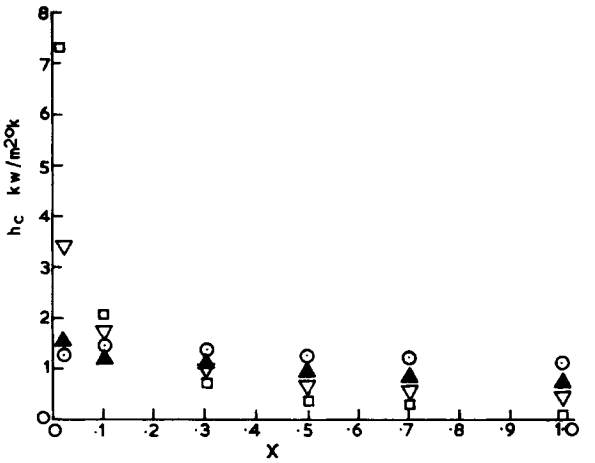

Fig. 2 Comparison of different models for heat transfer coefficient for pentane-water system.

Models	Symbols
Eqn (15)	▲
Tochitani Eqn (16)	▽
Sideman Eqn (17)	□
Sideman Run No 14	⊙

The value of h_c obtained by Sideman and Isenberg (1967) has the form:

$$h_c = K_c \left(\frac{3U_\infty}{2\pi R\alpha_c}\right)^{1/2} \left((\text{Cos}\beta - \frac{1}{3}\text{Cos}^3\beta + \frac{2}{3}\right)^{1/2} \qquad (17)$$

The mass balance for constant mass bubble Figure 1 yields:

$$H^2(3R - H) = \frac{4(mR_o^3 - R^3)}{m - 1} \qquad (18)$$

or in terms of the weight percent vapor content x, we have:

$$\frac{R^3}{R_o^3} = 1 + x(m - 1) \qquad (19)$$

where, $H = R(1 + \text{Cos}\beta)$ is now time dependent. (20)

Lumping the last three equations together we get,

$$(3\,\text{Cos}\beta - \text{Cos}^3\beta + 2) = \frac{4(1 - x)}{1 + x(m - 1)} \qquad (21)$$

For various values of angle β in Eq. 21, we get the corresponding values of x. The experimental data of Sideman and Taitel (1964) for the Pentane-water system has been used for investigation. Knowing the values of x, the values of velocity and radius can be calculated with the aid of Eq. 19 and the experimental expressions. The value of α is then calculated from Eq. 2. The values thus obtained are substituted in Eqs. 15, 16 and 17 to get the theoretical values of h_c. The experimental data for heat transfer coefficients are calculated on similar lines as carried out by Sideman and Taitel (1964). From Figure 2, it is clear that our model gives values that are very close to the experimental values as compared to those of Tochitani et al. (1977) and Sideman and Isenberg (1967).

The higher values of h_c obtained by Tochitani et al. (1977) during the early stages of evaporation are due to the higher contribution of the angle term at the lower values of α and the reverse is the case towards the later stages of evaporation.

NOTATION

K = thermal conductivity
m = ratio of liquid to vapor density of the bubble
r = radial distance in spherical co-ordinates
R = radius of two-phase bubble
R_o = initial radius of the drop of dispersed phase
T = temperature
T_L = interface temperature between continuous and dispersed phases
S = spreading coefficient
T_∞ = bulk temperature
U = rise velocity of two-phase bubble
$\dot{u}$ = velocity gradient
u_τ = tangential velocity
x = weight percent vapor
μ = dynamic viscosity
σ = tension at interface
α_c = thermal diffusivity

Subscript

c = continuous phase
d = dispersed phase

LITERATURE CITED

Baird, M. H., and A. E. Hamielec, "Forced convection transfer around spheres at Intermediate Reynold's Numbers," *Can. J. Chem. Eng.*, **40**, 119 (1962).

Mori, Y. H., "Configurations of Gas-Liquid Two-Phase Bubbles in Immiscible Liquid Media," *Int. J. Multiphase Flow*, **4**, 383 (1978).

