

Dynamic modelling of a three-phase catalytic slurry intensified chemical reactor

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Abstract: Three-phases chemical reactions are widely applied industrially. They are highly non-linear, multivariable, exothermal processes. The aim of the present work is to propose a dynamic model of an intensified continuous three-phases mini-reactor. This model is developed to enable the transient phase monitoring of the mini-reactor. The reactor is treated as an association of J stirred tank reactors in series with back mixing effect. The model is used to describe the dynamic behaviour of the reactor during the hydrogenation of o-cresol on Ni/SiO₂ catalyst. The model consists in mass and energy balance equations for the catalyst particles, the gas and liquid bulk phases. The transient heat transfers between the metal body of the reactor, the coolant fluid and the bulk fluid are also taken into account.

Keywords: Intensification; Three-phase reactor; Hydrogenation; Dynamic modelling; Control; Dynamic behaviour.

1. INTRODUCTION

The pharmaceutical and the fine chemical industries produce molecules of high added values mainly in batch or fed-batch agitated reactors. Indeed, batch reactors, even if they provide the characteristics of flexibility and versatility required in the field of fine chemicals production, have a number of limitations: in particular, poor conditions of heat released by the chemical reactions leads to a serious safety problem for highly exothermal chemical reactions.

For some years, there is an alternative in the use of batch reactors, thanks to process intensification progresses and to mini-reactors development. The idea is to perform the reactions in continuous intensified reactors. On the one hand, the intensification leads to a better control of heat transfer that allows concentrating the reagent and thus limiting the quantities of solvent to be treated. On the other hand, intensification leads to reduce mass transfer limitations in the case of multiphase chemical reactors.

Nowadays, the control and safety of these reactors are important features in the design as well as in the operation of industrial processes. Such processes carry out complex reactions with constraints on thermal stability and/or selectivity as, for example, exothermal hydrogenation reactions (Vasco de Toldeo *et al.*, 2001).

Hydrogenation reactions are widely applied industrially. Development of efficient and reliable models for three phase reactors is still a difficult task because it involves many aspects including hydrodynamics, gas-liquid and liquid-solid

mass transfer, heat transfer, reaction kinetics (Bergault *et al.*, 1997).

In the literature, we can find many studies proposing dynamic modelling of catalytic three phase reactors (P.A Ramachandran and J.M. Smith, 1976; R.J. Wörnä and T. Salmi, 1995; Vasco de Toldeo *et al.*, 2001) but as far as we know, the problem of mini-reactors modelling is not addressed.

The aim of this paper is to propose a dynamic model of a continuous three-phases intensified mini-reactor. This model is developed to enable the transient period monitoring of the three phases mini-reactor. It will allow better predictions of the behaviour of the system and therefore secure and effective studies of the reactor control.

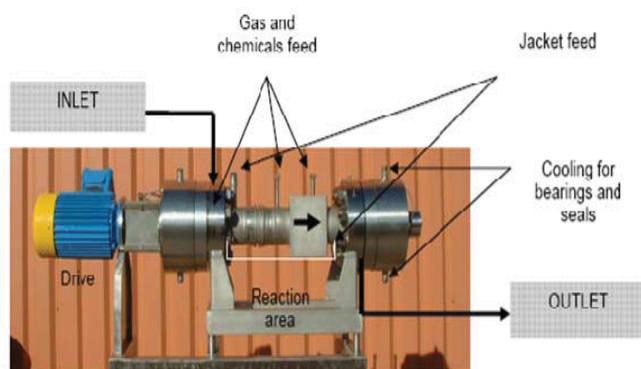


Fig.1. The “RAPTOR® (Réacteur Agité Polyvalent à Transfert Optimisé Rectiligne)”.

The mini-reactor under consideration, the “RAPTOR®” (presented by the figure 1) is developed by AETGOUP SAS Company a French society whose main activity is to offer a broad range of services mainly focused on chemical process industrialisation, in the field of pharmaceuticals, fragrances and aromas, cosmetics and specialty chemicals. For confidentiality reasons, we cannot give here a detailed description of the RAPTOR®.

