

# ANALYTICAL SOLUTIONS FOR NON-LINEAR CONVERSION OF A POROUS SOLID PARTICLE IN A GAS—I. ISOTHERMAL CONVERSION

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**Abstract**—Analytical descriptions are presented for non-linear heterogeneous conversion of a porous solid particle reacting with a surrounding gas. Account has been taken of a reaction rate of general order with respect to gas concentration, intrinsic reaction surface area and pore diffusion, which change with solid conversion and external film transport. Results include expressions for the concentration distributions of the solid and gaseous reactant, the propagation velocity of the conversion zone inside the particle, the conversion time and the conversion rate. The complete analytical description of the non-linear conversion process is based on a combination of two asymptotic solutions. The asymptotic solutions are derived in closed form from the governing non-linear coupled partial differential equations pertaining to conservation of mass of solid and gaseous reactant, considering the limiting cases of a small and large Thiele modulus, respectively. For a small Thiele modulus, the solutions correspond to conversion dominated by reaction kinetics. For a large Thiele modulus, conversion is strongly influenced by internal and external transport processes and takes place in a narrow zone near the outer surface of the particle: solutions are derived by employing boundary layer theory. In Part II of this paper the analytical solutions are extended to non-isothermal conversion and are compared with results of numerical simulations.

## 1. INTRODUCTION

Reactions between a gas and a solid are of considerable industrial importance. Such reactions are frequently encountered in the process industry. Knowledge of the conversion behaviour is a prerequisite to the analysis of existing processes and to the design of new installations.

For gas–solid reactions, internal and external transport and reaction kinetics have to be considered simultaneously. It depends on the relative magnitudes of the rates of transport and the rate of reaction whether or not important gradients inside and around the particle are built up or not. Furthermore, since the solid is involved in the reaction, the conditions inside the particle will change with solid conversion. Effective pore diffusion coefficients will change as a result of evolution of the pore structure, reaction rates as a result of development of internal reaction surface. Taking account of these dependencies, the governing partial differential equations pertaining to conservation of mass of solid and gaseous reactant are of an essentially non-linear, coupled form.

Analytical descriptions of the conversion process are generally based on solutions of linearized or otherwise simplified representations of the general equations. In the shrinking particle model, the particle is assumed to be impervious to gaseous reactants, reaction only occurring on the external surface of the shrinking particle (Field *et al.*, 1967; Caram and Amundson, 1977; Spalding, 1979). In the volumetric reaction model or progressive conversion model, the

reaction gas is allowed to penetrate into the particle, assuming a static internal solid structure, i.e. constant effective diffusivity and constant reaction surface area (Wen 1968; Ishida and Wen, 1968, 1971; Froment and Bischoff, 1979; Prins, 1987). An extensive collection of solutions of the simplified differential equations has been presented by Aris (1975). Applying a transformation allowed Del Borghi *et al.* (1976) and Dudokovic (1976) to reduce the coupled set of partial differential equations, for first-order reactions in gas and with constant diffusivity, into a single partial differential equation. More sophisticated models dealing with pore branching and pore enlargement are presented by Simons (1979), Gavalas (1981), Sotirchos and Burganos (1986), Reyes and Jensen (1986) and Tseng and Edgar (1989).

Studies of the complete problem in which account is taken of non-linear reaction rates and conversion-dependent diffusion constants are generally involved with application of numerical simulation techniques (Wen, 1968; Ishida and Wen, 1968; Yang, 1983; Sotirchos and Amundson, 1984; Prins, 1987; Loewenberg *et al.*, 1987). Accurate numerical solution of the underlying coupled non-linear partial differential equations, however, requires an extremely fine grid structure involving long computational time and high costs. A complete numerical approach is an elaborate and time-consuming method to identify the effect of process parameters and to provide a general insight into the conversion process.

An alternative to the numerical approach is presented in this paper. Rather than numerical ones, analytical solutions for the complete problem are given. The method for deriving these solutions consists of distinguishing two limiting cases which are

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associated with the value of the Thiele modulus  $\phi_0$ : viz.  $\phi_0 \ll 1$  and  $\phi_0 \gg 1$ . For both cases, closed-form solutions are given which are subsequently combined to arrive at analytical descriptions which are applicable over the entire range of  $\phi_0$  values. The solutions provide an improved means for assessing the non-linear conversion behaviour of a solid particle reacting with a gas.

## 2. BASIC EQUATIONS

The conversion of a solid particle includes external and intra-particle mass transfer, chemical kinetics and changing particle properties during conversion (e.g. pore structure). In this section a macroscopic approach is presented for modelling the conversion of a solid particle in a gas. The general assumptions for the modelling are:

- The particle is spherically symmetric.
- Continuum description of the porous solid particle. This assumption presumes that the largest length scale characteristic of the porous structure is much smaller than the characteristic length associated with concentration gradients. A criterion for the validity can be derived from the present study.
- The particle is composed of one solid reactant and mineral matter only. The solid reactant is the only reactive matter during particle conversion. The mineral matter is the source of ash and is considered as inert. No catalytic effect of the mineral matter is included in the model.
- Only one heterogeneous reaction is taking place, characterized by a stoichiometric coefficient.
- The rate of reaction is assumed to be  $m$ th-order with respect to the gaseous reactant concentration.
- The reaction takes place on the internal surface area of the particle.
- Transport of the gaseous reactant inside the char particle is by diffusion only, i.e. isobaric conditions are assumed for which a criterion for the validity is given by Froment and Bischoff (1979).
- Initially, the particle reacts with constant size until the surface porosity reaches a critical value, which causes fragmentation of the local ash matrix. At that instant, the particle size will decrease.
- A pseudo-steady state exists for gas–solid reactions. Diffusion of the gaseous reactant inside the particle is fast compared to the solid consumption (Froment and Bischoff, 1979).
- The temperature of the particle is uniform throughout the particle volume (isothermal conversion). In Part II of this paper results will be extended to the case for non-isothermal conversion.

