Kinetic modeling of solid-gas reactions at reactor scale: A general approach

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Loïc FAVERGEON [a], Jacques MORANDINI [b], Michèle PIJOLAT [a], Michel SOUSTELLE [a]
[a] Centre SPIN, Ecole Nationale Supérieure des Mines, Saint-Etienne, FRANCE
[b] ASTEK Rhône-Alpes, Echirolles, FRANCE

Abstract

Understanding the industrial reactors behavior is a difficult task in the case of solid state reactions such as solid-gas reactions. Indeed the solid phase is a granular medium through which circulate gaseous reactants and products. The properties of such a medium are modified in space and time due to reactions occurring at a microscopic scale. The thermodynamic conditions are driven not only by the operating conditions but also by the heat and mass transfers in the reactor.

We propose to numerically resolve the thermohydraulic equations combined with kinetic laws which describe the heterogeneous reactions. The major advantage of this approach is due to the large variety of kinetic models of grains transformation (~40) compared to the usual approach, especially in the case of surface nucleation and growth processes which need to quantitatively describe the grain conversion kinetics at a microscopic scale due to nucleation frequency and growth rate laws obtained in separate isothermal and isobaric experiments.

The heat and mass transfers terms entering in the balance equations at a macroscopic scale depend on the kinetics evaluated at the microscopic scale. These equations give the temperature and partial pressure in the reactor, which in turn influence the microscopic kinetic behavior.

Keywords: kinetics, simulation, heat and mass transfers, multi-scale

1. Introduction

Solid-gas reactions are of great interest in many industrial fields such as nuclear, chemistry, metallurgy, CO_2 capture, etc… Industrial reactors where these reactions take place are difficult to understand. Indeed the solid phase is a granular medium through which circulate gaseous reactants and products. The properties of such a medium are modified in space and time due to reactions occurring at a microscopic scale. The thermodynamic conditions are driven not only by the operating conditions but also by the heat and mass transfers in the reactor. Several models have been developed to account for the complexity of these transformations such as the grain model [1] and the pore model [2] and all the related incremented models. However most of these models are based on the law of additive reaction times of Sohn [3] for which the order respective to the gas in the kinetic rate equation must be equal to 1. However such condition is scarcely encountered in many gas-solid reactions so that erroneous results may be obtained using this simplified approach.

Moreover, such approaches necessitate to describe the reaction kinetics using the shrinking core model or similar laws, that is to say using rate equations for which dα/dt is the product of an Arrhenius

term by a f(α) function [1,2]. Such a behavior is unfortunately not always encountered for several reasons, especially in the case of reactions involving surface nucleation and growth processes [4].

In order to overcome such problems, we have developed a multi-physic approach based on the finite elements method which combines the resolution of the thermohydraulic equations with the kinetic laws describing the heterogeneous reactions at the scale of dense particles.

We propose [4] a large variety of models at the microscopic scale based on a general equation which accounts for the real influence of the partial pressures P_i of the relevant gases:

$$\frac{d\alpha}{dt} = \phi(T, P_i, ...) S_m(t, \phi, \gamma, r_0) \qquad (1)$$

where $\phi(T, P_i, ...)$ is the areic reactivity of growth, function of the thermodynamic conditions only (temperature, partial pressure, etc…) and $S_m(t, \phi, \gamma, r_0)$ is a function of the initial and current morphology of the sample and therefore of time, of ϕ, of the areic frequency of nucleation γ, and of the grains dimensions (e.g.: r_0 is the radius for spherical grain).

Using equation (1), about forty kinetic models may be derived based on various assumptions on the nucleation and growth processes in order to simulate heterogeneous reactions. These models can be simulated using CIN3 software (N° IDDN FR001130014.000.SP.2009.000.30625). Nevertheless CIN3 is able to simulate reactions where temperature and partial pressure of gases are uniform inside the granular medium. In the case of heterogeneous reactors where mass and heat transfers induce spatial and temporal variations of both temperature and partial pressures, it is necessary to couple kinetics of a grains population with the resolution of mass and heat transfers. This is the aim of the multi-physic software CIN4.

Section 2 presents the various scales approach and the main assumptions made in CIN4. Then section 3 summarizes a simplified presentation of the different mathematical models used, for kinetic modeling at grains scale as well as for heat and mass transfers at reactor scale. And finally section 4 presents the simulation of a thermobalance experiment, including both kinetic curves and mass and heat variations inside the system.

