

Barea et al.: Approximate Prediction of Gas-Solid Conversion in Fluid Beds

APPROXIMATE PREDICTION OF GAS-SOLID CONVERSION IN FLUIDIZED BED REACTORS

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ABSTRACT

A simple method is proposed to evaluate the performance of fluidized bed reactors where a single n^{th} -order gas-solid reaction occurs. The method accounts for the fluid dynamics of the fluidized bed by a two-phase flow model and the resistance to mass transfer at particle scale (internal and external) by a simplified particle model. Approximate analytical expressions are derived in terms of three effectiveness factors: interphasic, external and intraparticle, accounting for the individual contributions to the overall mass-transport resistances. Gas conversion is expressed in terms of four dimensionless governing quantities and reaction order, facilitating computations.

INTRODUCTION

The performance of reacting systems in fluidized beds (FBs) have been described by several approaches. Early models treated FB reactors as if the gas and solids were mixed, avoiding the multiphase nature of the bed. These 'single-phase' models assumed that the reactor performance was determined by the residence time of the gas. The two-phase theory, originally proposed by Toomey and Johnstone (1), was a breakthrough, allowing consideration of the multiphase nature of the FB. After the models of Orcutt et al. (2) and Davidson and Harrison (3) the concept of 'contact time distribution' was recognized as a key factor for taking into account the time that the gas is in contact with the solid reactant (Grace, (4)). More recently Mostoufi et al. (5) have compared the predictive capability of two- and single- phase models. There are several thorough reviews of existing approaches for modeling of FB reactors (Horio and Wen (6), Grace, (4), Van Swaaij (7), Davidson et al. (8)). Generally, solutions for two-phase models were presented in terms of two dimensionless groups: one representing the dimensionless reaction rate and the other accounting for the interphase mass-transfer resistance (Horio and Wen (6), Grace (4), Mostoufi (5), Van Swaaij (7), Davidson et al. (8)). Analytical solutions have been reported for a variety of simple kinetics schemes, such as 1st, 2nd ...-order kinetic (see for instance Table 11.5 in Grace (4)). Solutions for more complex kinetics schemes have also been presented for catalytic reactions, based on conventional two-phase

models and Kunii-Levenspiel's model (Kunii and Levenspiel (9), Irani et al. (10)).

A limitation associated with the aforementioned simplified solutions is that they do not explicitly account for diffusional limitations at a particle scale. If diffusional film and intraparticle mass transfer are not rapid enough, the overall reaction rate is influenced by diffusional effects. Dedicated models have been developed for particular situations where these limitations are of concern, but they are generally complex, making derivation of simple solutions difficult. In addition, existing shortcut methods do not explicitly include the individual assessment of diffusional and fluid-dynamic effects. Moreover, the analytical solutions available in literature do not explicitly account for non-catalytic reactions, i.e. for changes of properties during the progress of reaction, and they are not developed for general n^{th} order kinetics, van Swaaij (7), Davidson et al. (8).

The present work aims at presenting a tool that is useful for simple estimates of conversion in bubbling FBs when both fluid-dynamic and particle-scale effects can be of importance. The treatment is applicable for general n^{th} -order reactions, allowing the effective properties to change and the particle to shrink as the reaction proceeds. The model is based on the treatment of Gómez-Barea et al. (11). A major goal of this work is to keep the model as simple as possible, as the objective is mainly to discern leading order effects. While the model of Gómez-Barea et al. (11) was focused on the assessment of mass-transport effects during kinetic experiments in FB (by gas measurements), the treatment presented here shows solutions for reactor performance, i.e. it shows how to obtain the conversion of gas from intrinsic kinetics and other available physico-chemical data.

MODEL

Figure 1 illustrates the problem dealt with. The fluidization gas is introduced into the reactor with a concentration c_{in} of the reactant. It passes through the bed as bubbles (free of solids) in plug flow with a concentration c_b , and through the well mixed emulsion phase, where the reaction takes place with concentration c_e . The gas-solid reaction occurs in the emulsion, which remains at minimum fluidization velocity. For reaction to occur in the active particles embedded in an inert emulsion phase, the gaseous reactant has to overcome various resistances on its transfer from the bubbles to the reacting sites. These resistances are shown in Fig. 1. They are: (1) resistance from bubble to emulsion phase, (2) external particle film resistance around the solid particles, and (3) internal porous resistance inside the particle.

