

MODELING OF GAS-CARBON REACTION IN PORE DIFFUSION CONTROL REGIME

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Abstract—A model is developed for pore diffusion controlled gas-carbon reactions where the reaction is limited to a narrow region on the exterior surface of the carbon particle. A planar geometry is used and an isothermal condition is assumed. However, the effects of pore structure change with conversion are included. The model can predict the penetration depth, the porosity profile, the reaction surface area profile and the concentration profile in the reaction zone. The model is an extension of Gavalas model[1] and an improvement over Desai and Yang's model[2]. The model predictions are compared with available experimental data and with those of Desai and Yang's model.

INTRODUCTION

The rate of a gas-carbon reaction could be controlled by three different processes: surface reaction kinetics, pore diffusion or external film diffusion. The majority of previous studies has been done for the reaction in kinetic controlled regime, although reactions in pore diffusion controlled regime are of more practical importance. This study is concerned with the reaction in pore diffusion controlled regime where the reaction is limited to a narrow region on the exterior surface of a carbon particle. Therefore, the particle can be assumed as a planar infinite slab. An isothermal condition is assumed neglecting the temperature gradient in the reaction zone.

If a carbon particle is exposed to a reactant gas, the carbon is removed by the reaction between the carbon and the reactant gas. The effective diffusivity and the available reaction surface area change with conversion. When the surface porosity reaches a critical porosity close to unity, the pore walls merge and disintegrate, and the surface starts moving at a steady state velocity. When the structural changes of pores with conversion are neglected, the classical model of Thiele can predict the behavior of a reaction in pore diffusion controlled regime; the steady state reaction rate, the penetration depth, and the reactant gas concentration profile in the reaction zone. However, the effect of the pore structure change with conversion may not be negligible in many gas-carbon reactions. Gavalas [1] pro-

posed an analytical model to calculate the steady state reaction rate with the effect of pore structure change included. At about the same time, Desai and Yang [2] reported a model to determine not only the steady state reaction rate but also the reactant gas concentration profile and the penetration depth.

The Desai and Yang's model assumes a linear porosity profile in the reaction zone and requires numerical iterations about the reactant gas concentration profile. The present model relaxes the assumption of the linear porosity profile and eliminates numerical iterations providing a solution in an integral form. This model uses an approach similar to that of Gavalas model in the determination of the steady state reaction rate, but the main portion of this model, i.e., determination of the porosity profile, the concentration profile and the penetration depth, is a new development. The simulation results from the present model will be compared with available experimental data in the literature [3] and with those of Desai and Yang's model.

MODEL DEVELOPMENT

The present model is developed on the assumptions that the gas-carbon reaction is first order with respect to the reactant gas concentration and that the penetration depth is small relative to the particle size, therefore adopting a plane geometry. Fig. 1 illustrates the reaction system. Further, a pseudo steady state is assumed for the gas-carbon reaction system [4], and the effective diffusivity and the reaction surface area are assumed to be functions of conversion of carbon. The following differential equations in the moving co-

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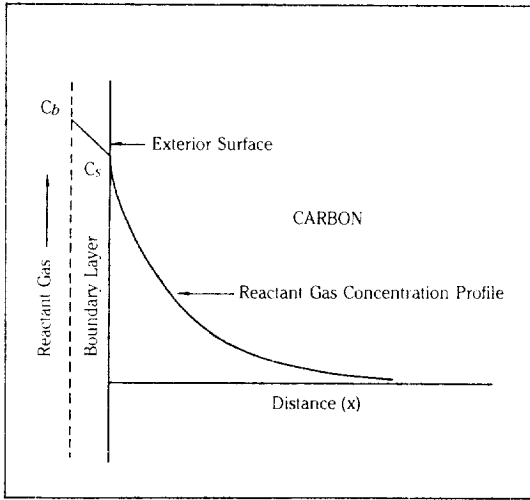


Fig. 1. The gas-carbon reaction system.

ordinate x can be derived from the mass balances of the carbon and the reactant gas in the reaction zone.

