reactant before any reaction has taken place (Bhatia and Perlmutter, 1980).

These model developments are limited, however, to isothermal conditions. When the heat transfer mechanism of a reacting particle is insufficient to maintain the particle isothermal, the temperature changes of the particle can have significant effects on the reaction kinetics. In the case of exothermic reactions such as char oxidation, this thermal effect can even result in particle ignition. This is especially to be avoided in a steam-oxygen char gasifier where particle ignition consumes excessive char intended for steam reaction.

Particle ignition temperature has frequently been used to characterize char reactivity (Hoffman and Schnitzer, 1968; Patrick and Shaw, 1972; Pai Vernekar et al., 1982). A particle ignites when the energy generated by exothermic reactions exceeds the energy removed by convection or radiation to the extent that the particle temperature suddenly jumps to a high temperature steady state. It should be noted that the temperature steady states referred to here are based on a specific conversion level, even though the conversion will change with time as reaction proceeds. The rate of energy generation is directly proportional to the reaction rate, which is affected by the pore structure development as demonstrated in Eq. 1. Consequently, the particle ignition characteristic is expected to be affected by its pore structure. Although the temperature rise and particle ignition phenomena in gas-solid reactions have been theoretically studied by various workers (Vulis, 1961; Luss and Amundson, 1969; Sohn, 1973; Stevenson et al., 1973), there seems to have been no attempt to address specifically the effect of pore structure on the ignition behavior until the recent experimenal work of Pai Vernekar et al. (1982). These latter authors suggested that the ignition temperature of a coal pellet is a function of the pellet porosity. In the work reported in this communication, the temperature rise will be considered for a porous solid reacting with gas exothermically in the chemical kinetic control regime. Emphasis is on the affect of the pore structure on the particle ignition characteristics.

ENERGY CONSERVATION

The following formulation of the energy movements in a reacting particle is based on three constraints:

1) Convective heat transfer between an individual particle and a flowing gas, is the sole mechanism of heat transfer.
2) The pseudosteady-state assumption is applicable.
3) There is no significant temperature gradient within the particle.

With regard to the first of these, char gasification in the chemical kinetic control regime usually occurs at relatively lower temperatures where the radiation affects are minimal and convection is the predominant heat transfer mechanism. Stevenson et al. (1973) have suggested that in a conventional brown-coal burner the contribution of radiation to ignition of the coal is much less than the contribution of convection. Calculations to be described in this study will further support such an argument.

The assumption of pseudosteady-state behavior is commonly used in numerical studies of gas-solid reaction models. For char oxidation where both CO_2 and CO have been identified as primary products, $C_p/-\Delta H \cong 3.3 \times 10^{-5}$ and 1.2×10^{-4} K^{-1} for CO_2 or CO production, respectively. This suggests that an adiabatic change of 1 K in the temperature of the solid could only drive the reaction to a conversion of between 3.3×10^{-5} to 1.2×10^{-4}. Therefore, the sensible heat required for transient heating of any likely magnitude can be responsible for only a very small fraction of the reaction. The pseudosteady-state argument is thus applicable; temperature transients are taken as very rapid and convective heat transfer is considered the only energy sink. The application of a pseudosteady-state not only simplifies the energy equation, but is also very useful in clarifying ideas on the unignited and ignited states.

Finally, the last point is justified by the lack of intraparticle diffusion in the chemical kinetic control regime, as well as by the high thermal conductivity of carbon which Perry and Chilton (1973) give as 6.23 and 5.89 W/m·K for carbon stock and petroleum coke, respectively. Following these arguments, energy conservation for the particle can be written as

$$\frac{\rho}{M} V(1 - \epsilon_o)(-\Delta H) \frac{dX}{dt} = h\, A(T - T_o) \qquad (3)$$

Combining Eqs. 2 and 3 in dimensionless form and introducing the rate constant k_s in Arrhenius form as

$$k_s = k_{so} \exp(-E/R'T) \qquad (4)$$

one obtains

$$\exp\left[-\gamma \left(\frac{1-\theta}{\theta}\right)\right] = \frac{\beta}{(1-X)\sqrt{1-\psi ln(1-X)}} (\theta - 1) \qquad (5)$$

PARTICLE IGNITION

For given conditions of β, γ, ψ, and X, the temperature of the reacting particle can be obtained by solving Eq. 5. As illustrated in part in Figure 1, the lefthand side of Eq. 5 produces a sigmoidal heat generation curve with respect to θ, whereas the right hand side is represented by a heat removal straight line with an intercept at $\theta = 1$ and slope equal to $\beta/[(1 - X)\sqrt{1 - \psi ln(1 - X)}]$. The multiple intersections correspond to the multiple solutions for θ in Eq. 5. For $\psi > 2$, the slope of the heat removal straight line decreases with conversion from the initial condition to conversion level X_{max} where $(1 - X)\sqrt{1 - \psi ln(1 - X)}$ reaches a maximum value; it then increases without bound to $X = 1.0$.