2. MATHEMATICAL MODELLING

The model is used to describe the dynamic behaviour of the reactor during the hydrogenation of o-cresol on Ni/SiO₂ catalyst, taken as an example. A three-phase catalytic reactor is a system in which gas and liquid phases are in contact with a porous solid phase. The reaction occurs between a dissolved gas and a liquid-phase reactant in presence of a catalyst on the surface of the porous solid support (P.A. Ramachandran and R.V. Chaudhari, 1983), according to the following global stoichiometric equation:



The chemical process involves several steps in series (see figure 2):

- diffusion of A from gas-liquid interface to the bulk liquid;
- diffusion of A and B from bulk liquid through liquid-solid interface;
- intraparticle diffusion of A and B into the pores of the solid;
- adsorption of the reactants;
- adsorbed phase reaction.

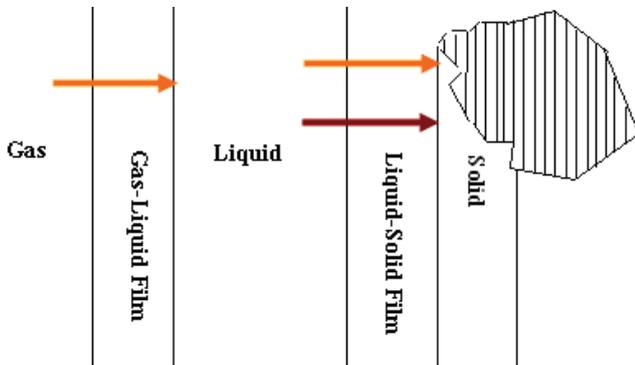


Fig.2. Steps of catalytic reaction.

The reactor is treated as an association of J stirred tank reactors in series with back mixing effect. Similarly, the jacket is treated as an association of J perfectly stirred tank reactors series. This way to consider the flows in the reactor is highly flexible and leads to a finite dimension model. Since an intensified reactor has to be compact, the influence of the reactor body itself may be significant with respect to the thermal transient behaviour of the system. Consequently, a piece of reactor body is associated to each perfectly mixed reactors used to model the flows (see figure 3).

The model consists in mass and energy balance equations for the catalyst particles, the gas phase and liquid-bulk phase,

and also energy balance equations for the body of the reactor and for the coolant fluid into the jacket.

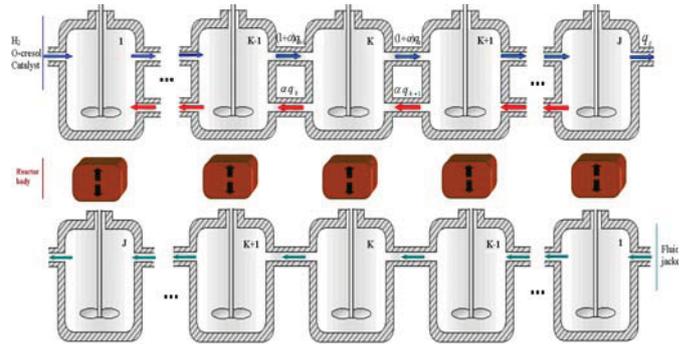


Fig.3. Flow model of the mini-reactor.

2.1 Kinetic model

Hydrogenation of o-cresol on Ni/SiO₂ catalyst (Hichri *et al.*, 1991) is taken as an example of chemical process that can be intensified. In this case, hydrogen reacts with o-cresol without any solvent due to the high heat and mass transfer capacities of the mini-reactor. The reaction can be represented by equation (1). In this case, A stands for hydrogen, B for o-cresol, C for 2-methylcyclohexanol.