### 2.1. Mass balance and reactivity equations

The pseudo-steady-state mass balance of the gaseous reactant can be expressed by the summation of diffusion and the mass consumed by reaction in the control volume as shown in the following equation:

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left[ D_e(\epsilon_S) r^2 \frac{\partial C_A}{\partial r} \right] - R_A = 0. \quad (2.1)$$

The mass balance of the solid reactant can be written as

$$\frac{\partial C_S}{\partial t} = -R_S \quad (2.2)$$

where  $C_A$  = local concentration of the gaseous reactant,  $C_S$  = local concentration of the solid reactant,  $\epsilon_S$  = local porosity of the particle,  $D_e(\epsilon_S)$  = the effective diffusivity,  $r$  = radial co-ordinate, and  $t$  = time.

The reaction rate  $R_A$  of the gaseous reactant can be written as

$$R_A = a k_s C_A^m A_g(\epsilon_S) \quad (2.3)$$

while the reaction rate of the solid reactant is

$$R_S = k_s C_A^m A_g(\epsilon_S) \quad (2.4)$$

where  $a$  = stoichiometric coefficient of the reaction (i.e. the number of moles of the gaseous reactant required for 1 mol of the solid reactant),  $k_s$  = reaction rate constant,  $m$  = order of reaction with respect to the gaseous reactant, and  $A_g(\epsilon_S)$  = reaction surface area per unit of volume. The initial conditions are

$$t = 0, \quad C_A = 0, \quad C_S = C_{S,0}, \\ \epsilon_S = \epsilon_{S,0} \text{ and } r_s = R. \quad (2.5)$$

For symmetry reasons we have

$$r = 0, \quad \frac{\partial C_A}{\partial r} = 0 \text{ and } \frac{\partial C_S}{\partial r} = 0. \quad (2.6)$$

The boundary condition at the external surface of the particle is

$$r = r_s, \quad D_e \frac{\partial C_A}{\partial r} = k_d (C_{A,\infty} - C_{A,s}) \quad (2.7)$$

where  $C_{S,0}$  = initial solid reactant concentration of the particle,  $C_{A,\infty}$  = gaseous reactant concentration in the bulk,  $C_{A,s}$  = gaseous reactant concentration at the external surface of the particle,  $\epsilon_{S,0}$  = initial porosity of the particle,  $k_d$  = mass transfer coefficient in the external gas layer,  $r_s$  = particle radius, and  $R$  = initial particle radius.

To allow for changes in the particle radius in the course of the reaction process, we consider, analogous to Gavalas (1981), that the particle shrinks because of disintegration of its structure at some critical value of the particle porosity  $\epsilon^*$ :

$$r_s = r(\epsilon_S = \epsilon^*). \quad (2.8)$$

The reaction rate constant  $k_s$  is expressed in the Arrhenius form and has to be estimated experimentally. The mass transfer coefficient  $k_d$  can be calculated from empirical correlations [e.g.

Ranz–Marshall (1952) for a convective flow, and Prins (1987) for a fluidized bed].

The stoichiometric coefficient  $a$  is determined by the reaction scheme. For char combustion  $a$  is equal to unity if the main gaseous product of char oxidation is  $\text{CO}_2$ , and  $a$  is equal to  $\frac{1}{2}$  if the main product is  $\text{CO}$ .

Both the effective diffusivity  $D_e$  and the reaction surface area  $A_p$  are functions of the solid porosity  $\varepsilon_s$ .

The porosity of the particle satisfies the relation (Wen, 1968)

$$\frac{1 - \varepsilon_s}{1 - \varepsilon_{s,0}} = \frac{\rho}{\rho_0} \quad (2.9)$$

where  $\rho$  is the density of the particle, and  $\rho_0$  is the initial density. The density of the particle is the average density of the density of the solid reactant and the ash density (mineral matter). Assuming that the ash density remains constant during the conversion of the particle, eq. (2.9) can be written as follows:

$$\frac{1 - \varepsilon_s}{1 - \varepsilon_{s,0}} = X_{\text{ash}} + (1 - X_{\text{ash}})S \quad (2.10)$$

where  $X_{\text{ash}}$  = initial ash concentration of the particle, based on mass, and  $S (C_s/C_{s,0})$  = reduced concentration of the solid reactant.

Hence, both  $D_e$  and  $A_p$  can explicitly be written as a function of the solid concentration  $S$ .

## 2.2. Dimensionless equations

The gas reactant mass balance of eq. (2.1) can be written in dimensionless form as

$$\frac{1}{\xi^2} \frac{\partial}{\partial \xi} \left[ D(S) \xi^2 \frac{\partial C}{\partial \xi} \right] - \phi_0^2 C^m A(S) = 0 \quad (2.11)$$

where  $\phi_0$  is the Thiele modulus based on initial conditions:

$$\phi_0 = R \sqrt{\frac{a k_s A_{g,0} C_{A,\infty}^{m-1}}{D_{e,0}}} \quad (2.12)$$

while  $\xi = r/R$ ,  $C = C_A/C_{A,\infty}$ ,  $S = C_s/C_{s,0}$ ,  $D = D_e/D_{e,0}$ , and  $A = A_p/A_{p,0}$ .