Formulation of the two-phase model. Evaluation of η_{ph}

By applying these assumptions, a molar balance for the gas in the bubble and emulsion phases leads to the following dimensionless equations (Gómez-Barea et al. (11))

$$\frac{dC_b}{dy} = \left[\frac{1}{\beta} \frac{k_b \varepsilon_b}{u_o / L_f} \right] (C_e - C_b); \quad (1 - \beta) C_e = \int_0^1 \frac{k_b \varepsilon_b}{u_o / L_f} (C_b - C_e) dy + \text{Da}_R (1 - C_e)^n \quad (1)$$

where the reaction is

$$(-R) = \eta_p (k c_e^n) \quad (2)$$

η_p is the particle effectiveness factor, which accounts for the resistance at particle scale (internal and external). By integrating and combining the two expressions² of

Eq. (1), the following equation is found (Gómez-Barea et al. (11))

$$1 - \beta \cdot \exp(-NTU/\beta) = Da_R (1 - C_e)^n / C_e \tag{3}$$

where the parameter, Da_R is the Damköhler number at reactor scale defined by

$$Da_R = \varepsilon_{s,b} \eta_p k_c^{n-1} / (u_o / L_f) \tag{4}$$

This number expresses the relative importance of the gas residence time L_f/u_o and the reaction time $\varepsilon_{s,b} k_c^{n-1}$ when mass transport effects are absent. $\varepsilon_{s,b}$ is the bulk concentration of the solid reactant. The number of transfer units, NTU and the dimensionless excess gas flow β , are defined as

$$NTU = \varepsilon_b k_b / (u_o / L_f) \quad \beta = (u_o - u_{mf}) / u_o \tag{5}$$

The expression β assumes that all gas in excess of that of minimum fluidization velocity flows through the bed in the form of bubbles (Toomey and Johnstone (1)). A throughflow factor can readily extend this concept to other particle systems, where β in Eq. (5) should be corrected. Corrections applicable for a number of particulate systems have been presented by Horio and Wen (6) and Chavarie and Grace (12). A thorough comparison and experimental verification of competing models can be found in several publications (Stergiou et al. (13), Chavarie and Grace (14)). Extensions and improvements of conventional two-phase models have been reviewed and explored by Chavarie and Grace (15). By defining the concentration efficiency in the bed (Gómez-Barea et al. (11)) as $N_a = (c_{in} - c_{out}) / (c_{in} - c_e)$ and assuming plug flow for the gas in the bubble phase entering with the concentration $c_{in} = c_{b,in}$, it is easy to verify that N_a is related to NTU and β according to $N_a = 1 - \beta \exp(-NTU/\beta)$. Figure 2 displays this relationship, illustrating the interpretation of N_a as a concentration efficiency of the bed. Then, Eq. (3) can be expressed as

$$N_a / Da_R = (1 - C_e)^n / C_e \tag{6}$$

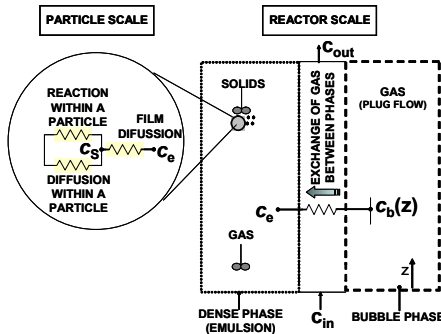
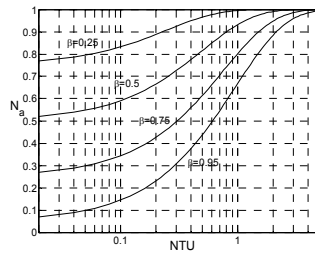
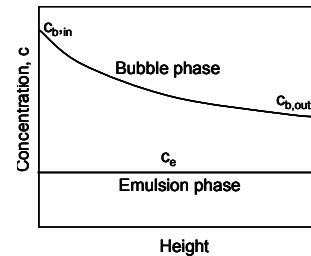


Fig. 1. Problem description



(2.a)



(2.b)

Fig. 2. Solution of $N_a = (NTU, \beta)$ (a) and interpretation (b)