Sambi, S. S., and P. D. Grover, "Direct contact heat transfer to evaporating drop in immiscible liquids," I.I.Ch.E., 32nd Annual Session Bombay (December, 1979).

Selecki, A., and L. Gradon, "uber den Verdampfungs mechanismus eines sich in einer nicht misch beren Flussigkbewegenden Flussigkeitstropfe," *Chemie-Ingr-Tech.*, **44**(18), 1077 (1972).

Sideman, S., and J. Isenberg, "Direct contact Heat Transfer with change of phase: Bubble growth in three-phase systems," *Desalination*, **2**, 207 (1967).

Sideman, S., and Y. Taitel, "Direct Contact Heat Transfer with change of phase: Evaporation of drops in an Immiscible liquid medium," *Int. J. Heat Mass transfer*, **7** 1273 (1964).

Tochitani, Y., T. Nakagawa, Y. H. Mori, and K. Komotori, "Vaporization of Single Liquid Drops in an Immiscible liquid, Part II: Heat Transfer Characteristics," *Warme-und Stoffuber-tragung*, **10**, 71 (1977).

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An Improved Single Particle Char Gasification Model

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Reactions between porous solids and gases are usually interpreted in terms of idealized models based on sharply defined reaction zones within the particle. For example the widely employed homogeneous and shrinking core models represent the extremes that might be encountered in the limits of very rapid and very slow diffusion of the reacting gases. Srinivas and Amundson (1980) recently proposed a model for the gasification of a single char particle in the presence of steam, hydrogen, carbon monoxide,

carbon dioxide and methane. The exceptional feature of the Srinivas-Amundson model is its ability to bridge the gap between these two idealized models thus making it possible to define regions of applicability for each.

Because of the complex algebra involved, Srinivas and Amundson were forced to make some assumptions which make quantitative predictions from the model questionable. Most notably, it was assumed that the diffusivities of all components are identical except for hydrogen which is infinite. No provision was made for Knudsen diffusion, although some consideration of this phenomenon appears to be reflected in the value chosen for the component diffusivities. In the present contribution these limitations will be avoided, and a quite general method of solution will be detailed which allows for any number of reactions and any number of components.

In order to provide the most meaningful comparison between our calculations and the computations of Srinivas and Amundson, we have utilized the same reaction rate expressions and the same char properties as employed by the previous authors. We have also used the expression of Dutta et al. (1977), for the relative available surface area as a function of carbon conversion.

REACTION RATE EXPRESSIONS

Following Srinivas and Amundson, we consider 1) the steam-carbon reaction, 2) the carbon dioxide-carbon reaction, 3) the hydrogen-carbon reaction, and 4) the water gas shift reaction:

1. $C + H_2O \rightarrow CO + H_2$
2. $C + CO_2 \rightarrow 2\,CO$
3. $C + 2H_2 \rightarrow CH_4$
4. $CO + H_2O \rightleftarrows CO_2 + H_2$

We also assume that the water-gas shift reaction is in equilibrium, a realistic assumption for many coal gasification systems. To do otherwise would require a knowledge of the kinetics of this reaction. The rate expressions for Reactions 1, 2, and 3 are:

$$R_{S1} = \frac{3.85 \times 10^7 \exp(-34231/T)C_1}{1 + 95.7 \exp(7299.3/T)C_2} \tag{1}$$

$$R_{S2} = 370 \exp(-29832/T)C_4 \tag{2}$$

$$R_{S3} = 4.839 \times 10^{-7} T \exp(-17921/T)C_2 \tag{3}$$

where component 1 = H_2O, component 2 = H_2, component 3 = CO, component 4 = CO_2, and component 5 = CH_4. The appropriate dimensions for use in these equations are provided in the Notation.