The reduced solid reactant mass balance in dimensionless form becomes

$$\frac{\partial S}{\partial \Theta} = -C^m A(S) \quad (2.13)$$

where

$$\Theta = k_s C_{A,\infty}^m A_{g,0} t / C_{s,0} \quad (2.14)$$

The initial and boundary conditions are

$$\Theta = 0, \quad C = 0 \quad \text{and} \quad S = 1 \quad (2.15)$$

$$\xi = 0, \quad \frac{\partial C}{\partial \xi} = 0 \quad \text{and} \quad \frac{\partial S}{\partial \xi} = 0 \quad (2.16)$$

$$\xi = \xi_s, \quad D \frac{\partial C}{\partial \xi} = Bi_m (1 - C_s) \quad \text{and} \quad S = S^* \quad (2.17)$$

where  $\xi_s = r_s/R$ ,  $C_s$  is the reduced gaseous reactant concentration at the external surface of the particle,

and  $Bi_m$  is the Biot number for mass transfer defined as

$$Bi_m = R \frac{k_d}{D_{e,0}} \quad (2.18)$$

The critical solid surface concentration  $S^*$  in eq. (2.17) can be obtained from eq. (2.10) taking  $\varepsilon_s$  equal to the critical porosity  $\varepsilon^*$ .

## 3. ASYMPTOTIC SOLUTIONS

The differential eqs (2.11) and (2.13) together with the boundary conditions (2.15)–(2.17) form a complete set for describing the reduced solid reactant concentration  $S$  and the reduced gaseous reactant concentration  $C$  inside the particle. Solving these equations in closed form is complicated as the effective diffusivity  $D$  and the reaction surface area  $A$  are general functions of the solid reactant,  $S$ , and the reaction rate is of general order with respect to the gaseous reactant,  $C$ . Because of the non-linearity of these terms, no general analytical solution in closed form seems to be attainable.

The method of this paper for arriving at analytical solutions of the governing equations consists of making a distinction between two limiting cases. These are associated with the value of the Thiele modulus  $\phi_0$  and correspond to  $\phi_0 \ll 1$  and  $\phi_0 \gg 1$ . For both cases, closed-form solutions are derived from the governing equations which are asymptotically valid for  $\phi_0 \rightarrow 0$  and  $\phi_0^{-1} \rightarrow 0$ , respectively. In Section 4, these solutions are combined to arrive at an analytical description of the main conversion parameters which is applicable over the entire range of values of  $\phi_0$ .

### 3.1. Solutions asymptotically valid for $\phi_0 \ll 1$

In the case when  $\phi_0 \ll 1$ , the gaseous reactant mass balance of eq. (2.11) can be well approximated by the following equation, with a relative error of  $O(\phi_0^2)$ :

$$\frac{1}{\xi^2} \frac{\partial}{\partial \xi} \left[ D \xi^2 \frac{\partial C}{\partial \xi} \right] = 0. \quad (3.1)$$

Integration of this equation and application of the boundary conditions (2.16) and (2.17) yields  $C = 1$ . Hence, the gaseous reactant fully penetrates the particle and the concentration of the gaseous reactant is time-independent.

Substitution of  $C = 1$  in eq. (2.13) yields

$$\frac{\partial S}{\partial \Theta} = -A(S) \quad (3.2)$$

and subsequent integration of this equation and application of initial condition (2.15) gives the time necessary to reach a solid concentration  $S$  of the solution:

$$\Theta = \int_S^1 \frac{dS}{A(S)}. \quad (3.3)$$

The inverse of eq. (3.3) represents the solid concentration  $S$  as a function of time.

It is clear from the above solutions that the particle reacts uniformly throughout its volume ( $S$  is independent of the radius of the particle). Hence, the size of the particle remains the same while the porosity increases during conversion.

The fractional conversion  $X$  of the solid reactant will be defined as follows:

$$X = 1 - \frac{\int_0^R 4\pi r^2 C_s dr}{\int_0^R 4\pi r^2 C_{s,0} dr} = 1 - 3 \int_0^1 S \xi^2 d\xi. \quad (3.4)$$

Since  $S$  is independent of  $\xi$  in this case, the above equation yields, for the conversion:

$$X = 1 - S. \quad (3.5)$$

From this equation and eq. (3.2), one obtains, for the conversion rate  $(d/d\Theta)X$ :

$$\frac{dX}{d\Theta} = A(S)_{S=1-X}. \quad (3.6)$$

The time  $\Theta$  necessary to reach a certain degree of conversion  $X$  can be written as

$$\Theta = \int_{1-X}^1 \frac{dS}{A(S)}. \quad (3.7)$$

The above solutions conform to solutions for the kinetics-controlled regime ( $\phi_0 \ll 1$ ) given by Del Borghi *et al.* (1976), Gavalas (1980), Simons (1983) and Tseng and Edgar (1984).