Langmuir-Hinshelwood model represents in a realistic way the adsorption phenomena involved in heterogeneous catalysis processes. The reaction rate is calculated as follows (Hichri *et al.*, 1991):

$$R = k \frac{K_A K_B C_{As} C_{Bs}}{(1 + K_A C_{As})(1 + K_B C_{Bs})} \quad (2)$$

C_{As} and C_{Bs} are respectively the hydrogen and o-cresol concentrations within the catalyst pores. The Arrhenius law gives the variation of the rate constants k with temperature while adsorption constants K_A and K_B variations derive from mass action law. The following expressions are taken from (Hichri *et al.*, 1991):

$$k(\text{mol/kg.cat.s}) = 5,46.10^8 \exp(-82220/RT_s) \quad (3)$$

$$K_A(\text{m}^3/\text{mol}) = 10,55.10^{-3} \exp(+5003/RT_s) \quad (4)$$

$$K_B(\text{m}^3/\text{mol}) = 7,54.10^{-6} \exp(+16325/RT_s) \quad (5)$$

where T_s (K) is the catalyst pellet temperature.

2.2 Mini-reactor model

The following assumptions are considered to derive the model (Vasco De Toledo *et al.*, 2001; Santana, 1999):

- the liquid and gas phases homogeneous suspension is considered as a pseudo-fluid with respect to the temperature;
- a global mass transfer coefficient is used to represent hydrogen transfer from the liquid surface to the bulk. Equilibrium conditions at the liquid surface are assumed;

- the pressure variations are negligible;
- the resistances to mass and heat transfer at the catalyst pellet surface and within the pores are lumped into global heat and mass transfer coefficients;
- the material balance in the gas phase, that is assumed to be pure hydrogen, is written at steady state.

Mass balance of reactant A in the gas phase

$$F_{Ag}^{0k} + V_k k_l a^k (C_{Al}^{k*} - C_{Al}^k) = F_{Ag}^{Ik} \quad (6)$$

Mass balance of reactant A in the liquid phase

$$\varepsilon_l^k V_k \frac{dC_{Al}^k}{dt} = (1 + \alpha) q_l^{k-1} C_{Al}^{k-1} + \alpha q_l^{k+1} C_{Al}^{k+1} - (1 + 2\alpha) q_l^k C_{Al}^k - V_k k_s a (C_{Al}^k - C_{As}^k) + V_k k_l a^k (C_{Al}^{k*} - C_{As}^k) \quad (7)$$

Mass balance of reactant A in the solid phase

$$\varepsilon_s V_k \frac{dC_{As}^k}{dt} = (1 + \alpha) q_s^{k-1} C_{As}^{k-1} + \alpha q_s^{k+1} C_{As}^{k+1} - (1 + 2\alpha) q_s^k C_{As}^k + V_k k_s a (C_{Al}^k - C_{As}^k) - v_A \varepsilon_s \rho_s V_k R(C_{As}^k, C_{Bs}^k, T_s^k) \quad (8)$$

Mass balance of reactant B in the liquid phase

$$\varepsilon_l^k V_k \frac{dC_{Bl}^k}{dt} = (1 + \alpha) q_l^{k-1} C_{Bl}^{k-1} + \alpha q_l^{k+1} C_{Bl}^{k+1} - (1 + 2\alpha) q_l^k C_{Bl}^k - V_k k_s a (C_{Bl}^k - C_{Bs}^k). \quad (9)$$

Mass balance of reactant B in the solid phase

$$\varepsilon_s V_k \frac{dC_{Bs}^k}{dt} = (1 + \alpha) q_s^{k-1} C_{Bs}^{k-1} + \alpha q_s^{k+1} C_{Bs}^{k+1} - (1 + 2\alpha) q_s^k C_{Bs}^k + V_k k_s a (C_{Bl}^k - C_{Bs}^k) - v_B \varepsilon_s \rho_s V_k R(C_{As}^k, C_{Bs}^k, T_s^k) \quad (10)$$

Energy balance in the fluid (gas + liquid) phase

$$V_k (\varepsilon_g^k \rho_g C_{pg} + \varepsilon_l^k \rho_l C_{pl}) \frac{dT_f^k}{dt} = hS (T_m^k - T_f^k) + V_k h_s a_{ls} (T_s^k - T_f^k) - (\varepsilon_g^k \rho_g C_{pg} + \varepsilon_l^k \rho_l C_{pl}) \left((1 + \alpha) q_{k-1} (T_f^k - T_f^{k-1}) + \alpha q_{k+1} (T_f^k - T_f^{k+1}) \right) \quad (11)$$