The interphasic effectiveness factor η_{ph} is defined as the ratio of the intrinsic reaction rate under emulsion conditions to that under inlet gas conditions

$$\eta_{ph} = (c_e / c_{in})^n = (1 - C_e)^n \tag{7}$$

The gas conversion X_g is expressed in dimensionless form as

$$X_g = 1 - (c_{out} / c_{in}) = C_e N_a \tag{8}$$

By substituting Eq. (7) in Eq.(6) an expression for η_{ph} as a function of N_a and Da_R is

$$\eta_{ph} / (1 - \eta_{ph}^{1/n}) = N_a / Da_R \tag{9}$$

As seen, η_{ph} is only a function of the group N_a/Da_R and the order of reaction n . Similarly, by substituting Eq. (8) in Eq. (6) an expression for X_g/N_a as a function of

N_a/Da_R results

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$$\frac{(1 - X_g / N_a)^n}{X_g / N_a} = \frac{N_a}{Da_R} \quad (10)$$

Obviously, X_g is a function of two groups: N_a and N_a/Da_R , as well as of the reaction order, n . Equations (9) and (10) can be combined to eliminate Da_R

$$\eta_{ph} = [1 - X_g / N_a]^n \quad (11)$$

The equations and correlations needed to calculate NTU and β and the parameters appearing therein can be found in various references (Kunii and Levenspiel (9), and Oka (16)). They depend on reactor configuration and flow regime. For instance, for deep bubbling FBs the correlations presented in Table 1 in Gómez-Barea et al. (11) can be used. In that work Eq. (11) is the starting point to evaluate the interphasic mass-transport effects during measurements in an FB. In that context Eq. (11) is useful, since it enables computation of the effectiveness factor from gas concentration measurements. In the present work the intrinsic kinetics are given, and the objective is to evaluate the performance of the FB, i.e. the gas conversion. The solution of this case is presented in the following.

Analytical solution for η_{ph}

To obtain an explicit solution for η_{ph} as a function of Da_R and N_a for n^{th} -order kinetics the following approximation formula can be used (Gómez-Barea (17)):

$$\eta_{ph} = \left(\left[\{ (1-n)(Da_R/N_a) \}^{1/n} + 1 \right]^n + n(Da_R/N_a) \right)^{-1} \quad \text{with } 0 < n \leq 1 \quad (12)$$

$$\eta_{ph} = 2n \left[(2n)^{1/n} - 1 + (1+2n)(Da_R/N_a)^{1/n} \right]^{-n} \quad \text{with } 1 < n \leq 2.7 \quad (13)$$

Once η_{ph} is known the gas conversion is determined by a combination of Eqs. (10) and (11) to yield $X_g = Da_R \eta_{ph}$. Analytical solutions for various n have been reported (Grace, (4)). It can be demonstrated that the solution of equation with the expressions of Eqs. (12) and (13) includes as particular cases the analytical expressions existing in literature (Gómez-Barea (17)). In Fig. 3 the lines made of symbols represent the solution by the modified Orcutt model reported by Grace in Grace (4) for irreversible reactions with $n=1/2$, $n=1$ and $n=2$. The solid lines in Fig. 3 are drawn using Eqs. (12) and (13). The difference is very small for the three values of n shown. Actually, the difference is entirely associated with Frank-Kamenetskii's approximation used to derive Eq. (12) and (13) from Eq. (10). In fact Eq. (10) is equivalent to the solutions of Orcutt's model but the present formulation provides an additional scheme for simple estimation of diffusion limitations at the particle scale. In effect, in the Damköhler number defined in Eq. (4) the interphasic effectiveness factor is not included and it is then decoupled from the multiphase effect associated with the bubbling nature of the bed. Therefore, gas conversion is a function of two parameters, N_a and N_a/Da_R . The group N_a/Da_R establishes the drop in concentration between entrance and emulsion. Two factors are responsible for that drop: the consumption of the reactant along the bed and the resistance to transfer of the reactant gas between bubble and emulsion. Limiting values of N_a are 0 and 1: If $N_a \sim 1$ the heterogeneous flow pattern associated with the phases in the bed loses importance for the reaction. However, the heterogeneity at the particle scale remains to be analyzed, as will be shown below.