CHAR PROPERTIES AS A FUNCTION OF CARBON CONVERSION

The reaction rate expressions must be converted to a particle volume basis for substitution into the component mass balance equations. This requires a knowledge of the surface area as a function of carbon conversion. The effective diffusivities, for both ordinary diffusion and Knudsen diffusion, depend upon the particle porosity. We assume that $D^e_{Ki} = \epsilon^2 D_{Ki}$ and $D^e_{ij} = \epsilon^2 D_{ij}$, consistent with the previous development. Furthermore, the Knudsen diffusivity is dependent upon the average pore radius which we calculate as $\bar{r}_p = 2V_p/S$. Thus a knowledge of the porosity and the average pore radius as functions of carbon conversion is also required. It is important to recognize that point values of the surface area, porosity, and average pore radius are needed since these quantities will vary within the particle under mass transfer limited conditions.

We assume that the char consists only of carbon and material which does not gasify (i.e., ash). Also, it is assumed that the chemical composition (or more specifically the weight) of the ash remains unchanged during gasification, and no shrinkage or expansion of the char particle is allowed. Following Srinivas and Amundson the relative total surface area at any point in the particle is related to the carbon conversion by the expression:

$$a = 1 + 100\, X_c^{4.125} \exp(-5.5\, X_c) \tag{4}$$

On the basis of this equation and the above considerations one can develop the following relations:

$$R_V = aS_o\rho_o W_b(1 - X_c)R_S \tag{5}$$

$$\epsilon = \epsilon_o + X_c W_b \rho_o/\rho_c \tag{6}$$

$$\bar{r}_p = \frac{2\epsilon}{aS_o\rho_o(1 - X_c W_b)} \tag{7}$$

The char properties calculated from these equations appear to be in qualitative agreement with available experimental results (e.g., Johnson, 1979).

GASEOUS COMPONENT MASS BALANCES

Upon invoking the steady-state approximation we can write the gaseous component mass balances for a spherical char particle as follows

$$\frac{1}{r^2}\frac{d}{dr}(r^2 N_i) = -\sum_{k=1}^{s} \nu_{ki} R_{Vk} \qquad i = 1, 2 \ldots 5 \tag{8}$$

For the diffusive transport equations we call upon the dusty-gas theory of Mason et al. (1967) which gives for each component:

$$\frac{dC_i}{dr} = -\frac{N_i}{D^e_{Ki}} - \frac{1}{C_{TS}} \sum_{j=1}^{n} \frac{C_j N_i - C_i N_j}{D^e_{ij,s}} \qquad i = 1, 2 \ldots 5 \tag{9}$$

We have neglected the viscous flow contribution to the component fluxes. In a previous paper it was shown that this simplification can be incorporated into calculations of this type with essentially no loss of accuracy (Haynes, 1978). In general the particle will not be isobaric when the contribution from Knudsen diffusion is significant (Hite and Jackson, 1977; Haynes, 1978).

For the boundary condition at the particle surface we write:

$$N_{iS} = k_c(C_{iS} - C_{iB}) + y_{iS} \sum_{j=1}^{5} N_j$$

in accordance with the recommendations of Bird et al. (1960). Upon combining this equation with the definition of the Sherwood number and substituting for the pseudo-binary diffusivities using the Stefan-Maxwell equations we obtain for $i = 1,2 \ldots 5$:

$$C_{iB} = C_i(r_c) - \frac{2r_c}{C_{TS}\mathrm{Sh}} \sum_{j=1}^{5} \frac{C_j(r_c)N_i(r_c) - C_i(r_c)N_j(r_c)}{D_{ij,s}} \tag{10}$$

At the center of the particle we have

$$N_i(0) = 0, \qquad i = 1,2 \ldots 5 \tag{11}$$

Now Eqs. 8 and 9 with the boundary conditions, Eqs. 10 and 11 constitute ten equations with ten unknowns, the five component concentrations and the five components fluxes. These equations thus represent a complete solution to the problem (at any given state of carbon conversion). However, the equations can be simplified with no loss of generality by utilization of the two stoichiometric equations. (Only three of the reactions 1-4 are independent.) These are:

$$N_1 + N_2 + 2N_5 = 0 \tag{12}$$

$$N_1 + N_3 + 2N_4 = 0 \tag{13}$$

Furthermore, upon imposing the water-gas shift equilibrium, we have:

$$K_c = \frac{C_2 C_4}{C_1 C_3} \tag{14}$$

and therefore:

$$\frac{1}{C_1}\frac{dC_1}{dr} + \frac{1}{C_3}\frac{dC_3}{dr} = \frac{1}{C_2}\frac{dC_2}{dr} + \frac{1}{C_4}\frac{dC_4}{dr} \tag{15}$$

