DYNAMIC MODELLING OF A THREE-PHASE CATALYTIC SLURRY REACTOR CONSIDERING THE PHASE CHANGE PHENOMENON

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Abstract: This work deals with the development of a model capable to simulate via deterministic modelling the phenomenon of phase change observed in three-phase catalytic slurry reactors, that occurs in the reacting medium and in the refrigerant fluid. A dynamic heterogeneous non-isothermal model was formulated to evaluate the impact of this phenomenon in the dynamic behaviour of the reactor. A multicomponent flash calculation was used to reproduce this effect in the reacting medium and an appropriate correction procedure of the global coefficient of heat transfer to analyse the effect in the refrigerant fluid. *Copyright © 2003 by the authors*

Keywords: Reactor, Modelling, Three-Phase, Catalytic, Slurry, Phase Change.

1. INTRODUCTION

The development of an efficient and reliable model of three-phase catalytic reactors is still a difficult task, because it involves many aspects including hydrogenation, gas-liquid and liquid-solid mass transfers, heat transfer, pore diffusion, reaction kinetics and deactivation. Model assessment has mostly been reported for a single reaction, or reactions obeying simplified kinetic laws, under isothermal conditions. Nevertheless, exothermic reactions undergoing a multi-step reaction scheme and complex kinetics are industrially of a main interest and rigorous comparison of the performances of several multiphase reactors, for such reactions, has hardly ever been published (Vasco de Toledo et al., 2001). Therefore, despite the large amount of effort put into the modelling of three-phase catalytic reactors, many issues still remain to be solved, for instance, the phenomenon of phase change in both reacting medium and refrigerant fluid, which occurs, frequently, in three-phase reactors.

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The impact of the phase change in the dynamic behaviour of the reactor can be very intensive, compromising seriously the efficiency of the controllers in their function of the maintenance of a stable operation of the reactor. The previous knowledge, obtained through simulations, of the operating conditions at which this phenomenon can occur is very important. So, the aim of the developed model presented in this work is to allow the user to simulate different aspects involving the phase change.

2. DESCRIPTION OF THE DYNAMIC MODEL

The main phenomena present in three-phase reactors were incorporated into the dynamic model. The model consists of mass and energy balance equations, and also an equation for the refrigerant fluid. Another aspect contemplated is the consideration of the variation of the physicochemical properties and of the mass and heat transfer coefficients, through correlations available in the literature. This work considers the hydrogenation of o-cresol on Ni/SiO_2 catalyst (Hichri et al., 1991).

However, as there are many other hydrogenation reactions of industrial interest, the model can easily incorporate other reactions due to the generality adopted during its development.

The hypotheses adopted to the dynamic model of the tubular reactor are:

1) a pseudo-homogeneous media is assumed for the liquid and the solid with respect to solid movement. This means that there is no velocity difference between solid and liquid;

2) negligible pressure variations;

3) reaction of the type $A_{(g)} + \nu B_{(l)} \rightarrow \nu C_{(l)}$ taking place in the catalyst and having a kinetic that is dependent on the concentrations of A and B;

4) phase change happens in the system.

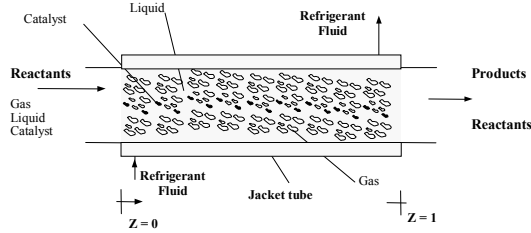The scheme utilized to represent the tubular reactor is displayed in Figure 1.

Fig. 1. Three-phase tubular reactor

The radial dispersion has been neglected for the fluid phase, which is a very common assumption in multi-phase reactors as normally found in literature (Gianetto and Silverston, 1986). The superficial velocities and the hold-ups are updated taking into account the changes in temperature, pressure and concentration. Some discussion on the formulation of dynamic models are presented elsewhere: Warna and Salmi (1996), Lange et al. (1999), Julcour et al. (1999), Salmi et al. (2000), Vasco de Toledo and Maciel Filho (2002) and Mariano (2003).

Aiming to adapt the equations of the model to the units (kmol/s) usually employed in multicomponent flash calculation, it was necessary to multiply the mass balance equations by the feed volumetric flow of the liquid phase (Q_l), that is a constant value and for this reason the results generated by the model are not changed.