Energy balance in the solid phase

$$\varepsilon_s V_k \rho_s C_{ps} \frac{dT_s^k}{dt} = V_k h_s a_{ls} (T_f^k - T_s^k) - (\rho_s C_{ps}) \left((1 + \alpha) q_{sk-1} (T_s^k - T_s^{k-1}) + \alpha q_{sk+1} (T_s^k - T_s^{k+1}) \right) - \varepsilon_s V_k \rho_s \Delta_r HR (C_{As}^k, C_{Bs}^k, T_s^k). \quad (12)$$

Energy balance of the body of the mini-reactor

$$(V_k \rho C_p)_m \frac{dT_m^k}{dt} = hS (T_f^k - T_m^k) + h_j S (T_j^k - T_m^k) \quad (13)$$

Energy balance of the refrigerant fluid into the jacket

$$(V_k \rho C_p)_j \frac{dT_j^k}{dt} = h_j S (T_m^k - T_j^k) - (\rho C_p)_j q_j^{k-1} (T_j^k - T_j^{k-1}). \quad (14)$$

3. SIMULATION RESULTS

Kinetic and thermodynamic parameters are taken from (Hichri *et al.*, 1991). The other physical parameters are taken from (Vasco de Toledo *et al.*, 2001; Adriano Pinto Mariano *et al.*, 2005).

We have performed a sensitivity study to define the optimum conditions that enable to achieve a high conversion rate under the constraint of the thermal runaway. One can see on the figure 5 the dynamic behaviour of the reactor and on the figure 4 the steady-state conversion profile that we have obtained. The operating conditions resulting from the sensitivity analysis lead to a conversion up to 90% at the reactor outlet, which is a very common industrial target.

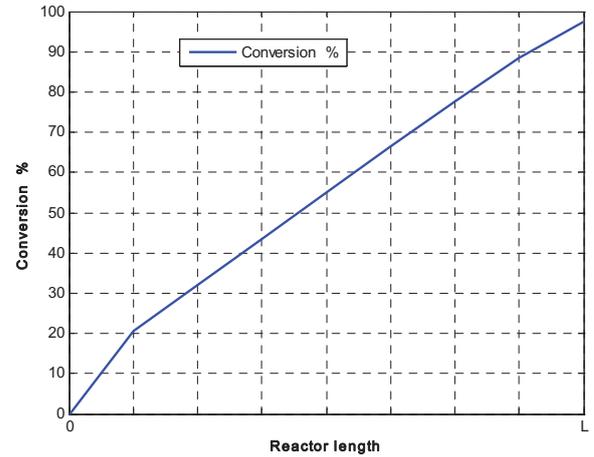


Fig.4. The steady-state conversion profile along the mini-reactor.

In figure 5, the dynamic behaviour of the reactor outlet temperature is represented. We observe that the fluid temperature is limited and increases by 24 %.

The catalyst temperature is slightly higher than that of reactant fluid since the reaction takes place in the pores catalyst. We also observe that the jacket temperature remains nearly constant while the temperature of the reactor body heats up by 15%. In fact the reactor body tends to store up the energy released by the reaction; it therefore appears that the reactor can work in hard reactive conditions, but safely.

When the optimum operating conditions have been established, we performed a steady-state characterization of the model; this feature allows not only steady analysis of model sensitivity with respect to the variation of input variables, but also consistency verification of the model.

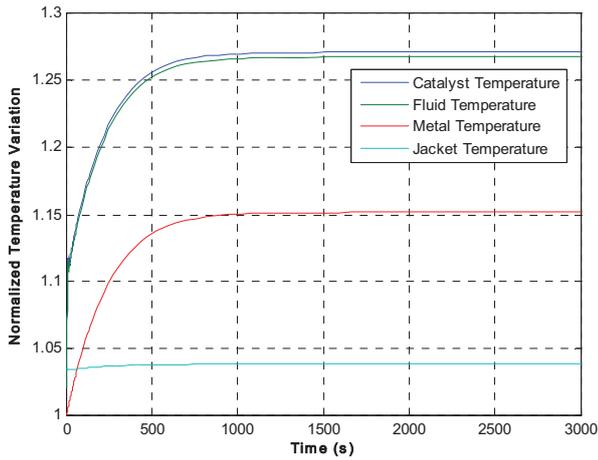


Fig.5. The dynamic behaviour of outlet reactor temperatures.