Equations 12 to 15 can be used to eliminate four of the differential equations, Eqs. 8 and 9. The equations must be combined in such a fashion that R_{V4} is eliminated since the kinetics of reaction no. 4 are irrelevant due to the equilibrium assumption. A set of equations convenient for numerical solution can be written:

$$\frac{dN_5}{dr} = R_{V3} - \frac{2N_5}{r}, r \neq 0 \tag{16}$$

$$\frac{d(N_1 + N_4)}{dr} = -R_{V1} - R_{V2} - \frac{2(N_1 + N_4)}{r}, r \neq 0 \tag{17}$$

$$\frac{dC_1}{dr} = \frac{C_1}{C_{TS}}(-N_1 f_1 + h_1) \tag{18}$$

$$\frac{dC_2}{dr} = \frac{C_2}{C_{TS}}(-N_2 f_2 + h_2) \tag{19}$$

$$\frac{dC_3}{dr} = \frac{C_3}{C_{TS}}(-N_3 f_3 + h_3) \tag{20}$$

$$\frac{dC_5}{dr} = \frac{C_5}{C_{TS}}(-N_5 f_5 + h_5) \tag{21}$$

$$C_4 = K_c C_1 C_3 / C_2 \tag{14}$$

$$N_1 = \frac{(N_1 + N_2)(2f_3 + f_4 + 2g_3 - g_4) - N_5(2f_2 - 2g_2 + g_5)}{(f_1 + f_2 + f_3 + f_4 + g_1 - g_2 + g_3 - g_4)} \tag{22}$$

$$N_2 = -N_1 - 2N_5 \tag{12}$$

$$N_4 = (N_1 + N_4) - N_1 \tag{23}$$

$$N_3 = -N_1 - 2N_4 \tag{13}$$

where

$$f_i = \frac{1}{C_i}\left[\frac{C_{TS}}{D^e_{Ki}} + \sum_{\substack{j=1 \\ j\neq i}}^{5} \frac{C_j}{D^e_{ij,s}}\right] \tag{24}$$

$$g_i = \sum_{\substack{j=1 \\ j\neq i}}^{4} \frac{(-1)^j}{D^e_{ij,s}} \tag{25}$$

$$h_i = \sum_{\substack{j=1 \\ j\neq i}}^{5} \frac{N_j}{D^e_{ij,s}} \tag{26}$$

Also, when $r = 0$ Eqs. 16 and 17 must be replaced by Eqs. 27 and 28

$$\frac{dN_5}{dr} = \frac{1}{3}R_{V3}, r = 0 \tag{27}$$

$$\frac{d(N_1 + N_4)}{dr} = -\frac{1}{3}(R_{V1} + R_{V2}), r = 0 \tag{28}$$

as can be verified by application of l'Hospitals rule to the last term in Eqs. 16 and 17.

The system of differential equations, Eqs. 16 to 21 constitutes a split boundary value problem. The component fluxes are known at the particle center, Eq. 11, and the component concentrations are known at the particle surface (or in the bulk fluid), Eq. 10. The complex algebra associated with these equations prompted us to attempt a shooting method of solution utilizing the Runge-Kutta algorithm. This approach was recently employed by Kaza et al. (1980), to solve the equations for intraparticle diffusion in the methanation reaction.

The component fluxes are zero at the particle center, Eq. 11. With guesses of the component concentrations at $r = 0$, Eqs. 16 to 21 were integrated using the 4th order Runge-Kutta algorithm to obtain the component fluxes, $N_i(r_c)$, and concentrations, $C_i(r_c)$ at the particle surface. The corresponding bulk concentrations were calculated from Eq. 10. The calculated bulk concentrations were then compared with the known bulk concentrations and in the event of a discrepancy new values of the $C_i(0)$ were assumed and the calculation repeated. In a sense our computational scheme is a generalization of the method of Weisz and Hicks (1962) who also integrated from the inside-out.