Influence of transport effects at particle scale: Evaluation of η_p

To evaluate Da_p (more precisely, to evaluate the reaction time in Eq. (4)), the particle effectiveness factor η_p has to be known. If the mass transfer rates are high enough, this factor is close to unity, and the formulation given above is closed. However, if the rates are not high, the particle effectiveness factor had to be determined. For this purpose external and internal effectiveness factors are calculated, η_e and η_i , yielding η_p as: $\eta_p = \eta_e \eta_i$. The external effectiveness is defined as the ratio of the intrinsic reaction rate for the condition at the surface and that in the emulsion surrounding the particle, $\eta_e = (c_s/c_e)^n$. Under pseudo-steady-state conditions, the isothermal mass transfer problem for n^{th} -order kinetics can be converted to (Gómez-Barea (17)),

$$\eta_e = (1 - Da_p \eta_p)^n \tag{14}$$

where a second Damköhler number Da_p , evaluated for emulsion conditions is

$$Da_p = (kL_{equ} / k_G) c_e^{n-1} \tag{15}$$

Applying again Frank-Kamenetskii's approximation to Eq.(14), the following approximate explicit solution for η_e is obtained

$$\eta_e = \left(\left[\{(1-n)Da_p \eta_i\}^{1/n} + 1 \right]^n + n Da_p \eta_i \right)^{-1} \quad \text{with } 0 < n \leq 1 \tag{16}$$

$$\eta_e = 2n \left[(2n)^{1/n} - 1 + (1 + 2n Da_p \eta_i)^{1/n} \right]^{-n} \quad \text{with } 1 < n \leq 2.7 \tag{17}$$

where the intraparticle effectiveness, η_i , is defined as the ratio of the observed total reaction rate $(-R)$, at any instant and the total reaction rate at that instant, assuming the concentration of the reactant to be equal to that at the surface $\eta_i = (-R) / kc_s^n$. The additional equation needed comes from the solution of the intraparticle problem. To include non-catalytic reactions, whose reaction rate changes as a function of the progress of reaction, we have assumed the following model behaviour for $(-R)$

$$(-R) = 1/V_p \int (-r) d\Omega = \rho_{s0} (1 - x_c)^{\delta-1} (dx_c / dt) \tag{18}$$

where appropriate values of δ are chosen, ranging from $\delta = 0$ for a shrinking-particle to $\delta = 1$ for uniform conversion. The intraparticle efficiency is obtained by an approximate solution of the reaction-diffusion problem in a particle (Gómez-Barea (11)) yielding:

$$\eta_i = \frac{\tanh\left(\eta_e^{(n-1)/2} M_e\right)}{M_e \eta_e^{(n-1)/2}} \quad M_e = \phi_e G(x_c) \quad \phi_e = L_{equ} \left[\frac{n+1}{2} \frac{k c_e^{n-1}}{D_{e0}} \right]^{1/2} \tag{19}$$

where k is the kinetic constant, ϕ_e the classical Thiele module, M_e the Thiele module dependent on conversion, and $G(x_c)$ a function accounting for the changes in reactivity and effective diffusivity with conversion (Gómez-Barea et al. (17)). In summary, Eqs. (16)-(17) together with Eq. (19) allow the solution of η_e and η_i and so, η_p . ϕ_e is evaluated under emulsion conditions, but c_e is only known when η_{ph} has been determined ($c_e = c_{in} \eta_{ph}^{1/n}$). However, η_{ph} is coupled to η_e , and the general case, where diffusional effects in the particle are of concern, has to be solved iteratively. It is best to start by solving η_{ph} , assuming $\eta_p \sim 1$ in Eq. (12) or (13). If the calculated value of η_p is not unity, the procedure is repeated until convergence.

Example of applications

The final objective of the model developed is the calculation of gas conversion X_g , as a function of the following parameters: N_a , Da_R , Da_p , M_e , and n . Given the hardware of the FB reactor (bed diameter, distributor design, ...), the intrinsic kinetics (reaction order n and the Arrhenius parameters for k), the empirical factor for the kinetic model