2. General presentation

2.1 The scales for modeling

Several geometrical scales characterize all phenomena which occur in a reactor. A rigorous description of our modeling process requires a precise definition of these different scales. We have deliberately set these scales from the objects: mesh, grain, grains population, agglomerate and reactor. In this paper, only three scales will be discussed: grain, grain population and reactor. At the grain scale, the nuclei appear at the grain surface[1] and grow at the expense of the initial solid phase: the kinetics is governed by the shape of the grain, the type of growth, the localization of the rate limiting-step of growth, the direction of development of the new phase. Then a microscopic population is a set of grains in the same thermodynamic conditions, i.e. the gradients of temperature and gas partial pressure are extremely small inside the population. Statistical considerations allow to define average behavior of this population from grain's one. And finally at the reactor scale, the chemical reaction is coupled with mass and heat transfers.

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[1] Avrami's laws cannot be used for solid-gas heterogeneous reactions involving powders since they are based on bulk nucleation in an infinite volume, which is not physically acceptable.

2.2 The assumptions of the model

Six assumptions are done in this model:

A1: gas production and consummation by the reaction do not disturb the total pressure distribution,

A2: the gases are diluted in a carrier gas,

A3: gases flow rates are low (less than 5 l.h^{-1} for a circular section of 2 cm),

A4: the gases are considered as ideal,

A5: the growth process can be described by a succession of elementary steps, one of them controls the growth kinetics (rate-determining step approximation),

A6: the grains shape and size distribution are known.

3. Mathematical modeling

3.1 Kinetic laws at grain and microscopic population scale

As previously recalled, in order to model reactions which involve surface nucleation and growth of the nuclei, one can use equation (1). For isothermal and isobaric conditions, the S_m function can take various expressions calculated from assumptions on the growth type (isotropic or anisotropic), the development direction of the new phase (inwards or outwards), the localization of the rate determining step of growth and the grains shape (spheres, cylinders, plates). Soustelle [5] has detailed the laws establishment and the expressions of S_m for each model.

The software CIN4 is able to solve forty-two kinetic models. Some of these models are derived at grain scale: in this case nucleation is considered as instantaneous compared to growth, so all the grains take the same kinetic law. Other models are derived at microscopic population scale: both nucleation and growth are taken into account, which leads to two kinds of models. According to the growth type (isotropic or anisotropic), two methods are used to calculate the fractional conversion of the reaction:

- in the case of isotropic growth of the nuclei, we used a statistical approach based on the works of Johnson and Mehl [6] and Mampel [7], then of Delmon [8],
- in the case of anisotropic growth, each grain starts its transformation at various times and the whole microscopic fractional conversion can be obtained considering the nuclei appearing on each grain of the microscopic population.

Moreover, CIN4 enables the calculation for a real grain size distribution.

3.2 Heat and mass transport at reactor scale

The macroscopic scale is the center of heat and mass exchanges that are described by the thermal and hydrodynamic models, as well as by a mass transfers equation.

3.2.1 Thermal model

Heat transfer is described by the following equation valid throughout each part of the reactor Ω^T :

$$\left[(1-\varepsilon)\rho_s c_{ps} + \varepsilon \rho_g c_{pg} \right] \frac{\partial T}{\partial t} + \varepsilon \rho_g c_{pg} \vec{u} \bullet \vec{\nabla} T + \vec{\nabla} \bullet \left(-k \vec{\nabla} T \right) = Q^T \tag{2}$$

where s and g indexes refer to solids and gases respectively.

This equation is accompanied by two kinds of boundary conditions:

- Neumann conditions which impose the value of the heat flow on $\partial \Omega_N^T$ boundary:

$$-k \vec{\nabla} T \bullet \vec{n} = \phi_{imposed} + h(T - T_a) + \varepsilon_r \sigma \left(T^4 - T_a^4 \right) \tag{3}$$

- Dirichlet conditions which impose the value of the temperature on $\partial\Omega_D^T$ boundary:

$$T = T_D \tag{4}$$

These equations are valid for each part of the reactor: solid (ε=0), gas (ε=1), porous media ($0<\varepsilon<1$).