More precisely, the problem was set up as an optimization problem in which a set of $C_i(0)$ were obtained which minimized (i.e., $\phi = 0$) the objective function:

$$\phi = \sum_{i=1}^{5} (C_{iB} - C'_{iB})^2 \tag{29}$$

A computational algorithm based on a Taylor series linearization of the C'_{iB} was found to converge typically after two or three iterations.

CARBON MASS BALANCE:

At any point within the char particle a carbon material balance gives:

$$\left(\frac{\partial X_c}{\partial t}\right)_r = R_g / C_{co} \tag{30}$$

where $R_g = R_{V1} + R_{V2} + R_{V3}$ is the total carbon gasification rate. The total carbon conversion and average carbon gasification rate at any point in time are calculated from integrations across the particle, Eqs. 31 and 32 respectively:

$$\bar{X}_C = \frac{3}{r_C^3}\int_0^{r_C} r^2 X_C dr \tag{31}$$

$$\bar{R}_g = \frac{3}{r_C^3}\int_0^{r_C} r^2 R_g dr \tag{32}$$

The solution of Eq. 30 was obtained using the modified Euler predictor-corrector method.

RESULTS

These equations were solved with the same parameter values employed by the previous authors where possible. Our bulk diffusivity values were calculated from the Chapman-Enskog equation. Other parameter values are available in Table 1 of Srinivas and Amundson (1980).

Initial concentration profiles for two cases of interest are plotted as mole fractions to make possible a direct comparison with the previous author's computations. Also plotted in these figures is the total pressure gradient. Our Figures 1 and 2 are for the same con-

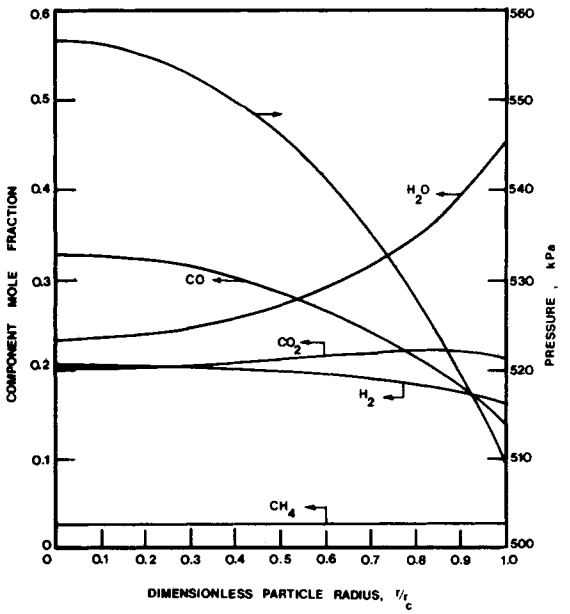

Figure 1. Gas phase concentration profiles at $t = 0$. ($T = 1{,}300$ K, $P = 506.5$ kPa, $y_{1B} = 0.50$, $y_{2B} = 0.15$, $y_{5B} = 0.03$.)

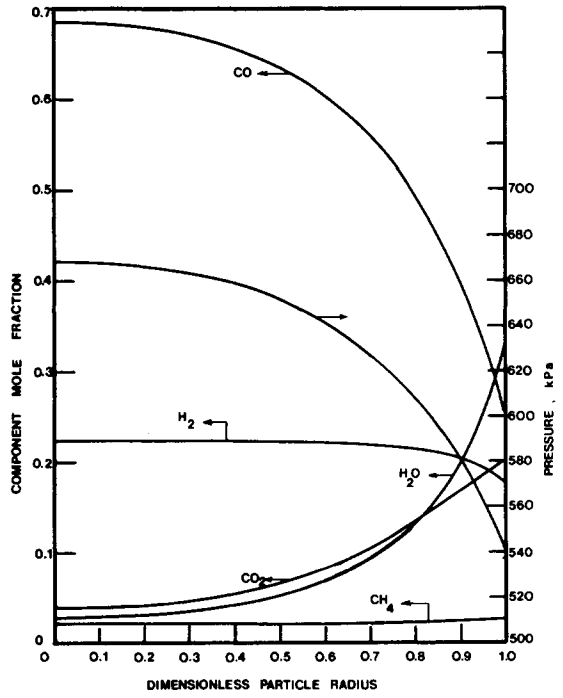

Figure 2. Gas phase concentration profiles at $t = 0$. ($T = 1{,}400$ K, $P = 506.5$ kPa, $y_{1B} = 0.50$, $y_{2B} = 0.15$, $y_{5B} = 0.03$.)