As far as intensified reactors are concerned, where the reaction takes place at very high temperature, the jacket plays a dual role in the evolution of the reaction. On the one hand, it is related to safety problems since the jacket fluid allows cooling the temperature of the bulk in order to avoid thermal runaway. On the other hand, it allows the indirect control of the outlet conversion by controlling the temperature of the bulk.

Figure 6 illustrates the steady-state characterization of outlet temperatures and conversion with respect to the inlet jacket fluid temperature (variations ranging from -5% to 5% around T_{j0}).

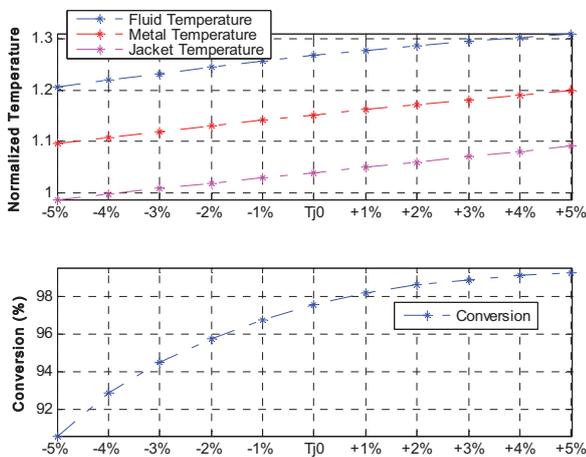


Fig.6. The steady-state characterization of outlet temperatures and conversion with respect to the inlet jacket fluid temperature.

From this figure, it is observed that both of outlet temperatures and conversion are very sensitive to changes in the inlet temperature of the jacket fluid. This sensibility of the dynamic behaviour of the reactor in relation to changes in the coolant fluid is observed mainly in industrial situations.

Figure 7 shows the steady characterization of outlet temperatures and conversion with respect to the inlet gas flow (ranging from -30% to 30% around q_{A0}). We can observe that

the variations of q_{A0} have more impact on the conversion than the outlet temperatures.

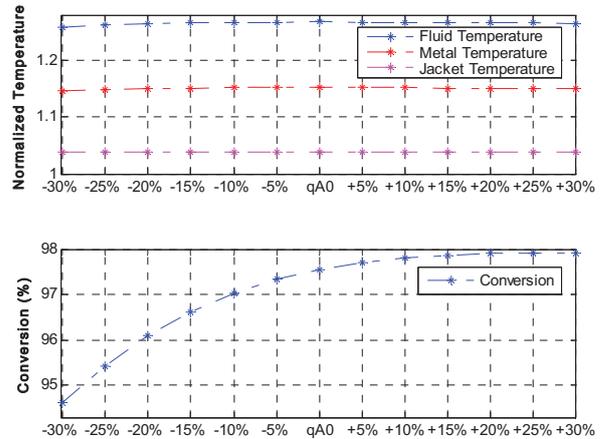


Fig.7. The steady-state characterization of outlet temperatures and conversion with respect to the inlet gas flow.

Figure 8 shows the effect of the inlet fluid temperature on the behaviour of outlet temperatures and conversion (variations ranging from -5% to 5% around T_{f0}). This figure points out that only conversion is sensitive to the variations of T_{f0} , as a result, disturbance on the inlet fluid temperature greatly affects the quality of the output product.

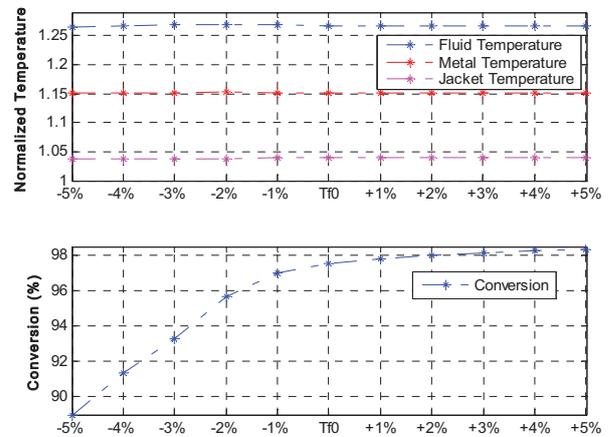


Fig.8. The steady-state characterization of outlet temperatures and conversion with respect to the inlet fluid temperature.