3.2.2 Hydrodynamic model

As the granular medium is static and as we consider solid-gas reactions, mass transfers are only due to the flowing of the gas produced or consumed inside the porous medium. The modeling of this flow inside the porous medium is based on notions of hydrodynamic charge and flow rate considerations. Hydrodynamic charge is calculated according to:

$$H = z + \frac{P}{\rho g} + \frac{1}{2g} u^2 \tag{5}$$

The flow rate is not the rate of fluidic particles inside the pores but an equivalent continuous rate. This flow rate is linked to the mass gradient according to the Darcy's law, which is expressed by:

$$\vec{u}_d = -\frac{K}{\eta}\vec{\nabla}(\rho g h) \approx -\frac{K}{\eta}\vec{\nabla}P = -k_p\vec{\nabla}P \tag{6}$$

The whole pressure field (or charge) is solution of a conservation equation. Neglecting source terms due to gas production and consummation (reaction is slow compared to the gas flow), hydrodynamic problem can be written as:

$$\vec{\nabla}\bullet\left(-k_p\vec{\nabla}P\right) = 0 \tag{7}$$

the boundary conditions being $-k_p\vec{\nabla}P\bullet\vec{n} = -u_n$ on $\partial\Omega_N^T$ and $P = P_D$ on $\partial\Omega_D^T$.

3.2.3 Mass transport

Gas phase is governed by the ideal gas law. Thus the total molar concentration inside the gas is equal to $C = \frac{P_r}{RT}$. The molar convective flow is due to the transport by the gas displacement and is expressed by:

$$\vec{J}_i^C = C\vec{u} = -\frac{P_i}{RT}\vec{u} \tag{8}$$

Diffusion in porous medium is a complex phenomenon including diffusion flow, Knudsen diffusion, Soret effect, which is well explained by Reid et al. [9]. Here, only diffusion flow is taking into account:

$$\vec{J}_i^D = -D_{ij}^D\vec{\nabla}C_j = -\frac{D_{ij}^D}{RT}\vec{\nabla}P_j \tag{9}$$

and finally each partial pressure is solution of the following equation:

$$\frac{\varepsilon}{RT}\frac{\partial P_i}{\partial t} + \frac{\varepsilon}{RT}\vec{u}_d\bullet\vec{\nabla}P_i - \vec{\nabla}\bullet\left(\frac{D_{ij}^D}{RT}\vec{\nabla}P_j\right) = Q_i^C \tag{10}$$

with the boundary conditions $-\frac{D_{ij}^D}{T}\vec{\nabla}P_j\bullet\vec{n} = R\phi_i$ on $\partial\Omega_N^T$ and $P_i = P_{iD}$ on $\partial\Omega_D^T$.

3.3 Coupling between the microscopic population scale and the reactor scale

At microscopic scale, the reaction fractional conversion is followed for a representative population of grains. By finite difference it is possible to evaluate the reaction rate $\dfrac{d\alpha}{dt}$. This rate allows to evaluate heat and mass sources produced by the reaction. Thus the heat source density is equal to:

$$Q^T = \sum_{i=1}^{n_g} \nu_i M_A \frac{1-\varepsilon}{V_{mA}} \frac{d\alpha}{dt} \Delta H_i \qquad (11)$$

and the mass (partial pressure) source density for a gas i is equal to:

$$Q_i^C = \nu_i \frac{1-\varepsilon}{V_{mA}} \frac{d\alpha}{dt} \qquad (12)$$

So, using these sources terms, microscopic reactions have an impact on the spatial and temporal evolution of the thermodynamic processes at the reactor scale. Inversely since it modifies the areic frequency of nucleation and the areic reactivity of growth, thermodynamic influences fractional conversion of the microscopic reaction. It is worthwhile to notice that CIN4 allows to simulate the behavior of reactions for which the kinetic rate at time t (at the microscopic population scale) depends on the local thermodynamic conditions that were established between t=0 and t. CIN4 highly improves the previous approaches which were limited to kinetic model based at grain scale only, excluding surface nucleation and growth models. The equations used in CIN4 require numerous physical properties (porosity, viscosity, density, heat capacity, thermal conductivity, diffusivity). CIN4's user should be able to calculate these properties using empirical laws or mathematical models like for example those given by Bird et al. [11].

4. Numerical modeling

At grain and microscopic population scales, two types of modeling are possible according to the type of growth: anisotropic or isotropic. In the first case, the method allows to calculate the evolution of the fractional conversion for all grains in each granulometric class. When the growth is isotropic, we used the Mampel's method [7] for three grain geometries: spheres, cylinders and plates. At reactor scale, for each equation (2), (7) and (10) (i.e. heat, hydrodynamic and mass transport problems), two finite element formulations were built, depending on the system symmetry (cylindrical or Cartesian coordinates). A classical way is followed to obtain weak formulations for each state variable: temperature, charge and partial pressures.