The equations of the heterogeneous dynamic model developed are:

Fluid Phase:

Mass balance of reactant A in the gas phase:

$$\varepsilon_g \frac{\partial FA_g}{\partial t} = \frac{D_{eg}}{L^2} \frac{\partial^2 FA_g}{\partial z^2} - \frac{u_g}{L} \frac{\partial FA_g}{\partial z} - (K_{gl})_A a_{gl} (FA^* - FA_l) \qquad (1)$$

$$\frac{D_{eg}}{L} \frac{\partial FA_g}{\partial z}\bigg|_{z=0} = u_g (FA_{g(z=0)} - FA_{gfo}) \qquad \frac{\partial FA_g}{\partial z}\bigg|_{z=1} = 0 \qquad (2)$$

Mass balance of reactant A and B and product C in the liquid phase:

$$\varepsilon_l \frac{\partial FA_l}{\partial t} = \frac{D_{el}}{L^2} \frac{\partial^2 FA_l}{\partial z^2} - \frac{u_l}{L} \frac{\partial FA_l}{\partial z} + (K_{gl})_A a_{gl} (FA^* - FA_l) - (K_{ls})_A a_{ls} (FA_l - FA_s^s) \qquad (3)$$

$$\frac{D_{el}}{L} \frac{\partial FA_l}{\partial z}\bigg|_{z=0} = u_l (FA_{l(z=0)} - FA_{lfo}) \qquad \frac{\partial FA_l}{\partial z}\bigg|_{z=1} = 0 \qquad (4)$$

$$\varepsilon_l \frac{\partial FB_l}{\partial t} = \frac{D_{el}}{L^2} \frac{\partial^2 FB_l}{\partial z^2} - \frac{u_l}{L} \frac{\partial FB_l}{\partial z} - (K_{ls})_B a_{ls} (FB_l - FB_s^s) \qquad (5)$$

$$\frac{D_{el}}{L} \frac{\partial FB_l}{\partial z}\bigg|_{z=0} = u_l (FB_{l(z=0)} - FB_{lfo}) \qquad \frac{\partial FB_l}{\partial z}\bigg|_{z=1} = 0 \qquad (6)$$

$$\varepsilon_l \frac{\partial FC_l}{\partial t} = \frac{D_{el}}{L^2} \frac{\partial^2 FC_l}{\partial z^2} - \frac{u_l}{L} \frac{\partial FC_l}{\partial z} - (K_{ls})_C a_{ls} (FC_l - FC_s^s) \qquad (7)$$

$$\frac{D_{el}}{L} \frac{\partial FC_l}{\partial z}\bigg|_{z=0} = u_l (FC_{l(z=0)} - FC_{lfo}) \qquad \frac{\partial FC_l}{\partial z}\bigg|_{z=1} = 0 \qquad (8)$$

Energy balance in the fluid (gas + liquid) phase:

$$(\varepsilon_g \rho_g C_{pg} + \varepsilon_l \rho_l C_{pl})\frac{\partial T}{\partial t} = \frac{(\varepsilon_g \lambda_g + \varepsilon_l \lambda_l)}{L^2} \frac{\partial^2 T}{\partial z^2} \qquad (9)$$
$$- \frac{(\varepsilon_g \rho_g C_{pg} u_g + \varepsilon_l \rho_l C_{pl} u_l)}{L} \frac{\partial T}{\partial z} + h_s a_{ls}(T_s^s - T)$$
$$- \frac{4U}{D_t}(T - T_r) - Q_{FLASH}$$

$$\frac{(\varepsilon_g \lambda_g + \varepsilon_l \lambda_l)}{L} \frac{\partial T}{\partial z}\bigg|_{z=0} = (\varepsilon_g \rho_g C_{pg} u_g + \varepsilon_l \rho_l C_{pl} u_l) \cdot \qquad (10)$$
$$(T_{(z=0)} - T_{fo})$$

$$\frac{\partial T}{\partial z}\bigg|_{z=1} = 0$$

Energy balance of the refrigerant fluid

$$\rho_r C_{pr} \frac{\partial T}{\partial t} = -\frac{\rho_r C_{pr} u_r}{L} \frac{\partial T}{\partial z} + \frac{4U}{D}(T - T_r) \qquad (11)$$

$$T_r = T_{ro}, \qquad z = 0$$

Solid Phase:

Mass balance of reactants A and B and product C in the solid phase:

$$\varepsilon_s \frac{\partial FA_s}{\partial t} = \frac{D_{ea}}{R_p^{\,2}} \frac{1}{r_p^{\,2}} \frac{\partial}{\partial r_p}\left(r_p^{\,2} \frac{\partial FA_s}{\partial r_p} \right) - \rho_s \, Q_l R_W(FA_s, FB_s, T_s) \qquad (12)$$

$$\left. \frac{D_{ea}}{R_p} \frac{\partial FA_s}{\partial r_p} \right|_{r_p=1} = (K_{ls})_A \left(FA_l - FA_s^s(r_p=1) \right) \qquad \left. \frac{\partial FA_s}{\partial r_p} \right|_{r_p=0} = 0 \qquad (13)$$

$$\varepsilon_s \frac{\partial FB_s}{\partial t} = \frac{D_{eb}}{R_p^{\,2}} \frac{1}{r_p^{\,2}} \frac{\partial}{\partial r_p}\left(r_p^{\,2} \frac{\partial FB_s}{\partial r_p} \right) - \nu\rho_s \, Q_l R_W(FA_s, FB_s, T_s) \qquad (14)$$

$$\left. \frac{D_{eb}}{R_p} \frac{\partial FB_s}{\partial r_p} \right|_{r_p=1} = (K_{ls})_B \left(FB_l - FB_s^s(r_p=1) \right) \qquad \left. \frac{\partial FB_s}{\partial r_p} \right|_{r_p=0} = 0 \qquad (15)$$

$$\varepsilon_s \frac{\partial FC_s}{\partial t} = \frac{D_{ec}}{R_p^2} \frac{1}{r_p^{\,2}} \frac{\partial}{\partial r_p}\left(r_p^{\,2} \frac{\partial FC_s}{\partial r_p} \right) + \nu\rho_s Q_l R_W(FA_s, FB_s, T_s) \qquad (16)$$

$$\left. \frac{D_{ec}}{R_p} \frac{\partial FC_s}{\partial r} \right|_{r_p=1} = (K_{ls})_C \left(FC_l - FC_s^s(r_p=1) \right) \qquad \left. \frac{\partial FC_s}{\partial r_p} \right|_{r_p=0} = 0 \qquad (17)$$

Energy balance in the solid phase

$$\rho_s \, C_{ps} \frac{\partial T_s}{\partial t} = \frac{\lambda_s}{R_p^{\,2}} \frac{1}{r_p^{\,2}} \frac{\partial}{\partial r_p}\left(r_p^{\,2} \frac{\partial T_s}{\partial r_p} \right) + \qquad (18)$$
$$\rho_s \, (-\Delta H_R) R_W(FA_s, FB_s, T_s)$$

$$\left. \frac{\lambda_s}{R_p} \frac{\partial T_s}{\partial r_p} \right|_{r_p=1} = h_s \left(T - T_s^s(r_p=1) \right) \qquad \left. \frac{\partial T_s}{\partial r_p} \right|_{r_p=0} = 0 \qquad (19)$$

2.1 Solution of the dynamic model.

The partial differential equations (PDEs) were converted to ordinary differential equations (ODEs) by discretization using the global orthogonal collocation method (Villadsen and Michelsen, 1978). After the discretization of the spatial coordinates in the particle and in the reactor, a system of ODEs and LEs (linear equations) are obtained. An important feature of the system is its stiffness (Salmi et al., 2000). This implies that specific calculation methods must be used. In this work, the software DASSL was used, which is a specific software for algebraic-differential stiff systems.

Intending to consider the variations of the physical-chemical properties, transfer coefficients of mass and heat and velocities of the fluid phase, without making difficult the numerical solution procedure, it was utilized the strategy normally employed in literature of calculating at each instant of integration the values of this terms through correlations found in literature. In the case of the physical-chemical properties, polynomials generated by the HYSYS® simulator were converted to FORTRAN90® language, utilized in this work.

2.2 Phase Change of the Reacting Medium.

During simulations, a multicomponent flash calculation can be or not considered to evaluate the effect of the phase change in the reacting medium in the dynamic behaviour of the reactor.