### 3.2. Solutions asymptotically valid for $\phi_0 \gg 1$

For  $\phi_0 \gg 1$ , the value of the second term on the left-hand side of eq. (2.11) is very large. This suggests as approximation of eq. (2.11) the equation

$$C^m A(S) = 0 \quad (3.8)$$

while eq. (2.13) reduces to

$$\frac{\partial S}{\partial \Theta} = 0. \quad (3.9)$$

Application of the initial conditions of eq. (2.15), and assuming  $m > 0$ , yields the solution

$$C = 0 \quad \text{and} \quad S = 1. \quad (3.10)$$

Evidently, this solution cannot satisfy the boundary condition imposed at the outer surface of the particle given by eq. (2.17). To overcome this problem, we have to introduce the concept of a boundary layer. The boundary layer is a narrow zone of conversion near the outer surface of the particle which moves inwardly with time. The boundary layer is the region within which the gaseous reactant concentration  $C$  and the solid reactant concentration  $S$  of the particle interior, as given by eq. (3.10), are adjusted to their values prescribed at the outer surface, as given by eq. (2.17). A formal mathematical procedure for connecting the solutions of the various regions is known as the method of matched asymptotic expansions

(Van Dyke, 1964). Application of this method leads to a consistent description of conversion variables, which is valid over the entire domain.

To arrive at the equations describing the concentrations in the boundary layer a boundary layer coordinate  $\eta$  is introduced:

$$\xi = \xi_s(\Theta) - \frac{\eta}{\phi_0} \quad (3.11)$$

where  $\xi_s$  is the reduced particle radius which reduces with time as a result of conversion. From eq. (3.11) we obtain, for the first derivative with respect to  $\xi$ :

$$\partial/\partial \xi = -\phi_0 \partial/\partial \eta \quad (3.12)$$

and the first derivative with respect to time becomes

$$\partial/\partial \Theta = \partial/\partial \Theta - u \partial/\partial \eta \quad (3.13)$$

where  $u$  is the reduced velocity of the outer surface or the velocity by which the conversion zone or boundary layer moves as a result of reaction:

$$u = -\phi_0 d\xi_s/d\Theta. \quad (3.14)$$

Consistent with the assumption of a thin boundary layer, effects of the curvature will be disregarded, i.e. terms in  $\xi^2$  in eq. (2.11) will be approximated as

$$\xi^2 = \left[ \xi_s(\Theta) - \frac{\eta}{\phi_0} \right]^2 \approx \xi_s^2(\Theta) \quad (3.15)$$

because  $\phi_0 \gg 1$  while  $\eta = O(1)$  in the boundary layer. Furthermore, from eq. (3.14) it can be verified that the time for overall conversion is of order of magnitude  $\phi_0/u$ , while from the right-hand side of eq. (3.13) it follows that the transient time is of order of magnitude  $1/u$ . In other words, the initial transient behaviour will last over a time which is of order of magnitude  $1/\phi_0$  compared to the time for overall conversion. Disregarding any effects of relative magnitude  $O(1/\phi_0)$  we omit the time derivative in the boundary layer equations and assume a constant boundary layer velocity  $u$ .

Up to a relative error of  $O(1/\phi_0)$ , the boundary layer approximation of the gas reactant mass balance as given by eq. (2.11) then becomes

$$\frac{d}{d\eta} \left[ D(S) \frac{dC}{d\eta} \right] - C^m A(S) = 0. \quad (3.16)$$

For the solid reactant mass balance we obtain, with a relative error of  $O(\phi_0^{-1})$ :

$$u \frac{dS}{d\eta} = C^m A(S). \quad (3.17)$$

The boundary conditions can be derived from boundary condition (2.17) and interior solution (3.10) as

$$\eta = 0 \quad D \frac{dC}{d\eta} = -\frac{Bi_m}{\phi_0} (1 - C_s) \quad \text{and} \quad S = S^* \quad (3.18)$$

$$\eta \rightarrow \infty, \quad \frac{dC}{d\eta} = 0, \quad \frac{dS}{d\eta} = 0, \quad C = 0 \quad \text{and} \quad S = 1. \quad (3.19)$$

It is noted in passing that, for  $m < 1$ , a so-called 'dead zone' can exist (Aris, 1975). In that case, conversion is limited to the region  $0 \leq \eta < \eta_0$ , while for  $\eta > \eta_0$  the conditions specified in boundary condition (3.19) exist. The solutions derived in the subsequent analysis are also valid for this case.

The above boundary layer equations were first formulated by Gavalas (1981). His formulation, however, resulted from a less formal derivation, leaving the error of the various approximations, and hence the area of validity of the solution, unspecified. The solutions presented by Gavalas (1981) are basically the same as those presented below, but are arrived at adopting a slightly different solution procedure.

The main objective of the subsequent mathematical treatment is to derive an expression for the boundary layer velocity  $u$ , which is also the velocity by which the particle shrinks with time as a result of conversion. Subtracting eq. (3.17) from eq. (3.16), integrating the resulting equation with respect to  $\eta$  and applying boundary conditions (3.19) yields

$$D(S) \frac{dC}{d\eta} + u(1 - S) = 0. \quad (3.20)$$

At the particle surface, where eq. (3.18) holds, eq. (3.20) can be written in the form

$$C_s = 1 - u \frac{\phi_0}{Bi_m} (1 - S^*) \quad (3.21)$$

where  $C_s$  is the reduced concentration of the gaseous reactant at the external surface of the particle. Combining eqs (3.21) and (3.17) for  $\eta = 0$ , while eliminating  $C_s$ , results in the following expression including the boundary layer velocity  $u$ :

$$u^{1/m} \left[ \frac{1}{A(S)} \frac{dS}{d\eta} \right]_{\eta=0}^{1/m} + u(1 - S^*) \frac{\phi_0}{Bi_m} = 1. \quad (3.22)$$