$$\frac{d}{dx} [D_e(f) \frac{dC}{dx}] = S(f)kC \quad (1)$$

$$\frac{df}{dx} = -\frac{Mk}{V\rho} S(f)C \quad (2)$$

Boundary conditions:

$$\begin{aligned} \text{At } x = 0, \quad C &= C_s \\ f &= f_s \end{aligned} \quad (3)$$

$$\text{At } x = \infty, \quad C = 0 \quad (4)$$

where x is the distance from the instantaneous surface boundary, $D_e(f)$ is the effective diffusivity, C is the reactant gas concentration, $S(f)$ is the relative reaction surface area or the ratio of instantaneous reaction surface area to the initial reaction surface, f is conversion of carbon, M is the molecular weight of carbon, k is the rate constant, V is the surface boundary moving velocity, ρ is density of carbon, C_s is the reactant gas concentration at the surface boundary and f_s is the conversion of carbon at the surface boundary. In Eqn. (1), the time derivative term for C is neglected using the pseudo-steady state approximation of Bischoff [4]. The time dependent partial differential equation for f is converted to Eqn.(2) in a time independent form by letting the substantial derivative for f be zero at the steady state. Instead of conversion(f) as the independent variable in equation (2), Gavalas used a different variable (q), the length by which the pore surface at position x has retreated due to the reaction during a given time interval, therefore the right hand side of equation (2) taking a different form. The reason for taking conversion as

the independent variable in this study is that conversion is more generally used in most of gas-carbon reaction studies. Let

$$x^* = x / L \quad (5)$$

$$C^* = C / C_s \quad (6)$$

$$D_e^* = D_e(f) / D_e^0 \quad (7)$$

where L is the characteristic length defined later and D_e^0 is the effective diffusivity at zero conversion. Then equations (1) and (2) can be rewritten to give equations (8) and (9) in dimensionless form, respectively.

$$\frac{d}{dx^*} (D_e^*(f) \frac{dC^*}{dx^*}) = \frac{L^2 S(f)k}{D_e^0} C^* \quad (8)$$

$$\frac{df}{dx^*} = -\frac{LMkC_s}{V\rho} S(f)C^* \quad (9)$$

Boundary conditions:

$$\begin{aligned} \text{At } x^* = 0, \quad C^* &= 1 \\ f &= f_s \end{aligned} \quad (10)$$

$$\text{At } x^* = \infty, \quad C^* = 0 \quad (11)$$

Starting from equations (8) and (9), we obtain eqns (12) and (13) by a mathematical manipulation in several steps similar to those in the Gavalas model.

$$V = \frac{MC_s(kD_e^0)^{\frac{1}{2}}}{\rho} \frac{1}{\left(2 \int_0^{f_s} G(f) df\right)^{\frac{1}{2}}} \quad (12)$$

where $G(f) = f / S(f) D_e^*(f)$

$$\frac{dC^*}{df} = \frac{V^2 \rho^2}{C_s^2 M^2 k D_e^0} \frac{G(f)}{C^*} \quad (13)$$

Rearranging equation (13) yields

$$C^* dC^* = \frac{V^2 \rho^2}{C_s^2 M^2 k D_e^0} G(f) df \quad (14)$$

On integration of both sides of equation (14) and substituting equation (12) for V in equation (14), equation (15) is obtained which relates the conversion to the reactant gas concentration.

$$C^* = \left[\int_0^f G(f) df / \int_0^{f_s} G(f) df \right]^{\frac{1}{2}} \quad (15)$$

It is interesting that C^* is a function of f only, being independent of other reaction variables such as the rate constant and the initial effective diffusivity. Substituting equation (15) into equation (9) yields

$$\frac{df}{dx^*} = -\left[\frac{L^2 k}{D_e^0} \right]^{\frac{1}{2}} S(f) \left[2 \int_0^f G(f) df \right]^{\frac{1}{2}} \quad (16)$$

By separation of variables and integration, we obtain equation (17) which can determine the conversion profile in the reaction zone.

$$x^* = - \left[\frac{D_e^0}{L^2 k} \right]^{\frac{1}{2}} \int_{f_s}^f df \{ S(f) \left[2 \int_0^f G(f) df \right]^{\frac{1}{2}} \}^{-1} \quad (17)$$

The characteristic length, L , in equation (17) is now defined as the distance from the surface boundary to a point where the conversion has the value of 0.01. L represents thickness of the reaction zone or penetration depth. The penetration depth may be defined in a different way as the distance from the surface boundary to a point where the concentration instead of the conversion has a predetermined small value. The penetration depth was measured by shelling the partially reacted carbon in the reaction zone layer by layer until the surface area or the density approached the bulk value [5]. The reason for defining L in the former way is that the penetration depth can be explicitly calculated from equation (18), otherwise iterations would be required.