Among the multiple intersections of these curves, the low temperature state is ordinarily the actual particle temperature in the early stages of conversion; however, the particle can ignite to the high temperature state if the slope of the heat removal line becomes less than the slope of the tangent to the sigmoidal heat generation curve at any level of conversion. Although one can computer θ at a high temperature steady state, the value does not have physical meaning because the particle would be completely reacted before its temperature reached the new state. The arguments used in deriving Eq. 5 such as chemical kinetic control, negligible radiation effects, and pseudosteady-state would not be applicable under such conditions. Figure 2 shows the changes of particle temperature θ with conversion at different values of the pore structure parameter

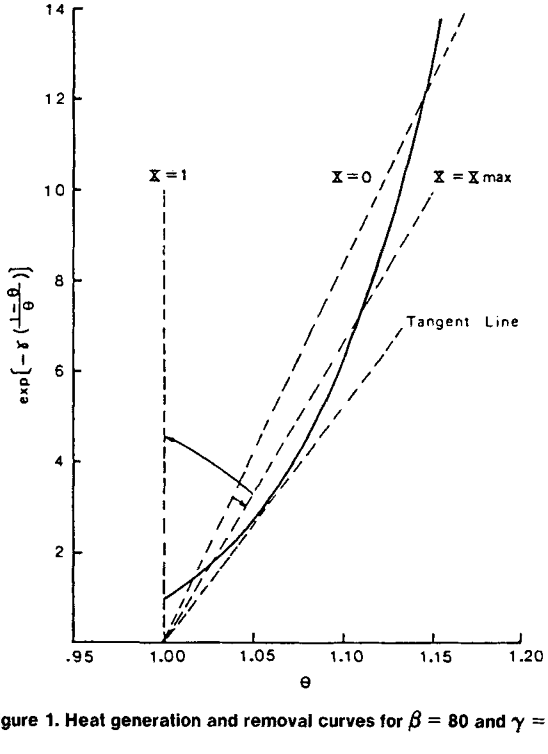

Figure 1. Heat generation and removal curves for $\beta = 80$ and $\gamma = 20$.

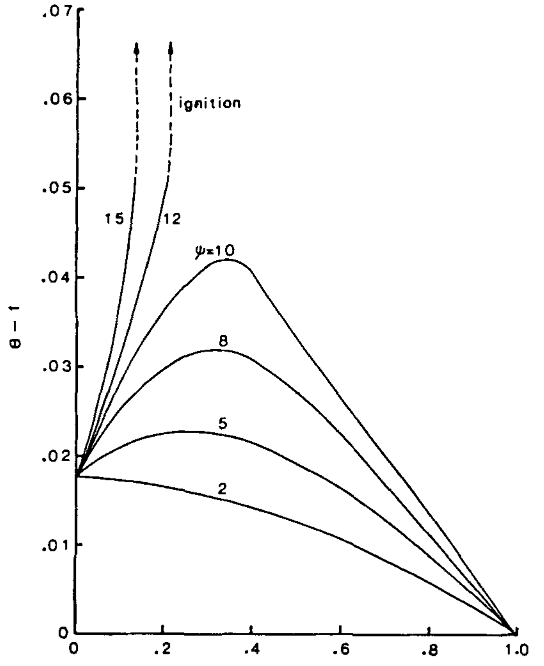

Figure 2. Changes of particle temperatures with conversion at different values of ψ. Parameter β = 80 and γ = 20.

ψ, using parameter $\beta = 80$ and $\gamma = 20$.