To assess  $[1/A(S)(dS/d\eta)]_{\eta=0}$ , we rearrange eq. (3.17) as follows:

$$C = \left[ u \frac{1}{A(S)} \frac{dS}{d\eta} \right]^{1/m}. \quad (3.23)$$

Differentiation of this equation with respect to  $\eta$ , and subsequent substitution in eq. (3.20), yields

$$D(S) \left[ \frac{1}{A(S)} \frac{dS}{d\eta} \right]^{1/m-1} \frac{d}{d\eta} \left[ \frac{1}{A(S)} \frac{dS}{d\eta} \right] = -mu^{1-1/m}(1 - S). \quad (3.24)$$

Integrating the above differential equation from  $\eta = 0$  to  $\infty$ , we obtain the following expression:

$$\left[ \frac{1}{A(S)} \frac{dS}{d\eta} \right]_{\eta=0}^{1+1/m} = (1 + m)u^{1-1/m} \int_{S^*}^1 \frac{1 - S}{D(S) A(S)} dS. \quad (3.25)$$

Substitution in eq. (3.22) yields

$$\left[ \frac{1 + m}{2} (\psi u)^2 \right]^{1/(1+m)} + u(1 - S^*) \frac{\phi_0}{Bi_m} = 1 \quad (3.26)$$

with

$$\psi = \left[ 2 \int_{S^*}^1 \frac{1 - S}{D(S) A(S)} dS \right]^{1/2}. \quad (3.27)$$

By means of eq. (3.26), which conforms with Gavalas (1981), we have obtained an algebraic expression which enables the value of the boundary layer velocity, i.e. the velocity of the narrow conversion zone near  $\xi = \xi_s$  apparent for  $\phi_0 \gg 1$ , to be assessed. The physical parameter  $\psi$  in eq. (3.26) represents the combined effect of pore surface area and effective diffusivity spatially averaged over the reaction zone where the solid concentration changes from  $S^*$  to unity. Noting that  $\psi$  depends solely on  $S^*$ , which depends on  $\varepsilon^*$  and  $\varepsilon_0$  [see eq. (2.10)], the parameter  $\psi$  is a constant determined a.o. by the initial pore size distribution of the particle.

For a number of reactions, it can be assumed that the reaction is first-order with respect to the gaseous reactant ( $m = 1$ ). In this case, eq. (3.26) can be rewritten and an explicit relationship for  $u$  can be derived as

$$u = \frac{1}{\psi + \frac{\phi_0}{Bi_m}(1 - S^*)}. \quad (3.27)$$

From eq. (3.24), we can obtain the solid concentration profile if  $A(S)$  and  $D(S)$  are known. Subsequently, from eq. (3.23), we can obtain the gas concentration profile.

Finally, we will derive expressions for conversion degree and conversion time in terms of the already given boundary layer velocity  $u$ . From eq. (3.4) we obtain, for the conversion of the solid:

$$X = (1 - \xi_s^3) - S^*(1 - \xi_s^3) \quad (3.28)$$

where the first term on the right-hand side represents the solid conversion due to the reaction, while the second term represents the solid loss due to abrasion (fragmentation) of the outer surface of the particle.

Noting that the boundary layer velocity  $u$  in eq. (3.26) is independent of time, i.e.  $Bi_m$  or the mass transfer coefficient  $k_d$  is independent of  $\xi_s$ , eq. (3.14) can be integrated. Substituting the result in eq. (3.28), the conversion of the solid as function of the time becomes

$$X = \left[ 1 - \left( 1 - \frac{u}{\phi_0} \Theta \right)^3 \right] (1 - S^*). \quad (3.29)$$

Differentiating this equation yields an expression for the conversion rate:

$$\frac{dX}{d\Theta} = 3 \left( 1 - \frac{X}{1 - S^*} \right)^{2/3} (1 - S^*) \frac{u}{\phi_0}. \quad (3.30)$$

The inverse of eq. (3.29) represents the time  $\Theta$  necessary to reach a certain degree of conversion  $X$ :

$$\Theta = \frac{\phi_0}{u} \left[ 1 - \left( 1 - \frac{X}{1 - S^*} \right)^{1/3} \right]. \quad (3.31)$$

The time required for ultimate conversion  $X_\infty$  is

defined as the time required for the particle radius to reach a final value of  $\xi_{s,\infty}$ . The time required for ultimate conversion then follows from eq. (3.31), substituting  $X = X_\infty$ , where

$$X_\infty = (1 - \xi_{s,\infty}^3)(1 - S^*). \quad (3.32)$$

In the case of complete conversion ( $X_\infty = 1$ ), which is only possible if both the final particle diameter  $\xi_{s,\infty}$  and the solid surface concentration  $S^*$  are zero, the time required for complete conversion is

$$\Theta_c = \frac{\phi_0}{u}. \quad (3.33)$$

### 3.3. Discussion

(i)  $\phi_0 \ll 1$ . From the solutions asymptotically valid for  $\phi_0 \ll 1$ , it is seen that the gaseous reactant fully penetrates the particle and the solid reactant reacts uniformly throughout the volume. Noting the non-dimensionalisation of the time given by eq. (2.14), it follows from solutions (3.6) and (3.7) that, for  $\phi_0 \ll 1$ , the conversion rate and conversion time are functions of the reaction degree and the evolution of the internal reaction surface, respectively. Conversion variables do not depend on effective pore diffusivity and external film transport. It can thus be concluded that, for  $\phi_0 \ll 1$ , the reaction kinetics is the rate-controlling step. This corresponds to the type of conversion usually referred to as regime I: e.g. see Laurendeau (1978). An illustration of the distribution of solid concentration  $S$  and gas concentration  $C$ , typical for the case  $\phi_0 \ll 1$ , is given in Fig. 1(a).