5. Results

Figures 1 to 3 present a thermobalance simulation achieved with CIN4. This simulation involves a model at the reactor scale coupled with a model of the reaction at the microscopic grains population scale. There, the system studied consists of a vertical cylindrical chamber in which a flow of reactive gas (G1) from the bottom up is maintained. In the middle position, crucible, whose base is porous, contains a granular medium initially composed of grains of A which are transformed into B according to the reaction:

$$A(s) + \frac{1}{2} G_1(g) \rightarrow 3B(s) + 2G_2(g) \qquad (13)$$
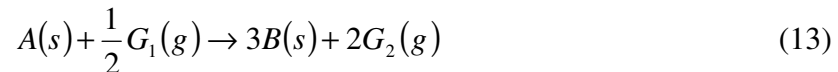
The system being axi-symmetric, we have used weak forms written in cylindrical coordinates. Figure 1 shows the mesh used for solving heat and mass transfers' equations throughout the reactor by the finite elements method (the mesh was done by using Gmsh freeware [11]).
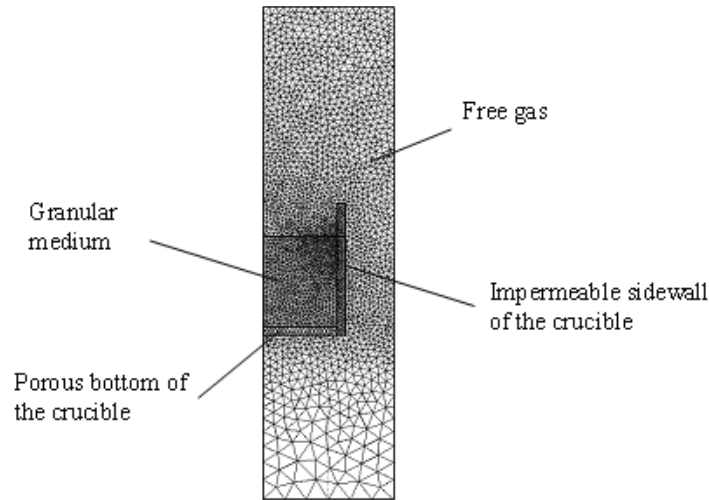
Figure 1: mesh of a thermobalance containing a crucible and a granular medium.

There are four areic regions in this mesh: the granular medium, the bottom of the crucible, the vertical wall of the crucible and the zone of free gas. We also the boundary conditions, which are:
- on the incoming boundary, the entering gaseous mixture is fixed: temperature, flow and composition (here 100% G1),
- on the outgoing boundary: free exit for the temperature, total pressure imposed at 1 atm,
- on the sidewall: the boundary is adiabatic and is impermeable for the mass flow,
- on the symmetry axis: the radial derivatives of all physical grandeurs are equal to 0.

In the following, the kinetic model is based on surface nucleation and anisotropic growth of the nuclei, the grains are spherical ($r_0 = 100\mu m$), the rate determining-step of growth is located at the internal interface, with inward development.