The foregoing not withstanding, criteria can be obtained to determine whether a particle would ignite during reaction. The minimum slope of the heat removal straight line occurs at X_{max} which, according to Bhatia and Perlmutter is

$$X_{max} = 1 - \exp[(2 - \psi)/2\psi] \quad \text{for} \quad \psi \geq 2 \tag{6}$$

and

$$X_{max} = 0 \quad \text{for} \quad \psi \leq 2 \tag{7}$$

Using Eqs. 6 and 7, one obtains

$$\min_{0 \leq X \leq 1} \{\beta/[\sqrt{(1 - X)}\sqrt{1 - \psi ln\,(1 - X)}]\} = \beta \bigg/ \left[\frac{\sqrt{\psi}}{2}\exp\left(\frac{2 - \psi}{2\psi}\right)\right] \quad \text{for} \quad \psi \geq 2 \tag{8}$$

and

$$\min_{0 \leq X \leq 1} \{\beta/[(1 - X)\sqrt{1 - \psi ln\,(1 - X)}]\} = \beta \quad \text{for} \quad \psi \leq 2 \tag{9}$$

The slope m of the tangent line to the sigmoidal curve with intercept at $\theta = 1$ can be obtained by simultaneously solving

$$m(\theta' - 1) = e^{-\gamma(1-\theta'/\theta')} \tag{10}$$

and

$$m = \frac{d}{d\theta}\{\exp[-(1 - \theta)/\theta]\}_{\theta=\theta'} = \frac{\gamma}{\theta'^2}e^{-\gamma(1-\theta'/\theta')} \tag{11}$$

where θ' is the value of θ at the tangent point. Combination of Eqs. 10 and 11 leads to

$$\theta' - 1 = \frac{\theta'^2}{\gamma} \tag{12}$$

Therefore,

$$\theta' = \frac{\gamma - \sqrt{\gamma^2 - 4\gamma}}{2} \tag{13}$$

Substituting Eq. 12 into Eq. 10, one obtains

$$m = \frac{\exp\theta'}{\theta' - 1}$$

Therefore, combining Eqs.8, 9 and 14, one can obtain the criteria for particle ignition as

$$\frac{\sqrt{\psi}}{2}\exp\left[\frac{2 - \psi}{2\psi}\right] > \frac{\beta(\theta' - 1)}{\exp\theta'} \quad \text{for} \quad \psi > 2$$
$$1 > \frac{\beta(\theta' - 1)}{\exp\theta'} \quad \text{for} \quad \psi > 2 \tag{15}$$

where the value of θ' can be calculated from Eq. 13.

RESULTS AND DISCUSSION

Equation 15 specifies the degree of dependence of ignition characteristics on the pore structure of a particle. The information required for the three parameters: pore structure, activation energy, and the ratio of heat removal to heat generation are all experimentally obtainable. Figure 3 shows the ranges of β and ψ values over which ignition occurs, using γ as parameter. The region to the left of each curve, including the curve itself, represents the conditions where particle ignition characteristics can be read from Figure 3; for $\beta = 80$ and $\gamma = 20$, for example, a particle with $\psi = 10$ will not ignite while one with $\psi = 12$ will ignite. (See also Figure 2.) For a porous solid with single pore size where according to Bhatia and Perlmutter (1981), $\psi = -1/ln(1 - \epsilon_o)$, this only requires a decrease of porosity from 0.095 to 0.080. For particles with the same initial surface area, the one with smaller porosity is more likely to ignite because its more significant surface area development would cause a greater rate increase and temperature rise.

Figure 3 can also be useful in planning experiments or determining reaction conditions. For reaction of a porous particle with $\gamma = 20$ and $\psi = 10$, for example, the convective heat transfer of the flowing gas must be large enough to give $\beta > 79$ in order to avoid particle ignition. Equation 15 can also be used to calculate the conversion level X_i at which ignition occurs. Such results are shown in Figure 4 for $\gamma = 20$. The ignition occurs earlier for those particles with larger ψ, due to the more significant surface area development. Although derived for reaction of a single porous particle, these results may also be applied to the study of spontaneous ignition in coal beds and coal dust, if the entire bed of coal particles is considered as a single porous material. Moreover, since diffusional limitations tend always to inhibit reaction, the lines shown in Figure 3 can be considered safe bounds to avoid ignition for such cases as well.