(ii)  $\phi_0 \gg 1$ . The solutions asymptotically valid for  $\phi_0 \gg 1$  depend upon  $u$ , the boundary layer velocity, which can be calculated from eq. (3.26). From eq. (3.26) it is noted that we may distinguish two limiting cases. These cases are associated with the value of the

Biot number for mass transfer  $Bi_m$  with respect to the value of the Thiele modulus  $\phi_0$ .

(iia)  $\phi_0 \gg 1$  and  $Bi_m \gg \phi_0$ . If  $Bi_m$  is very large with respect to  $\phi_0$ , eq. (3.26) can be approximated by the following relationship:

$$u = \sqrt{\frac{2}{1+m}} \frac{1}{\psi} \quad (3.34)$$

and we obtain from eq. (3.21), for the reduced concentration of the gaseous reactant at the external surface of the particle:

$$C_s = 1. \quad (3.35)$$

Figure 1(b) illustrates the concentration gradients inside the particle when  $\phi_0 \gg 1$  and  $Bi_m \gg \phi_0$ .

The time for conversion can be approximated by the relation

$$\Theta = \sqrt{\frac{1+m}{2}} \phi_0 \psi \left[ 1 - \left( 1 - \frac{X}{1-S^*} \right)^{1/3} \right]. \quad (3.36)$$

Referring to the expression for  $\psi$  given by eq. (3.27), it can be concluded that, for  $\phi_0 \gg 1$  and  $Bi_m \gg \phi_0$ , conversion depends on functions related to reaction surface area and internal pore diffusion. Conversion does not depend on external film transport. Conversion governed by pore diffusion and reaction is generally referred to as regime II. In cases termed regime II, however, concentration gradients can extend over a significant part of the particle interior. Such a situation would occur for the parameter range  $\phi_0 \geq O(1)$  and  $Bi_m \gg \phi_0$ . For  $\phi_0 \gg 1$  and  $Bi_m \gg \phi_0$ , pore diffusion becomes so limiting that conversion occurs in a boundary layer rather than in a region which extends over the entire particle volume. The case  $\phi_0 \gg 1$  and  $Bi_m \gg \phi_0$  can thus be considered as a limiting situation of the case usually referred to as regime II.

(iib)  $\phi_0 \gg 1$  and  $Bi_m \ll \phi_0$ . If  $Bi_m$  is very small with respect to  $\phi_0$ , we obtain from eq. (3.26), as approximation for the boundary layer velocity, the expression

$$u = \frac{Bi_m}{\phi_0(1-S^*)}. \quad (3.37)$$

From eq. (3.21) we obtain, for the concentration of the gaseous reactant at the external surface of the particle:

$$C_s = 0. \quad (3.38)$$

Figure 1(c) illustrates the concentration gradients inside the particle for  $\phi_0 \gg 1$  and  $Bi_m \ll \phi_0$ .

The time for conversion can be approximated by

$$\Theta = \frac{(1-S^*)\phi_0^2}{Bi_m} \left[ 1 - \left( 1 - \frac{X}{1-S^*} \right)^{1/3} \right]. \quad (3.39)$$

Hence, for low values of  $Bi_m$  with respect to  $\phi_0$ , the conversion process directly depends on  $Bi_m$ , which includes the external mass transfer coefficient  $k_d$ . Conversion variables do not depend on parameters related to reaction rate and internal pore diffusion.

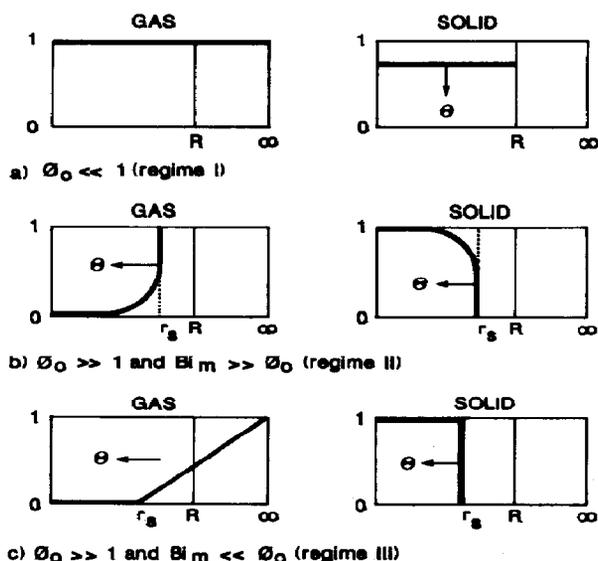


Fig. 1. Reduced gas and solid concentration profiles in and around the particle for different conversion regimes.