ditions as employed in the previous author's Figures 1a and 1b. Clearly the differences are substantial. Srinivas and Amundson calculate a much higher external mass transfer resistance than we find. At 1,300 K we find the resistance to external mass transfer to be minimal. The effect becomes somewhat more pronounced at 1,400 K, but still the major resistance to mass transfer is due to intraparticle diffusion. This is the situation normally expected for diffusion and reaction in porous media. Srinivas and Amundson find major contributions from external mass transfer at Sherwood Nos. as high as 25.

Concentration profiles five seconds into the reaction are plotted in Figure 3 for the same conditions as Figure 2. Over 80% of the carbon is gasified in the first five seconds at these conditions. Carbon conversion profiles corresponding to these same conditions are plotted in Figures 4 and 5. As noted by the previous authors,

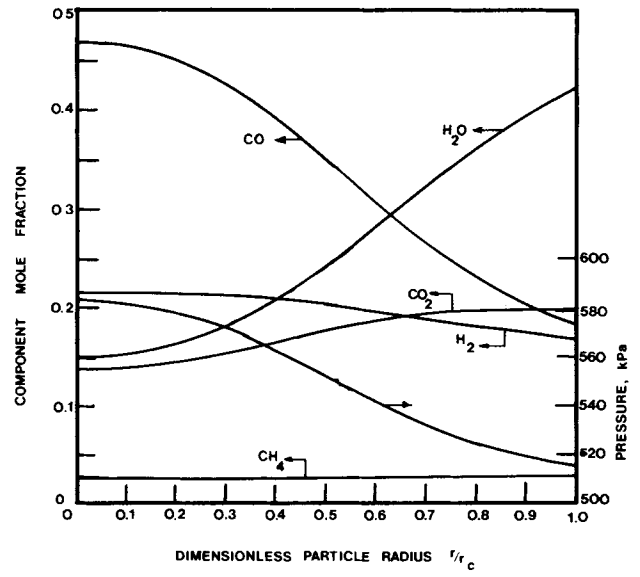

Figure 3. Gas phase concentration profiles at $t = 5$ s. ($T = 1{,}400$ K, $P = 506.5$ kPa, $y_{1B} = 0.50$, $y_{2B} = 0.15$, $y_{5B} = 0.03$.)

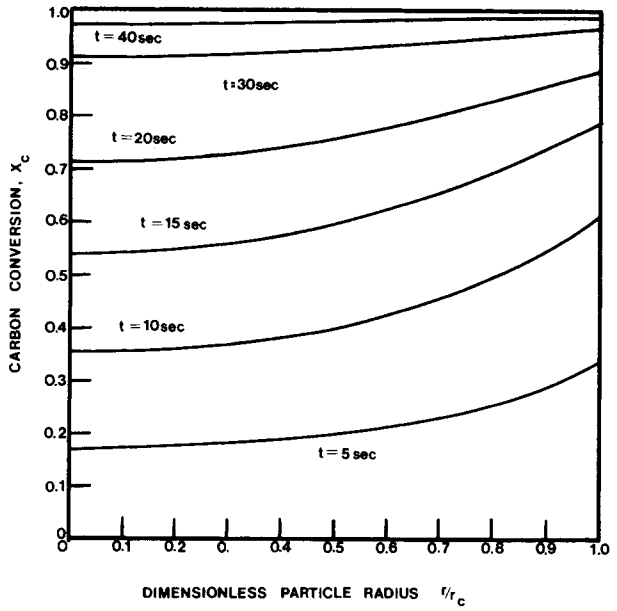

Figure 4. Carbon conversion profiles. ($T = 1{,}300$ K, $P = 506.5$ kPa, $y_{1B} = 0.50$, $y_{2B} = 0.15$, $y_{5B} = 0.03$.)