$$L = - \left[\frac{D_e^0}{k} \right]^{\frac{1}{2}} \int_{f_s}^{0.01} df \{ S(f) \left[2 \int_0^f G(f) df \right]^{\frac{1}{2}} \}^{-1} \quad (18)$$

The model requires inputs such as the rate constant(k), the initial effective diffusivity(D_e^0), the bulk concentration of the reactant gas, functions to calculate the reaction surface area and the effective diffusivity at a given conversion, and the critical porosity at which the pore walls merge and disintegrate. Three well-known models to calculate the reaction surface area are shown in Table 1. The effective diffusivity is calculated by

$$D_e(f) = D_g \epsilon / \tau \quad (19)$$

where τ is the tortuosity factor. Using the input data, the penetration depth, the conversion profile and the

concentration profile in the reaction zone can be explicitly calculated from equations (18), (17) and (15), respectively. The porosity profile is calculated from the conversion profile by

$$\epsilon = \epsilon^0 + (1 - \epsilon^0) f \quad (20)$$

where ϵ^0 is the initial porosity of the carbon particles. Iterations are required to calculate the surface boundary moving velocity(V) from equation (12). A value is assumed for C_s . The assumed value is compared with the value calculated from

$$C_s = C_b - \frac{V_o}{k_m M} \quad (21)$$

where k_m is the external mass transfer coefficient. Iterations are continued until a predetermined convergence criterion is met. If the resistance to external mass transfer is negligible, C_s can be assumed to be equal to C_b and the above iterative procedure is not necessary.

RESULTS AND DISCUSSION

In Fig. 2, the porosity profile predicted by this model is compared with that observed in a carbon rod gasification experiment [3]. Since the rate constant and the initial effective diffusivity for the carbon rod gasification are not available in the literature, they are treated as adjustable parameters and determined so that the reaction rate and the penetration depth predicted by this model match with the experimental data. The

Table 1. Reaction surface area models.

Model	Equation
Grain Model [7]	$S(f) = (1-f)^m$ $m=2/3$ for spherical grains $m=1/2$ for cylindrical grains $m=0$ for flat plate grains
Petersen Model [8]	$S(f) = \frac{\xi(2G-3\xi)}{(2G-3)}$ $f = \frac{\epsilon_o}{1-\epsilon_o} \left[\xi^2 \left(\frac{G-\xi}{G-1} \right) - 1 \right]$ $\frac{4}{27} \epsilon^0 G^3 - G + 1 = 0$
Random Pore Model [9]	$S(f) = (1-f) \sqrt{1-\Psi \ln(1-f)}$ $\Psi = [-\ln(1-\epsilon_o)]^{-1}$

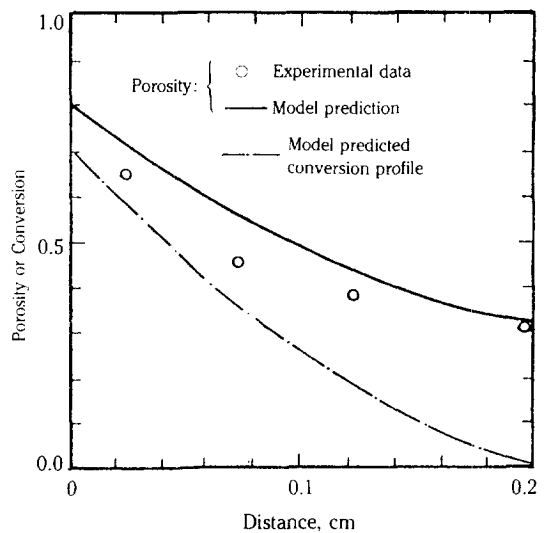


Fig. 2. Comparison of the porosity profile between experimental data and the model prediction. (Conversion of carbon predicted by the model is also shown.)