Hence, for  $\phi_0 \gg 1$  and  $Bi_m \ll \phi_0$ , transport through the external gas layer dominates the conversion process. This corresponds to conversion referred to as regime III.

4. COMPOSITE SOLUTION

In Sections 3.1 and 3.2, asymptotic closed-form solutions have been derived for the limiting cases  $\phi_0 \ll 1$  and  $\phi_0 \gg 1$ , respectively. To arrive at an analytical solution which is applicable over the entire range of  $\phi_0$  values, the asymptotic solutions will be combined. The combination is such that the resulting composite solution is consistent with the limiting cases, i.e. the composite solution approaches the results for conversion controlled by kinetics as  $\phi_0 \ll 1$ , and the results for conversion governed by internal and/or external transport as  $\phi_0 \gg 1$ .

The composite solution for the time  $\Theta$  necessary to reach a certain degree of conversion  $X$  is written as

$$\Theta(X) = [\Theta_1^\kappa(X) + \Theta_2^\kappa(X)]^{1/\kappa} \tag{4.1}$$

where  $\Theta_1(X)$  represents the time for conversion given by eq. (3.7), and  $\Theta_2(X)$  the time for conversion given by eq. (3.31). Noting that  $\Theta_1 = O(1)$  and  $\Theta_2 = O(\phi_0)$ , it can be verified from eq. (4.1) that, for  $\kappa > 0$ ,  $\Theta$  approaches  $\Theta_1$  as  $\phi_0 \rightarrow 0$ , and  $\Theta$  approaches  $\Theta_2$  as  $\phi_0 \rightarrow \infty$ . The fit parameter  $\kappa$  is used to adjust the behaviour of  $\Theta$  in the intermediate range of  $\phi_0$  values.

The time  $\Theta_c$  required for ultimate conversion follows from eq. (4.1) by substituting into the right-hand side the value of  $X$  at ultimate conversion  $X_\infty$ . Furthermore, the conversion rate  $\partial X/\partial \Theta$  as a function of the conversion degree  $X$  can be assessed by differentiating eq. (4.1), resulting in

$$\frac{dX}{d\Theta}(X) = \frac{[\Theta_1^\kappa(X) + \Theta_2^\kappa(X)]^{1-1/\kappa}}{\frac{\Theta_1^{\kappa-1}(X)}{(dX/d\Theta)_1} + \frac{\Theta_2^{\kappa-1}(X)}{(dX/d\Theta)_2}} \tag{4.2}$$

where  $(dX/d\Theta)_1$  represents the conversion rate given by eq. (3.6), and  $(dX/d\Theta)_2$  the conversion rate given by eq. (3.30).

A value for the fit parameter  $\kappa$  in the above composite solution can be obtained from a comparison with the solutions for the linear case, i.e.  $m = 1$ ,  $A(S) = 1$ ,  $D(S) = 1$ , and  $S^* = 0$ . For the linear case, exact solutions valid over the entire range of  $\phi_0$  values are known (Ishida and Wen, 1968).

In Fig. 2, a comparison is made between the exact solutions for the linear case and the present composite solutions taking various values of  $\kappa$ . It is concluded that, for the linear case,  $\kappa = 2$  gives a good fit to the exact solution. The same conclusion is drawn from the results given in Fig. 3. Here we have shown  $(d/d\Theta)X_{\text{exact}}$  and  $(d/d\Theta)X$  for various values of  $\kappa$  vs  $\phi_0$  for  $\Theta = 0$ , and assuming different values for the Biot number, i.e.  $Bi_m = 100$  and 1.

In Part II of this paper a comparison is made with results of numerical simulations executed for non-linear cases. Again it is found that  $\kappa = 2$  gives good agreement. Summarizing, the present composite solu-

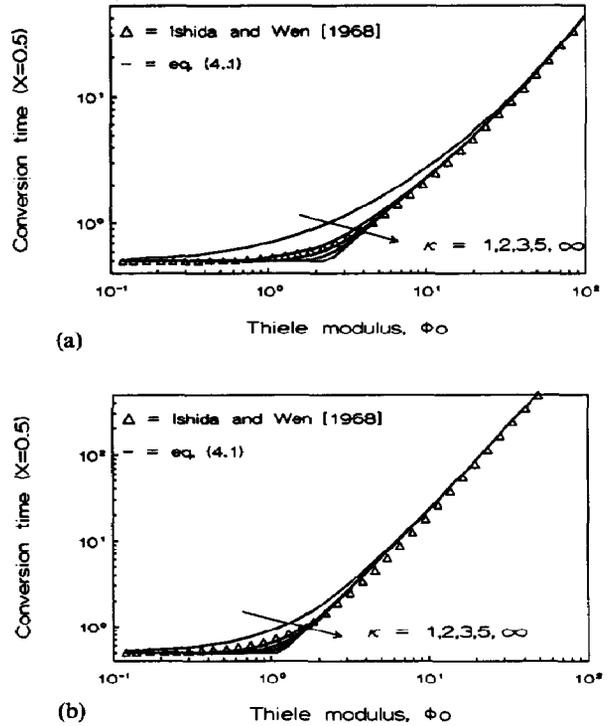


Fig. 2. Conversion time for  $X = 0.5$  vs Thiele modulus  $\phi_0$  for  $Bi_m = 100$  (a) and  $Bi_m = 1$  (b): a comparison between Ishida and Wen (1968) and eq. (4.1) for different values of  $\kappa$  (linear case).