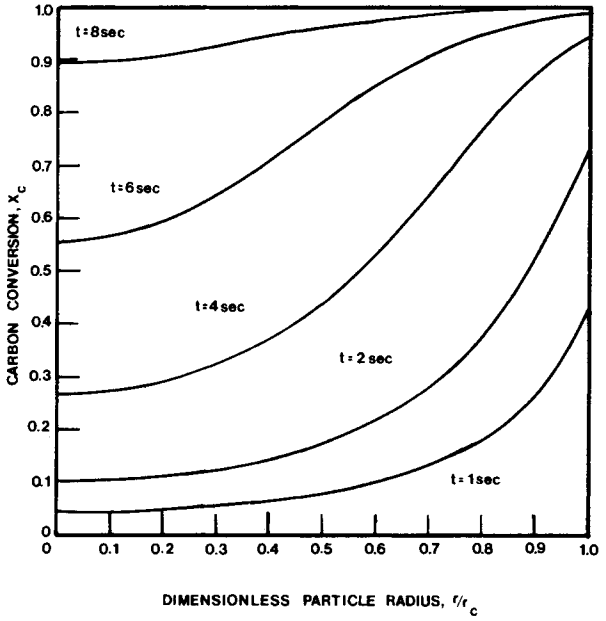

Figure 5. Carbon conversion profiles. ($T = 1{,}400$ K, $P = 506.5$ kPa, $y_{1B} = 0.05$, $y_{2B} = 0.15$, $y_{5B} = 0.03$.)

neither the Homogeneous model nor the Shrinking core model is applicable in these examples, Burnoff curves are plotted in Figure 6. In comparing these plots with the corresponding plots in Srinivas and Amundson it is evident that our calculations predict a much higher rate of gasification.

No doubt much of the difference between our computational results and the results of Srinivas and Amundson is due to approximations in the previous development. However, this will not likely explain the gross deviations observed. As already noted a major discrepancy between the two sets of computations is in the magnitude of the external mass transfer resistance. Srinivas and Amundson employed a diffusivity of $2 \times 10^{-6} m^2/s$ in their computations, and upon comparing this value with ordinary diffusivity values, it is clear that some consideration of Knudsen diffusion was incorporated into their estimate. While this value of diffusivity may be appropriate for computations of intraparticle diffusion, it is not appropriate to substitute this value into the Sherwood Number. An

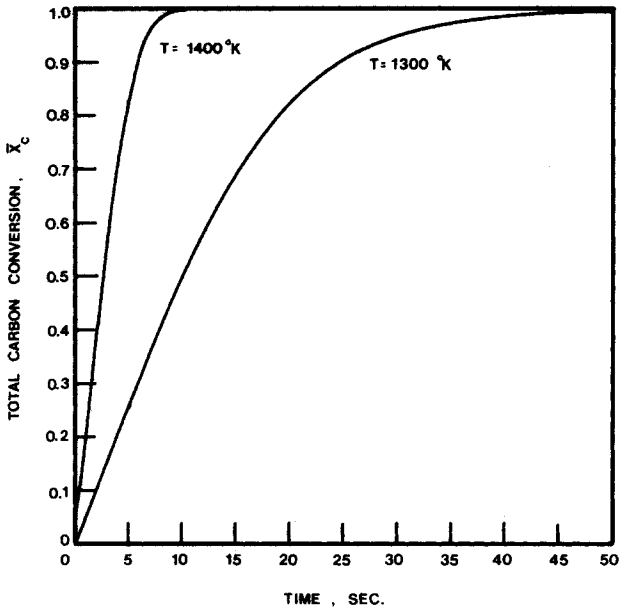

Figure 6. Carbon burnoff time. (P = 506.5 kPa, y_{1B} = 0.05, y_{2B} = 0.15, y_{5B} = 0.03.)

inordinately small value of the external mass transfer coefficient would result. This may explain the unusually large external mass transfer resistances and the relatively low rates of gasification of the previous investigation. We have not included an energy balance in our computations as we are in complete agreement with the approach of the previous authors.