In figure 9, the steady-state characterization of outlet temperatures and conversion with respect to the inlet fluid flow (ranging from -30% to 30% around q_{f0}) is highlighted. We remark that the temperatures and conversion are very sensitive to q_{f0} . In fact, a decrease in the inlet fluid flow (-30%) allows obtaining a good conversion (=99.9%) with better thermal conditions. However this result leads to lower productivity.

According to the observations of these figures, the steady-state characterization of the model confirms the consistency of the model sets.

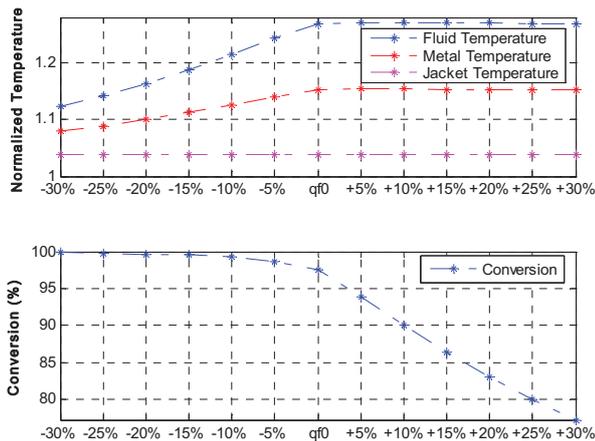


Fig.9. The steady-state characterization of outlet temperatures and conversion with respect to the inlet Fluid flow.

We observed that system's output variables are very sensitive to the variations of inlet jacket temperature. We could also highlight the fact that the conversion is very sensitive to the variations of inlet gas flow. Thus it may be concluded that these two variables may be chosen as an efficient control variables.

4. CONCLUSION

Reactions performed in multiphase catalytic intensified reactors have a complex behaviour due to heat and mass transfers and chemical kinetic interactions. The objective of the dynamic mathematical model developed in this work is to perform a detailed study of the process dynamic behaviour in order to define a suitable control structure. This structure has to control the outlet conversion and preserve safety conditions of the reactor. Others objectives such as high product quality and economy gain can also be considered.

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NOTATION

a	interfacial area, m^{-1}
C_A	concentration of the component A, $mol\ m^{-3}$
C_A^*	solubility of the component A, $mol\ m^{-3}$
C_B	concentration of the component B, $mol\ m^{-3}$
C_p	heat capacity, $J\ K^{-1}\ kg^{-1}$
F	molar flow, $mol\ s^{-1}$
h	heat transfer coefficient, $W\ m^{-2}\ K^{-1}$
k	kinetic constant, $mol\ kg^{-1}\ s^{-1}$
K	adsorption constant, $m^3\ mol^{-1}$
k_l	mass transfer coefficient gas-liquid, $m\ s^{-1}$
k_s	mass transfer coefficient liquid-solid, $m\ s^{-1}$
q	volume flow, $m^3\ s^{-1}$

R	reaction rate, $mol\ kg^{-1}\ s^{-1}$
S	surface, m^2
T	temperature, K
v	volume, m^3

GREEK LETTERS

$\Delta_r H$	heat of reaction, $J\ mol^{-1}$
v	stoichiometric coefficient
α	back mixing
ρ	density, $kg\ m^{-3}$
ϵ_g	gas hold up
ϵ_l	bulk hold up
ϵ_s	solid hold up

SUBSCRIPT

A	component A
B	component B
j	jacket fluid
f	fluid
g	gas
k	reactor number
l	liquid
m	metal
s	solid

SUPERSCRIPIT

k	reactor number
I	Inlet
O	Outlet

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