Before applying the multicomponent flash, it is necessary to check the existence of two phases. Two methods were tested: the thermodynamic Bubble and Dew point calculation and another criteria proposed by Hanika et al. (1976), that has been used in works related to the study of the phenomenon of phase change in three-phase reactors (Kheshgi et al. (1992), Khadilkar et al. (1999) and Cheng et al. (2001)).

With respect to the non-ideality of the liquid and vapour phases, it was considered in the flash calculation through, respectively, models for activity (Ideal, NRTL, UNIQUAC) and for fugacity (Ideal, Virial) coefficients.

The numerical strategy used to couple the flash calculation to the dynamic model is: during pauses in the integration, the bubble and the dew points of the reacting medium or, as another option, the Hanika criteria (Hanika et al., 1976) are evaluated for each axial position of the reactor discretization grid. If the temperature of the reacting medium at each axial position is found between the bubble and dew points or the criteria of Hanika is satisfied, the multicomponent flash is calculated. Consequently, the concentration values of the components are updated and the heat involved in the phase change (Q_{flash}) is computed by the energy balance of the fluid phase (Equation 9).

An important detail introduced in the calculation of the multicomponent flash is the factor F. The results obtained with the flash procedure are multiplied by F, ($0 \leq F \leq 1$). This factor allows the user of the model to adjust the effect of the phase change in order to represent the dynamic behaviour of the reactor as it is observed in practice. This is accounted for each control volume element that has the fraction of m^3 dimensionality. Thus, F is considered a parameter that corrects the flash results since the fraction of the mass flow, in the reacting medium, that is suffering phase change at one specific axial point in the reactor, is not known (Vasco de Toledo and Maciel Filho, 2002).

2.3 Phase Change of the Refrigerant Fluid.

The great amount of energy released in hydrogenation reaction may increase the temperature of the refrigerant until evaporation. For this reason, the regime flow of the refrigerant fluid can present two situations: monophase (liquid or steam) and two-phase (liquid+steam).

The transfer of heat in monophase regime flow is reasonably susceptible to a predictive treatment, having a large number of correlations that predict the convective coefficient (Incropera and De Witt, 1990). The estimation of coefficients of heat transfer in ebullition (two-phase regime flow) was possible due to the methodology proposed by Chen and described by Stephan (1992).

The numerical strategy to incorporate this phenomenon in the model of the reactor is described next. During the integration of the dynamic model of the reactor, at each axial position of the grid of discretization of the reactor, the temperature of the refrigerant fluid (T_r) is compared to its saturation temperature (T_{sat}), that is dependent of the pressure. From this comparison, the convective heat transfer coefficient of the refrigerant fluid (he) may be calculated differently in three cases:

1) If $T_r < T_{sat}$, then the flow is monophase and liquid, thus he is calculated by the equation in Incropera and De Witt (1990);

2) If $T_r = T_{sat}$, then the flow is two-phase, thus he is calculated by the methodology proposed by Chen and described by Stephan (1992);

3) If $T_r > T_{sat}$, then the flow is monophase and vapour, thus he is calculated by the equation in Incropera and De Witt (1990) using the vapour physical properties.

In accordance with the methodology proposed by Chen, during the phase change is necessary to evaluate the amount of refrigerant fluid vaporized or condensed taking into account the latent heat of the refrigerant fluid. Thus, a possible variation of he due to the conditions of vaporization above mentioned may cause a variation of the global coefficient of heat transfer (U), whose value affects the energy balance of the fluid phase and of the refrigerant fluid (Eqs. 9 and 11). In the case of study of this work, the refrigerant fluid is water, which is observed in many industrial processes.

3. RESULTS

The simulations monitored the temperature of the reacting medium at the end of the tubular reactor (T). The studies focused on this variable because its knowledge is fundamental for elaboration of efficient control strategies, simulation studies and reactor design. For each simulation, a step perturbation related to one specific operating parameter was introduced in the system. The parameters that showed to have more influence on the reacting medium temperature (Vasco de Toledo and Maciel Filho, 2002) are the inlet temperatures of the fluid phase, T_{fo}, and of the refrigerant fluid, T_{ro}.