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NOTATION

a = total surface area/total surface area at $X_c = 0$
C_i = component i concentration, kmol/m^3
C_{co} = $W_b\rho_o/12$ = 22.67 kmol carbon/m^3 particle
C_{TS} = total gas phase molar density at particle surface, kmol/m^3
D^e_{ij} = effective ordinary diffusivity, m^2/s
D_{im} = pseudo-binary ordinary diffusivity, m^2/s
D^e_{Ki} = effective Knudsen diffusivity, m^2/s
f_i = function defined by Eq. 24, s/m^2
g_i = function defined by Eq. 25, s/m^2
h_i = function defined by Eq. 26, kmol/m^4
K_c = water-gas shift equilibrium constant, Eq. 21
k_i = mass transfer coefficient, m/s
n = number of components
N_i = component i molar flux, kmol/m^2·s
r = radial coordinate, m
r_c = particle radius = 0.0005 m
R_g = total point carbon gasification rate = $R_{V1} + R_{V2} + R_{V3}$, kmol/m^3·s
$\bar{R}_g$ = total carbon gasification rate, kmol/m^3·s
$\bar{r}_p$ = mean pore radius = $2V_p/S$
R_S = reaction rate per unit carbon surface area, kmol/m^2·s
R_V = reaction rate per unit particle volume, kmol/m^3·s
s = number of reactions
S = total surface area, m^2/kg
Sh = Sherwood number = $2r_ck_i/D_{im}$
S_o = initial total surface area = 424,000 m^2/kg
T = absolute temperature, K
t = time, s
V_p = pore volume, m^3/kg
W_b = initial weight fraction carbon = 0.80
X_c = point carbon conversion
$\bar{X}_c$ = total carbon conversion
y_i = component i mole fraction

Greek Letters

ϵ = particle porosity
ϵ_o = initial partial porosity
ν = stoichiometric coefficient (negative for products)
ρ_o = initial partial density = 340 kg/m^3
ρ_c = carbon density = 1,447 kg/m^3
ϕ = optimization function, Eq. 29

Subscripts

S = particle surface quantity
B = bulk fluid quantity

LITERATURE CITED

Bird, R. B., W. E. Stewart and E. N. Lightfoot, *Transport Phenomena*, Chapt. 21, Wiley, New York (1960).

Dutta, S., C. Y. Wen, and R. J. Belt, "Reactivity of Coal and Char. 1. In Carbon Dioxide Atmosphere," *Ind. Eng. Chem., Process Design Develop.*, **16**, 20 (1977).

Haynes, H. W. Jr., "Calculations of Gas Phase Diffusion and Reaction in Heterogeneous Catalysts. The Importance of Viscous Flow," *Can. J. Chem. Eng.*, **26**, 582 (1978).

Hite, R. H. and R. Jackson, "Pressure Gradients in Porous Catalyst Pellets in the Intermediate Diffusion Regime," *Chem. Eng. Sci.*, **32**, 703 (1977).

Johnson, J. L., "Relationship Between Gasification Reactivities of Coal Char and Physical and Chemical Properties of Coal and Coal Char," *Kinetics of Coal Gasification*, Wiley, New York (1979).

Kaza, K. R., J. Villadsen and R. Jackson, "Intraparticle Diffusion Effects in the Methanation Reaction," *Chem. Eng. Sci.*, **35**, 17 (1980).

Mason, E. A., A. P. Malinauskas and R. B. Evans III, "Flow and Diffusion of Gases in Porous Media," *J. Chem. Phys.*, **46**, 3199 (1967).

Srinivas, B. and N. R. Amundson, "A Single-Particle Char Gasification Model," *AIChE J.*, **26**, 487 (1980).

Weisz, P. B. and J. S. Hicks, "The Behaviour of Porous Catalysts Particles in View of Internal Mass and Heat Diffusion Effects," *Chem. Eng. Sci.*, **17**, 265 (1962).

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