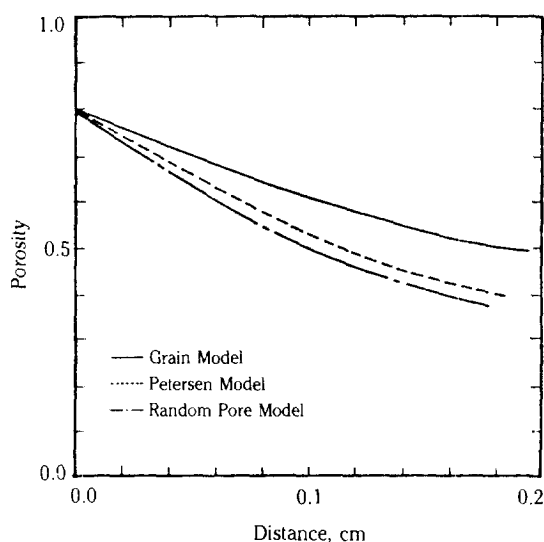


Fig. 3. Comparison of the porosity profile between different reaction surface area models.

critical porosity was observed to be about 0.8 in the carbon rod experiment, therefore the same value is used in the model calculation. The random pore model is used to determine the reaction surface area at a given conversion. The Petersen model and the grain model were also tested (Fig. 3). The Petersen model yields a result very similar to that of the random pore model, but the grain model gives considerably higher porosities than the other two models. The model prediction gives good agreement with the experimental data, considering that there may be uncertainties in

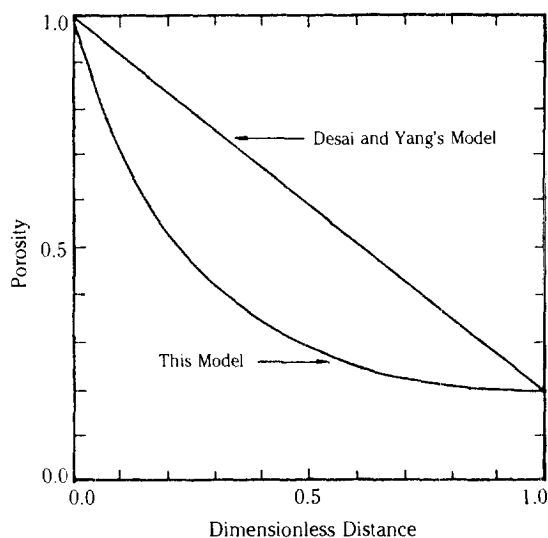


Fig. 4. Comparison of the porosity profile between the Desai and Yang's model and this model.

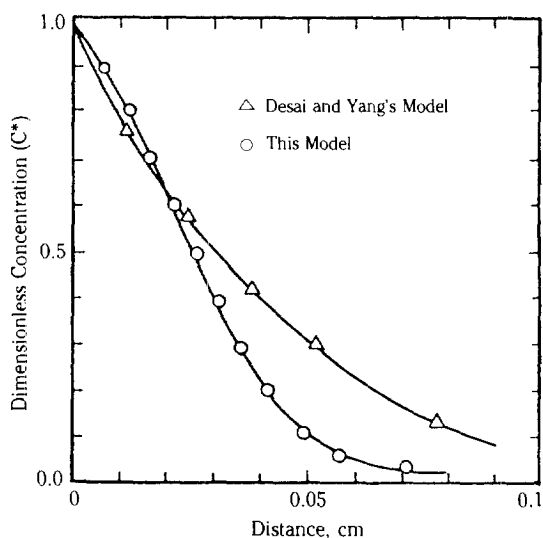


Fig. 5. Comparison of the concentration profile between the Desai and Yang's model and this model.

determining the local reaction surface area and the effective diffusivity with conversion and that the carbon rod is cylindrical in shape, while the model assumes a planar geometry. Other experimental data for further verification of the model are not available.

Comparisons in the porosity profile and the concentration profile between the Desai and Yang's model and this model are shown in Fig. 4 and Fig. 5, respectively. The data used for the comparison are shown in Table 2. A constant reaction surface area is assumed because the analytical solution of the Desai and Yang's model being compared is based on that assumption. As shown in Fig. 4, the local porosity of Desai and Yang's model, where the porosity profile is assumed to be linear, is higher than the porosity predicted by this

Table 2. Input data for the simulation.

