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
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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.

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
α-cresol on Ni/SiO₂ catalyst (Hichri et al., 1991).

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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) + vB(l) → vC(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](image)

The radial dispersion has been neglected for the fluid phase, which is a very common assumption in multiphase 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 \(Q\), 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:

\[
\begin{align*}
\frac{\partial F_A}{\partial t} &= \frac{D_A}{L} \frac{\partial^2 F_A}{\partial z^2} - \frac{u_z}{L} \frac{\partial F_A}{\partial z} + \left(K_g\right)_{\text{A}} \frac{\partial F_A - F_A}{\partial z} \\
D_A \frac{\partial F_A}{\partial z}|_{z=0} &= u_z \frac{F_A(z=0) - F_A_{\infty}}{\partial z} = 0
\end{align*}
\]  

(1)

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

\[
\begin{align*}
\frac{\partial F_A}{\partial t} &= \frac{D_A}{L} \frac{\partial^2 F_A}{\partial z^2} - \frac{u_z}{L} \frac{\partial F_A}{\partial z} + \left(K_l\right)_{\text{A}} \frac{\partial F_A - F_A}{\partial z} \\
D_A \frac{\partial F_A}{\partial z}|_{z=0} &= u_z \frac{F_A(z=0) - F_A_{\infty}}{\partial z} = 0
\end{align*}
\]  

(2)

Energy balance of the refrigerant fluid:

\[
\begin{align*}
\frac{\partial p_c C_p \frac{\partial T}{\partial t}}{L} &= \frac{\left[\frac{L}{u} + \frac{L}{u_2} + \frac{L}{u_3}\right] \frac{\partial T}{\partial z}}{L} + \left(K_l\right)_{\text{C}} \frac{\partial T - T}{\partial z} \\
\frac{\partial T}{\partial z}|_{z=0} &= 0
\end{align*}
\]  

(9)

Energy balance of the refrigerant fluid:

\[
\begin{align*}
\frac{\partial p_c C_p \frac{\partial T}{\partial t}}{L} &= \frac{\partial p_c C_p \frac{\partial T}{\partial z}}{L} + \frac{4U}{D_1} (T - T_f) \\
T_f &= T_{\infty}, \quad z = 0
\end{align*}
\]  

(10)
Solid Phase:

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

\[
\frac{\partial \rho_r T}{\partial t} - \frac{\partial}{\partial r} \left( \frac{1}{r} \frac{\partial}{\partial r} \left( r \rho_r T \right) \right) = \rho_r \frac{\partial Q_{r,\text{heat}}}{\partial r} - \left( \frac{\partial}{\partial r} \left( r \rho_r \nu_s \frac{\partial T}{\partial r} \right) \right) + \rho_{\text{inlet}} \frac{\partial Q_{\text{inlet}}}{\partial r} \tag{18}
\]

Energy balance in the solid phase

\[
\rho_r C_p \frac{\partial \rho_r T}{\partial t} = \lambda_s \frac{\partial}{\partial r} \left( \frac{\partial}{\partial r} \left( r \rho_r \nu_s \frac{\partial T}{\partial r} \right) \right) + \rho_{\text{inlet}} \frac{\partial Q_{\text{inlet}}}{\partial t} \tag{19}
\]

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 (Villardsen 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 the 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 \(Q_{\text{flash}}\) 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 monophasic 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 monophasic 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 monophasic 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 it 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, $T_{fr}$.

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 $T_{fo}$ and $T_{fr}$, 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.

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.
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. 4](image_url) Influence of the thermodynamic models (activity coefficients) on the outlet temperature profile of the reactor. Step perturbation in \( T_{ro} \).

![Fig. 5](image_url) 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 (~10°C). 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](image_url) Influence of the factor \( F \) on the outlet temperature profile of the reactor. Step perturbation in \( T_{ro} \).

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.


References