The granular medium is the seat of heat and mass sources calculated by simulation of reaction phenomena at the microscopic level. Figure 2 shows the gas rate field obtained as well as some views of fields of temperature, partial pressure, fractional conversion and reaction rate for one instant. Figure 3 presents the whole fractional conversion versus time, and the whole rate of reaction versus fractional conversion.
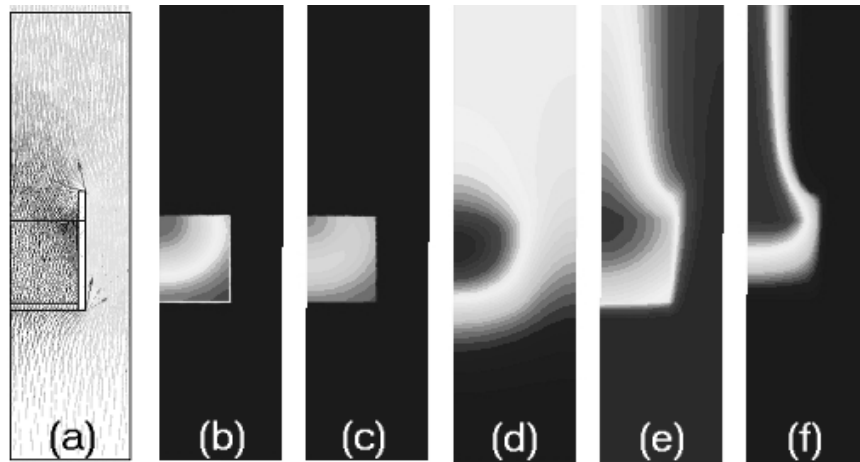
Figure 2: Representation of (a) the gas rate field, (b) the fractional conversion, (c) the rate of reaction, (d) the temperature, (e) G_1 partial pressure and (f) G_2 partial pressure in the thermobalance at a given time.
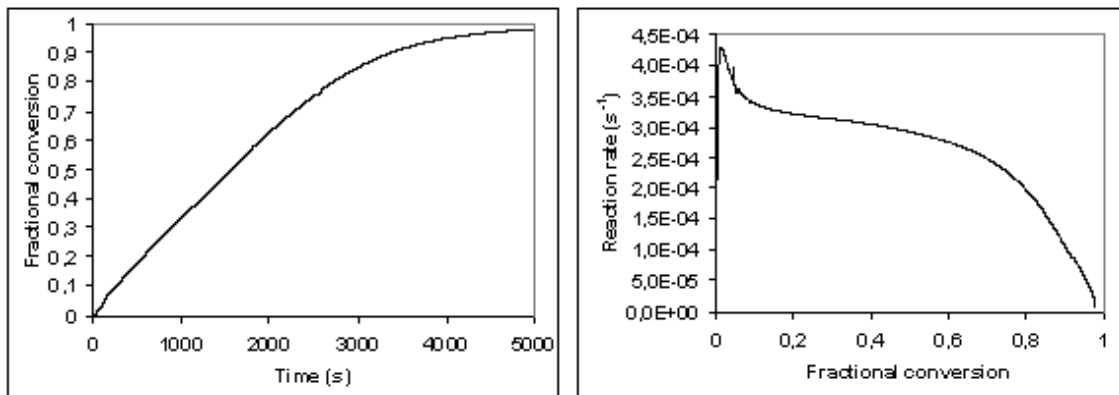

Figure 3: Whole fractional conversion vs. time, and rate of reaction vs. fractional conversion from the simulation.

6. Conclusions

We present a general approach for kinetic modeling of heterogeneous reactions by coupling kinetic models at grain and microscopic population scales with both heat and mass transfers by means of the finite element method. Kinetic models are based on a general method agreeing with physical reality, offering the possibility to simulate about forty models depending on the shape of the grains, the growth type (isotropic or anisotropic), the development direction of the new phase and the localization of the rate determining step of growth (internal interface, external interface or diffusion volume). Among these models, twenty-one include surface nucleation and growth processes. Heat and mass transfers are governed by differential equations and solved by a finite element method. This modeling process allows to simulate not only thermobalances but also industrial reactors.

Notations

α Fractional conversion of the powder
β Fractional conversion of a grain
C Concentration (mol.m^{-3})
c_p Heat capacity at constant pressure (J.kg^{-1}.K^{-1})
D Diffusivity (m^2.s^{-1})
D_{ij} Multicomponent diffusion coefficient (m^2.s^{-1})
S_m Space function (m^2.mol^{-1})
ε Porous medium porosity
ε_0 Initial porous medium porosity
ε_r Emissivity
ϕ Areic reactivity of growth (mol.m^{-2}.s^{-1})
g acceleration of gravity (m.s^{-2})
γ Areic frequency of nucleation (nuclei.m^{-2}.s^{-1})
h Heat transfer coefficient (W.m^{-2}.K^{-1})
H Hydrodynamic charge (m)
J^D Diffusion flow vector (mol.m^{-2}.s^{-1})
k Thermal conductivity (W.m^{-1}.K^{-1})
k_p diffusion coefficient (m^2.Pa^{-1}.S^{-1})

K Darcy's permeability (m^2)

M_i Molar mass for constituent i (kg mol^{-1})
η Dynamic viscosity of the fluid (Pa.s)
P Total pressure (Pa)
P_i Partial pressure of reactive gas (Pa)
Q_T Heat sources density (W.m^{-3})
Q_C Concentration sources density (mol.m^{-3}.s^{-1})
R Ideal gas constant (= 8.314 J.K^{-1}.mol^{-1})
r_0 Initial radius of the grain (m)
ρ Density (kg.m^{-3})
σ Stefan Boltzmann constant (W.m^{-2}.K^{-4})
T Temperature (K)
T_a Ambient temperature (K)
υ Rate vector (m.s^{-1})
υ_d Flowing rate vector (m^2.s^{-1})
u_n Incoming flow density (m.s^{-1})
V_{mA} Molar volume of A (m^3.mol^{-1})

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