of the particle (δ) and some physico-chemical properties of reacting particles (particle size, effective diffusivity) the values of N_a , Da_R , $Da_{p,in}$, M_{in} and n can be determined. As an example some values from a real case are taken: $N_a=0.75$, $Da_R=1.5$, $Da_{p,in}=0.6$, $M_{in}=1$ and $n=0.75$. With these data η_{ph} and η_p can be computed or read from graphs, such as presented on Figs 3 and 4. Fig. 3 presents η_{ph} as a function of Da_R/N_a for various n using Eqs (12) and (13). Similarly, Fig. 4 displays η_p as a function of M_e taking Da_p and n as parameters using Eqs (16) and (17)). From Fig. 3 with $Da_R/N_a = 2$, we obtain $\eta_{ph}=0.35$. With this value the following parameters at the particle scale are computed: $Da_{p,e}=0.6 \cdot 0.35^{-0.33}=0.85$; $M_e=1 \cdot 0.35^{-0.33}=1.41$. Entering these two values in Fig.4 yields a particle effectiveness of $\eta_p=0.47$. This is lower than the initial guess ($\eta_p=1$, since we used directly the value of Da_R evaluated for bulk conditions) and the procedure has to be repeated until convergence. In a second iteration we obtain $Da_R/N_a=2 \cdot 0.47=0.95$. The final result is $\eta_{ph}=0.53$ and $\eta_p=0.50$ ($\eta_e=0.75$, $\eta_i=0.67$) and a gas conversion of $X_g=0.53 \cdot 0.75=0.40$ (40 %). As shown, the method is easy to apply.

Limitation

The hold-up of the solid reactant, $\varepsilon_{s,b}$, is not known in non-catalytic systems. To calculate this quantity in such cases, an overall mass balance between the solid and gas reactants within the bed should be formulated. This provides an additional equation, which adds difficulty in the estimation of the inventory of solid reactant in the bed under steady-state conditions. The problem becomes more complex, but the method of solution is the same, since the inventory of solid reactant is included in the Damköhler number. The non-catalytic reactions need, in addition, a population balance to account for the residence times of the reactant particles. This is, however, outside of the objective of the present paper and will be addressed in coming work.

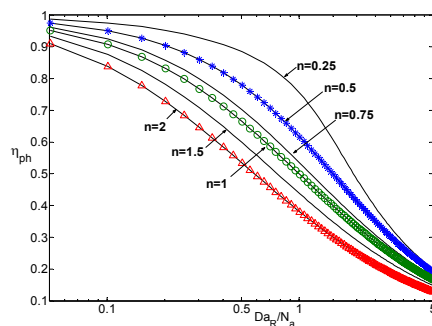


Fig. 3 $\eta_p = f(Da_R/N_a, n)$

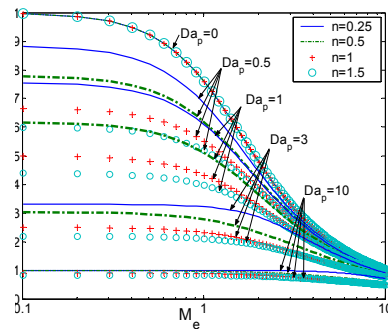


Fig. 4. $\eta_p = f(M_e, Da_p, n)$

CONCLUSION

A simple method was developed to evaluate the gas conversion in a fluidized bed. The main aim was to extend existing shortcut methods by formulation of a model allowing: (1) application of general n th order kinetics, (2) to explicitly include the individual assessment of fluid-dynamic and diffusional effects at a particle scale, (3) the analysis of non-catalytic reactions, i.e. changes of properties during the progress of reaction. A major goal was to keep the model as simple as possible, and so the solution is useful to discern leading order effects, for instance when rapid estimations are necessary, as in the simulation of complex flowsheets in a process simulator.

NOTATION

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c	gas concentration, $\text{mol}\cdot\text{m}^{-3}$
C	dimensionless gas concentration, $(c_{\text{in}}-c)/c_{\text{in}}$, –
D_e	effective diffusivity of reactant the porous reactant solid particle, $\text{m}^2\cdot\text{s}^{-1}$
d_s	instantaneous average diameter of the solid particles, m
Da_p, Da_R	Damköhler number at particle scale and reactor scale, respectively, –
$G(x_c)$	function of x_c , –
k	n^{th} -order kinetic constant, $(\text{mol}\cdot\text{m}^{-3})^{1-n}/\text{s}$
k_b	interchange coefficient between the bubble and emulsion, s^{-1}
k_G	external mass-transfer coefficient, $\text{m}\cdot\text{s}^{-1}$
L_{equ}	equivalent size of solid particle, m
L_f	bed height, m
M	Thiele module, function of conversion, –
n	reaction order, –
N_a	concentration efficiency, –
NTU	number of transfer units, –
$(-R)$	observed reaction rate, $\text{mol}\cdot\text{m}^{-3}\cdot\text{s}^{-1}$
$(-r)$	intrinsic reaction rate, $\text{mol}\cdot\text{m}^{-3}\cdot\text{s}^{-1}$
t	time, s
u	gas velocity, $\text{m}\cdot\text{s}^{-1}$
X_g	gas conversion, –
x_c	char conversion, –
y	dimensionless axial coordinate, –
V_p	volume of solid reactant, m^3
β	dimensionless excess of flow, –
δ	kinetic parameter, –
$\varepsilon_{s,b}$	char bed hold-up, $(\text{m}^3 \text{ solid reactant})/(\text{m}^3 \text{ bed})$
ε_b	bubble fraction $(\text{m}^3 \text{ bubbles})/(\text{m}^3 \text{ bed})$
$\eta_{ph,p,e,i}$	interphase, particle, external and internal effectiveness factors, –
ρ_s	density of solid reactant, $\text{kg}\cdot\text{m}^{-3}$
ϕ	Thiele module, –