Figures 2 and 3 show the effect of the phase change of the reacting medium in the dynamic behaviour of the reactor after a step perturbation in T_{ro} and T_{fo}, respectively. This phenomenon gives rise to steep temperature gradients within the reactor due to the

heat involved in the phase change according to the flash calculation. As a result, temperature increases when condensation occurs and it decreases as the reacting medium vaporizes, thus the reactor shows an oscillatory dynamic behaviour.
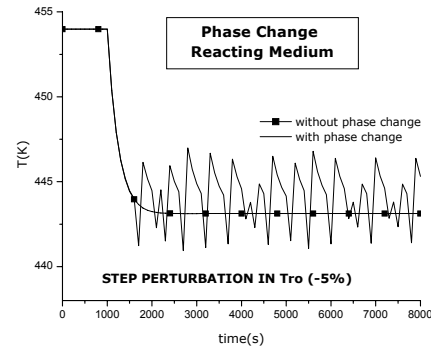

Fig. 2. Influence of the phase change of the reacting medium on the outlet temperature profile of the reactor. Step perturbation in T_{ro} (refrigerant fluid feeding temperature).
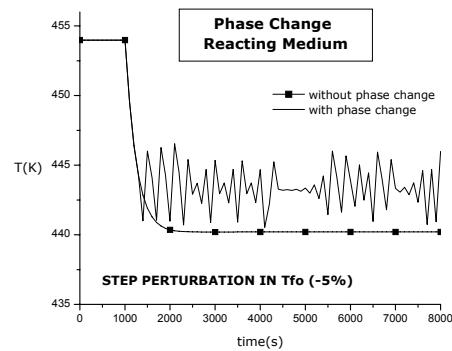

Fig. 3. Influence of the phase change of the reacting medium on the outlet temperature profile of the reactor. Step perturbation in T_{fo} (feeding temperature).

In Figures 4 and 5, the effects of considering the non-ideality of the, respectively, liquid and vapour phases, for the case displayed in Figure 2, can be seen. The differences between the results show that the hypotheses of ideal system may affect the dynamic behaviour of the reactor when, in fact, the system does not have these ideal characteristics. When the criteria of Hanika was used to check the occurrence of the phase change, in general, there was a conflict between the temperature pointed out by the criteria and the phase equilibrium equation (in flash calculation) that did not considered the values of temperature and pressure as conditions of existence for the two phases. Thereby, for this case of study, the flash calculation reached a better performance when the Bubble and Dew points option were utilized to check the temperature of the phase change.
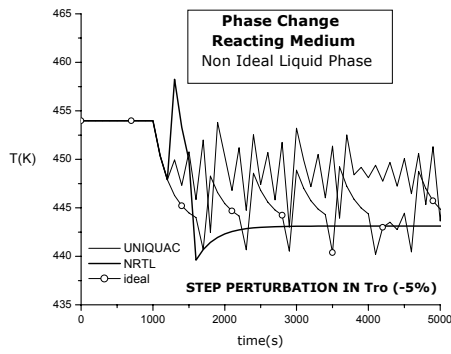
Fig. 4. Influence of the thermodynamic models (activity coefficients) on the outlet temperature profile of the reactor. Step perturbation in T_{ro}.
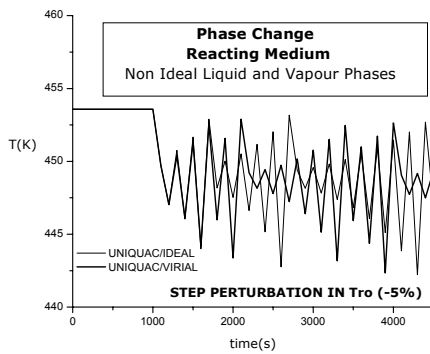

Fig. 5. Influence of the thermodynamic models (fugacity coefficients) on the outlet temperature profile of the reactor. Step perturbation in T_{ro}.

The simulations represented in Figure 6 show the influence of the factor F in the representation of the phenomenon of phase change of the reacting medium. According to the results, small values of F must be preferred, otherwise the variations in the temperature become wider than is observed in practice (~10ºC). Thus, the factor F allows the user of the model to adjust the effect of the phase change as it is observed in practice.
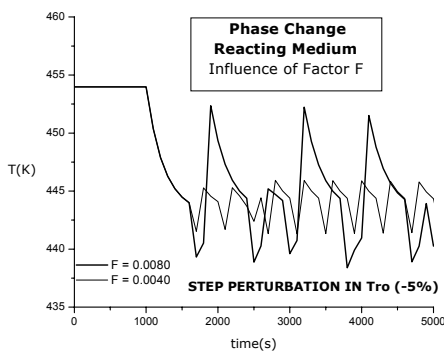

Fig. 6. Influence of the factor F on the outlet temperature profile of the reactor. Step perturbation in T_{ro}.