Temperature, °C	1,000
Pressure, atm	1.0
Reactant gas bulk mole fraction	0.21
Carbon bulk density, g/cm ³	1.0
Preexponential factor, 1/sec	2.0×10^{12}
Activation energy, cal/mol	59,300
Initial porosity	0.20
Molecular diffusivity at 25°C, cm ² /sec	0.15
Tortuosity factor	60/ ϵ
Reaction surface area model	random pore model

model, where the porosity profile is self-determined eliminating the linearity assumption. Therefore the reactant gas could penetrate deeper with the Desai and Yang's model giving a higher reaction rate. As shown in Fig. 5, the concentration profile predicted by the present model exhibits a shape different from what is commonly expected in gas solid reactions. Unlike the monotonous decrease of the concentration with distance as shown by the Desai and Yang's model, the concentration curve obtained from this model has an inflection point; the rate at which the concentration decreases with the distance increases until the inflection point is reached, thereafter the rate decreases. Fig. 6 shows the concentration curve can have an inflection point depending on the effective diffusivity profile (or porosity profile). The concentration curves in Fig. 6 are obtained by solving equation (8) for a known effective diffusivity profile. For varying reaction surface area, the Desai and Yang's model requires numerical iterations. A parabolic concentration profile is first assumed to begin the iteration, and then iterations are continued until the difference between the newly calculated concentration profile and the one in the previous step becomes smaller than a predetermined value. While, the present model can give an explicit solution for the concentration profile eliminating such iterative procedure.

The model developed here can be used to calculate the intrinsic kinetic data of coal-gas reactions from the apparent kinetic data obtained assuming the reaction occurs at the external surface only, or vice versa. The model can also be used for determination of the effective diffusivity from the reaction rate and the penetration depth measured under the pore diffusion controlled regime. The effective diffusivity can be measured

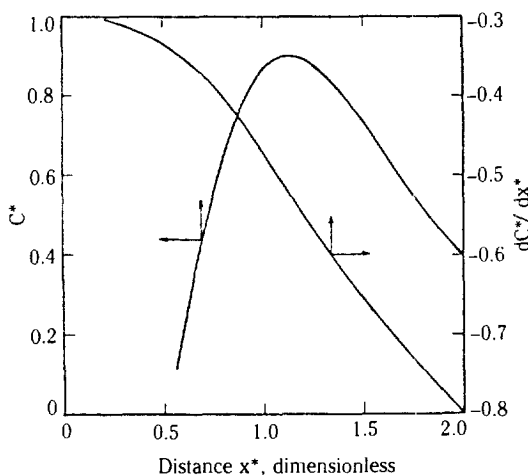


Fig. 6. The concentration profile for $D_e^* = e^{-2x}$ and $S(f)L^2k/D_e^* = 1$ in Eqn. (8).

directly by the physical method of Wicke-Kallenbach [10]. However, the direct measurement cannot take into account dead end pores present in carbonaceous materials like coals. Yang and Liu [9] reported that, for a carbon dioxide-carbon reaction, the effective diffusivity measured via the chemical reaction rate measurement was 60% higher than that obtained from the Wicke-Kallenbach method. Yang and Liu attributed the discrepancy to the presence of dead end pores.

CONCLUSION

An analytical model is developed for pore diffusion controlled gas-carbon reactions. The model can predict the penetration depth, the porosity profile, the reaction surface area profile and the concentration profile in the reaction zone. The model can also be used to determine the effective diffusivity for a gas-carbon reaction by measuring the penetration depth and the reaction rate. The model predictions exhibit good agreement with the experimental data for the carbon rod gasification. Compared to the Desai and Yang's model, this model gives an improvement in determining the porosity profile and requires less computational efforts.

NOMENCLATURE

- C : concentration of gas, (mol/cm³)
- D_e : effective diffusivity (cm²/sec)
- D_g : molecular diffusivity (cm²/sec)
- f : conversion of carbon
- $G(f)$: defined by equation (12)
- k : reaction rate constant (1/sec)
- k_m : mass transfer coefficient (cm/sec)
- L : penetration depth (cm)
- M : molecular weight (g/mol)
- q : the length by which the pore structure has re-treated during a given time interval (cm)
- $S(f)$: ratio of instantaneous reaction surface area to the initial surface area
- V : surface boundary moving velocity (cm/sec)
- x : distance (cm)

Greek Letters

- ρ : density, (g/cm³)
- ϵ : porosity
- τ : tortuosity factor

Superscripts

- * : dimensionless
- o : initial

Subscripts

- b : bulk

- e : effective
s : surface boundary

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