Subscripts

b,e, in, out	bubble, emulsion, inlet and outlet gas conditions, respectively
0	initial, superficial
s	surface

REFERENCES

1. Toomey, R.D., and Johnstone, H.F., 1952. Gaseous fluidization of solid particles, Chem. Eng. Prog. 48, 220–225.
2. Orcutt, J.C., Davidson, J.F., and Pigford, R.L., 1962. Reaction time distributions in fluidized bed reactors, Chem. Eng. Prog. Symp. Ser., 59, 1-15.
3. Davidson J.F., Harrison D., 1963. Fluidised particles. Cambridge University Press.

4. Grace, J.R., 1986. Fluid beds as chemical reactors, in Geldart, D. (Ed.), Gas Fluidization Technology, John Wiley & Sons Ltd.
5. Mostoufi, N., Cui, H.P., and Chaouki, J., 2001. A comparison of two- and single-phase models for fluidized bed reactors, Industrial and Engineering Chemistry Research 40, 5526–5532.
6. Horio, M. and Wen, C.Y., 1977. An assessment of fluidized-bed modelling. A.I.Ch.E. J. Symp. Ser. 73, 9–21.
7. van Swaaij, W.P.M., 1985. Chemical reactors, in: J.F. Davidson, R. Clift, D. Harrison (Eds.), Fluidization, 2nd Edition, Academic Press, London, (Chapter 18).
8. Davidson, J.F., Harrison, D., Darton, R.C., LaNauze R.D., 1977. The two-phase theory of fluidization and its application to chemical reactors, in: L. Lapidus, N.R. Amundson (Eds.), Chemical Reactor Theory, A Review, Prentice-Hall, Englewood Cliffs, NJ, 583–685.
9. Kunii, D., Levenspiel, O., 1991. Fluidization Engineering (second ed.), Butterworth-Heinemann, London.
10. Irani, R.K., Kulkarni, B.D., Doraiswamy, L.K., 1980. Analysis of Complex Reaction Schemes in a Fluidized Bed. Application of the Kunii-Levenspiel Model. Ind. Eng. Chem. Proc. Des. Dev. 19, 24-30.
11. Gómez-Barea A., Ollero P. and B. Leckner, Mass transport effects during measurements of gas-solid reaction kinetics in a fluidised bed, Chemical Engineering Science, doi:10.1016/j.ces.2006.10.018.
12. Chavarie, C., Grace, J.R., 1975. Performance Analysis of a Fluidized Bed Reactor. I. Visible Flow Behavior. Ind. Eng. Chem. Fundam. 14, 75-79
13. Stergiou, L., Laguerie, C., and Gilot, B., 1984. A discrimination between some fluidized bed reactor models for ammoxidation of propylene to acrylonitrile. Chem. Engng Sci. 39, 713–730.
14. Chavarie, C., Grace, J.R., 1975. Performance Analysis of a Fluidized Bed Reactor. III. Modification and Extension of Conventional Two-Phase Models. Ind. Eng. Chem. Fundam. 14, 86-91.
15. Chavarie, C., Grace, J.R., 1975. Performance Analysis of a Fluidized Bed Reactor. II. Observed Reactor Behavior Compared with Simple Two-Phase Models Ind. Eng. Chem. Fundam. 14, 79-86.
16. Oka, S.O., 2004. Fluidised Bed Combustion, Marcel Dekker, Inc., New York.
17. Gómez-Barea, A., 2006 Modelling of diffusional effects during gasification of biomass char particles in fluidised-bed, PhD thesis. University of Seville, Spain.