The effect of the phase change in the refrigerant fluid is represented in Figure 7 (the phase change of the reacting medium is not considered). The reactor temperature (T) falls during the vaporization of the refrigerant fluid because of an intensification of the heat exchange caused by a sharp rise in the convective heat transfer coefficient of the refrigerant fluid (he) (Figure 8) that affects the value of the global heat transfer coefficient (U). Otherwise, while the vaporization does not happen, T comes back to increase. Thus, an oscillatory dynamic behaviour is observed in the reactor.
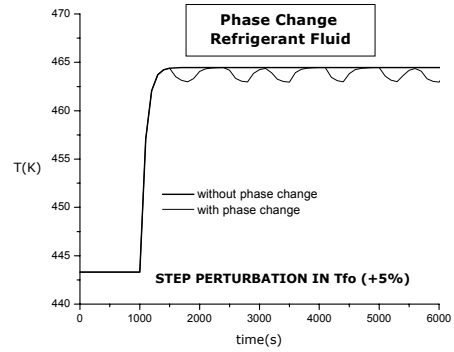

Fig. 7. Influence of the phase change of the refrigerant fluid on the outlet temperature profile of the reactor. Step perturbation in T_{fo}.
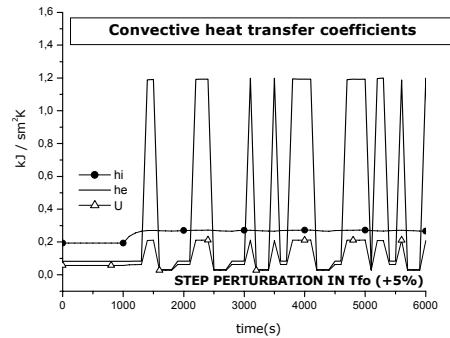

Fig. 8. Convective coefficients of heat transfer during simulation of Figure 7.

4. CONCLUDING REMARKS

The model developed and presented in this work allowed to simulate some aspects of the dynamic behaviour of three-phase slurry reactor. The model was capable to foresee the phenomenon of phase change of the reacting medium as well as of the refrigerant fluid that introduced perturbations on the temperature of the reactor that surely affect the product specifications. Therefore the knowledge obtained through the model is essential for a good design and control of three-phase catalytic slurry reactors.

NOTATION

a	interfacial area, m^{-1}
C_p	heat capacity, kj/kg.K
D_e	effective diffusivity, m^2/s
D_t	reactor intern diameter, m
D_{te}	reactor extern diameter, m
D_{ts}	diameter of the jacket tube, m
E	activity energy, J/mol
FA	molar flow of the component A, kmol/s
FB	molar flow of the component B, kmol/s
FC	molar flow of the component C, kmol/s
he	external convective heat transfer coefficient, kj/m^2.s.K
hi	internal convective heat transfer coefficient, kj/m^2.s.K
k	kinetic constant, kmol/ kg cat . s
K	mass transfer coefficients, cm/s
L	reactor length, m
Q_{flash}	heat of phase change of the reacting medium, kj/s
Q_l	liquid feed volumetric flow, m^3/s
r_p	dimensionless particle radial position
R_p	radius particle, m
R_w	rate of hydrogenation of *o*-cresol, kmol/kg-cat.s
T	temperature, K
t	time, s
u	linear velocity, m/s
U	global heat transfer coefficient, kj/m^2.s.K
w	catalyst concentration, $kgcat/m^3$
z	dimensionless reactor axial position

Greek letters

ΔH_R	heat of reaction, kj/kmol
λ	thermal conductivity, kj/m.s.K
ν	stoichiometric coefficient
ρ	density, kg/m^3
ε_g	gas phase hold-up
ε_l	liquid phase hold-up
ε_s	solid porosity
τ	tortuosity

Subscripts

g	gas phase
fo	feeding
l	liquid phase
i	initial value (reactor inlet)
p	particle
r	refrigerant fluid
s	solid

Superscripts

s	catalyst surface

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