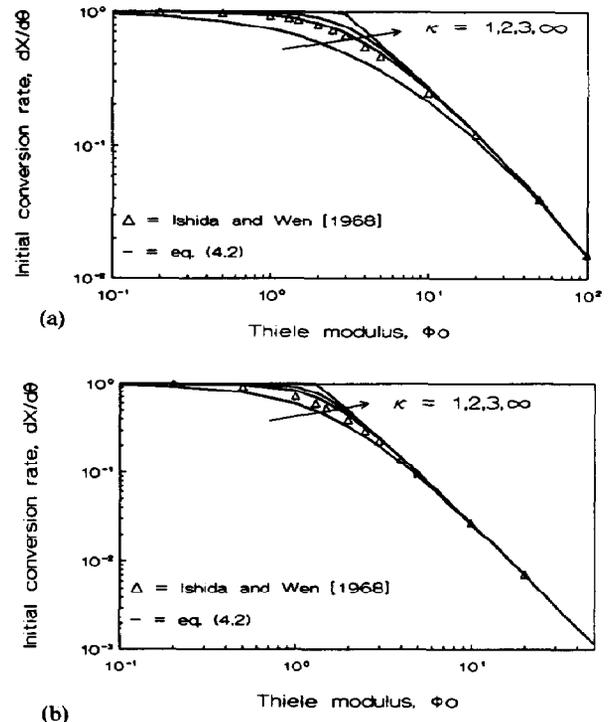


Fig. 3. Conversion rate at  $\Theta = 0$  vs Thiele modulus  $\phi_0$  for  $Bi_m = 100$  (a) and  $Bi_m = 1$  (b): a comparison between Ishida and Wen (1968) and eq. (4.2) for different values of  $\kappa$  (linear case).

tions are asymptotically exact in the limiting cases  $\phi_0 \ll 1$  and  $\phi_0 \gg 1$ . They agree well with exact and numerical results in the intermediate range of  $\phi_0$  values taking  $\kappa = 2$ .

### 5. CONCLUDING REMARKS

In the previous analysis, complete analytical solutions for the non-linear conversion of a porous solid particle in a gas have been developed. The solutions include heterogeneous reaction rates in non-linear form, effective pore diffusion which changes as a result of evolution of the pore structure, external gas film transport and decrease of the particle size due to solid conversion.

The complete analytical solutions consist of a combination of two closed-form solutions asymptotically valid for  $\phi_0 \ll 1$  and  $\phi_0 \gg 1$ , where  $\phi_0$  is Thiele modulus defined by eq. (2.12). For  $\phi_0 \ll 1$ , the solutions correspond to conversion determined by reaction kinetics. For  $\phi_0 \gg 1$ , the solutions correspond to conversion strongly influenced by internal and external transport processes and taking place in a narrow zone near the outer surface of the particle which reduces in size with time.

In Part II of this paper, the analytical solutions are extended to non-isothermal conversion and are compared with results of numerical simulations.

### NOTATION

$a$	stoichiometric coefficient of the reaction
$A$	reduced reaction surface area ( $A = A_g/A_{g,0}$ )
$A_{g,0}$	reference value of reaction surface area, e.g. initial value or maximum value
$A_g$	reaction surface area per unit of volume
$Bi_m$	Biot number for mass transfer ( $Bi_m = Rk_d/D_{e,0}$ )
$C$	reduced concentration of the gaseous reactant ( $C = C_A/C_{A,\infty}$ )
$C_A$	concentration of the gaseous reactant
$C_S$	concentration of the solid reactant
$D$	reduced effective diffusivity ( $D = D_e/D_{e,0}$ )
$D_e$	effective diffusivity
$k_d$	mass transfer coefficient in the external gas layer
$k_s$	reaction rate constant
$m$	order of reaction with respect to the gaseous reactant
$r$	radial co-ordinate
$r_s$	particle radius
$R$	initial particle radius
$R_A$	reaction rate of the gaseous reactant
$R_S$	reaction rate of the solid reactant
$S$	reduced concentration of the solid reactant ( $S = C_S/C_{S,0}$ )
$S^*$	critical solid concentration at outer surface of particle
$t$	time
$u$	reduced boundary layer velocity ( $u = -\phi_0 \partial \xi_s / \partial \Theta$ )
$X$	solid conversion

$X_{ash}$  initial ash concentration of the particle, based on mass

### Greek letters

$\varepsilon^*$	critical particle porosity causing breakage of the local particle structure at the outer surface
$\varepsilon_S$	particle porosity
$\eta$	boundary layer co-ordinate
$\Theta$	reduced time ( $\Theta = k_s C_{A,\infty}^m A_{g,0} t / C_{S,0}$ )
$\Theta_c$	time required for maximum conversion $X_\infty$
$\kappa$	fit parameter in the composite solution
$\xi$	reduced radial co-ordinate ( $\xi = r/R$ )
$\rho$	density of the particle
$\phi_0$	Thiele modulus based on initial conditions ( $\phi_0 = R \sqrt{ak_s A_{g,0} C_{A,\infty}^{m-1} / D_{e,0}}$ )
$\psi$	pore diffusion parameter given by eq. (3.27)

### Subscripts

0	initial value
1	first region, $\phi_0 \ll 1$
2	second region, $\phi_0 \gg 1$
$\infty$	final situation, at ambient conditions
A	gas reactant
max	maximum value
s	at external surface area of the particle
S	solid reactant

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