Finally, the contribution to heat transfer by radiation can be numerically evaluated. For a particle with radius of 150 micron reacting in a stagnant 673 K oxygen atmosphere (Nusselt number = 2.0) with $T/T_o = 1.05$ (see the ignition temperature in Figure 1), the heat transfered by radiation is found to be only 6.7% of that transferred by conduction, i.e.,

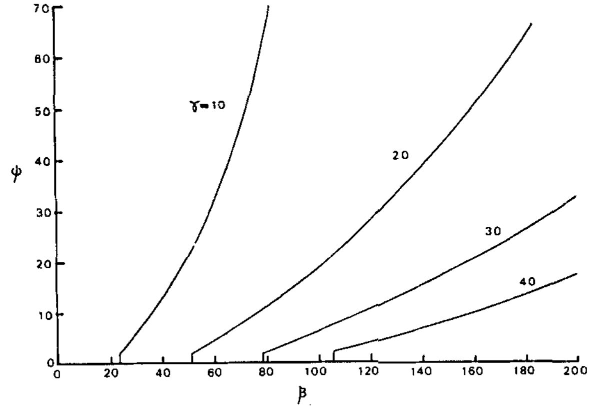

Figure 3. Ignition criteria for various values of β, γ, and ψ. The region to the left of each curve represents the conditions where particle ignition would occur.

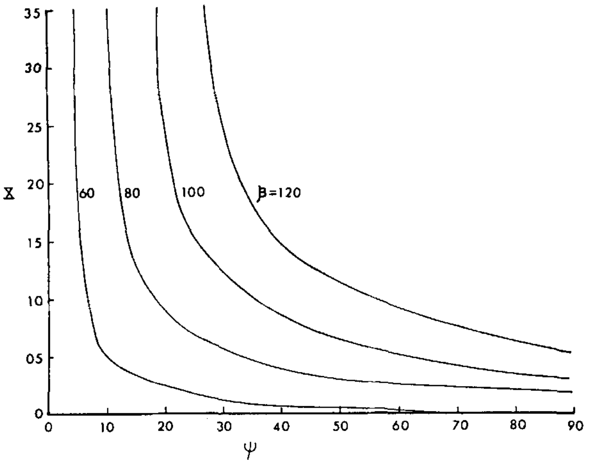

Figure 4. Effect of pore structure parameter ψ on the ignition conversion level x_i at different values of β. Parameter $\gamma = 20$.

$$\frac{H_r}{H_c} = \frac{\sigma(T^4 - T_o^4)}{\frac{Nu\,k}{2R}(T - T_0)} = \frac{1.8 \times 10^{-8}[(707)^4 - (673)^4]}{\frac{2(5.32 \times 10^{-2})}{2(150 \times 10^{-6})}(707 - 673)} = 0.067$$

This percentage will be even lower in a flowing gas where convection is significant, supporting the argument that radiation effects are negligible in the chemical kinetic control regime.

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NOTATION

A = exterior surface area of a single solit particle, m^2
C_o = ambient concentration of gas reactant, mol/m^3
C_p = heat capacity of solid reactant, J/mol·K
E = activation energy of reaction, J/mol
ΔH = heat of reaction, J/mol
H_r = energy transferred by radiation, J/s
H_c = energy transferred by convection, J/s
h = heat transfer coefficient, $J/m^2 \cdot K \cdot s$
k = thermal conductivity of gas, W/m·K
k_s = rate constant for surface reaction
k_{so} = preexponential factor of k_s
L_o = initial total pore length per unit volume of particle, m/m^3
M = molecular weight of solid reactant, g/mol
m = slope of the tangent line to heat generation curve
Nu = $2hR/k$, Nusselt number, dimensionless
n = reaction order of gasification reaction
R = particle size, m
R' = gas constant, 8.314 J/mol·K
S = surface area per unit volume of particle, m^2/m^3
S_o = S at $t = 0$
T = temperature of the reacting particle, K
T_o = temperature of ambient gas reactant, K
t = reaction time, s
V = volume of a single solid particle, m^3
X_i = conversion level at which particle ignition occurs
X = conversion dimensionless
X_{max} = conversion level at which reaction rate reaches maximum

Greek Letters

β = $hAT_o \Big/ \left[\frac{\rho}{M}V(-\Delta H)k_{so}C_o^n S_o\right]$, ratio of heat removal to heat capability, dimensionless
γ = $E/R'T_o$, activation energy parameter, dimensionless
ϵ_o = initial porosity, dimensionless
θ = T/T_o, dimensionless particle temperature
θ' = $[\gamma - \sqrt{\gamma^2 - 4\gamma}]/2$
ρ = density of solid reactant, g/m^3
σ = Stefan-Boltzmann constant, $1.798 \times 10^{-8}\ W/m^2 \cdot K^4$
τ = $k_s C_o t S_o/(1 - \epsilon_o)$, dimensionless time
ψ = $4\pi L_o(1 - \epsilon_o)/S_o^2$, a pore structure parameter, dimensionless

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