

Phenomenological approach to interpret the effect of liquid flow modulation in trickle bed reactors at the particle scale

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Abstract

This work analyzes the influence of liquid flow modulation on the behavior of a reaction occurring in a spherical porous particle within a trickle bed reactor. A single first-order reaction between a gaseous reactant and a non-volatile liquid reactant is considered. Non-steady-state mass balances for gas and liquid reactants are formulated and solved under isothermal conditions in order to focus the analysis on the mass transport effects. Dynamic reactant profiles inside the catalytic particle are obtained for different cycling and system conditions. The enhancement factor (ϵ) due to periodic operation is defined to evaluate the impact of induced liquid flow modulation on reaction rate. Influence of cycling and system parameters on the enhancement factor is also reported for a wide range of conditions. Experimental trends observed by several authors can be explained with this approach.

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1. Introduction

Trickle beds are among the most widely commercially employed three phase reactors for applications in quite diverse fields, from the petroleum and petrochemical industries to waste treatment, fine chemical and biochemical processes (Dudukovic et al., 2002). Traditionally, trickle bed reactors (TBRs) have been designed for steady-state operation. Internal and external mass transport rates strongly affect reaction rates. Therefore, the possibility of performance enhancement exists in these reactors by induced liquid flow modulation, i.e., periodic changes of the liquid loading between two predetermined values, since hydrodynamics and transport coefficients depend on the liquid velocity.

The application of periodic operation to TBR was suggested earlier by Gupta (1985). The work by Haure et al. (1989) represents one of the first experimental studies of periodic TBR operation. A growing number of contributions concerning liquid flow modulation in TBR have been presented in the last 15 years. Most of the studies reported in the open literature were restricted to gaseous reactant limited conditions. From the experimental results offered in the literature it is evident that, under proper conditions, periodic flow modulation can generate higher conversions than those found under steady-state operation (Lange et al., 1994; Khadilkar et al., 1999; Banchemo et al., 2004). In most contributions, only qualitative explanations of experimental results have been provided due to difficulties in disentangling the complex interactions among dynamics of reaction, mass transfer and hydrodynamics.

A few contributions have attempted the modeling of the periodic operation. Lange et al. (1999) and Stegasov et al. (1994) have proposed non-steady-state models for the whole

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reactor but they neglected the dynamics inside the particle. However, this phenomenon should not be ignored since internal diffusion dynamics can strongly influence catalytic processes for non-steady-state operations (Lee and Bailey, 1974). Boelhouwer (2001) solved dynamic mass balances considering internal diffusion for the case of wash coated catalyst particles with an impermeable core. Mass transfer between the dry and wet zones was not considered. Reactant and product profiles were obtained during fast cycling BASE-PEAK modulation but reactor enhancement was not evaluated. It was also found that the rate of internal diffusion largely determines the optimal cycle period.

A detailed dynamic model has been presented by Kouris et al. (1998) to study the behavior of a catalytic particle in the pulsing-flow regime, where regions enriched in gas and liquid rapidly pass through the reactor. Two parallel reactions between a volatile and two non-volatile components in a partially wetted catalyst were studied. Two approaches were considered: (i) a particle completely covered by liquid during the liquid pulse and completely covered by gas during the gas pulse; (ii) a particle covered by liquid in the upper section and by gas in the lower section during the liquid pulse, and the reverse during the gas pulse. They found that, as the period tends to zero, the particle is unable to follow the rapid changes in wetting and reaches a pseudo-stationary state. They concluded that catalyst performance can be enhanced in the pulsing-flow regime. Pulsing flow can be assimilated to a fast cyclic operation of a TBR. Intermediate and/or slow flow modulation has different characteristics, not examined by Kouris et al. (1998).

This work has the purpose of modeling the time course of the reaction rate for a catalyst particle in a TBR under ON–OFF cycling. Effectiveness factor for steady- and non-steady-state situations are calculated from the numerical resolution of the model. Therefore, an enhancement factor obtained under induced liquid flow modulation is defined and evaluated. Influence of cycling and system parameters on the enhancement factor is analyzed over a wide range of conditions. Experimental trends observed by several authors can be explained by means of the model.

2. Model development

A single reaction between a gaseous reactant (A) and a non-volatile liquid reactant (B) within a porous solid catalyst is considered. The active sites are uniformly distributed in the particle. The kinetic is assumed to be first-order with respect to A and zero-order with respect to B . The last assumption can be justified considering that B is in large excess, as in some oxidation and hydrogenation reactions. Besides, this rate expression allows for an easier verification of model results for steady-state and cycling operation if no depletion of B occurs. The usefulness and limitations of this kinetic expression have been pointed out by Harold and Ng

(1987) for steady-state conditions and can be extended to our study.

Isothermal conditions are assumed, to focus the analysis on the mass transport and accumulation effects. Non-steady-state mass balances for the gas and liquid reactants are formulated and solved for a spherical particle. Behavior during ON–OFF operation is described as a square-wave cycling. This hypothesis is valid mainly for intermediate to low liquid flow modulation. For fast liquid flow modulation, the square-wave assumption may not represent properly the system, as discussed in the next section. Total internal wetting is assumed during the whole cycle period. The catalyst particle can be completely or partially wet during the ON cycle. Once the liquid flow stops, the external mass transport resistances are considered negligible. This last assumption is supported by the significantly higher values of mass transfer coefficients in the gas phase, which would mostly determine the external resistances during the dry period of the cycle. This approach is valid if the time required to drain the particle is smaller than the extent of the dry cycle.

Taking into account these assumptions, the dimensionless differential mass balances for both reactants inside the catalyst are:

$$\frac{\partial \alpha_A}{\partial \tau} = \frac{\partial^2 \alpha_A}{\partial \rho^2} + \frac{2}{\rho} \frac{\partial \alpha_A}{\partial \rho} + \frac{\cot \theta}{\rho^2} \frac{\partial \alpha_A}{\partial \theta} + \frac{1}{\rho^2} \frac{\partial^2 \alpha_A}{\partial \theta^2} - \phi^2 \alpha_A H(\alpha_B), \quad (1a)$$

$$\frac{\partial \alpha_B}{\partial \tau} = \delta \left(\frac{\partial^2 \alpha_B}{\partial \rho^2} + \frac{2}{\rho} \frac{\partial \alpha_B}{\partial \rho} + \frac{\cot \theta}{\rho^2} \frac{\partial \alpha_B}{\partial \theta} + \frac{1}{\rho^2} \frac{\partial^2 \alpha_B}{\partial \theta^2} \right) - \phi^2 \zeta \alpha_A H(\alpha_B), \quad (1b)$$

where $H(\alpha_B)$ is the Heaviside function.

The model is solved in spherical coordinates considering radial and angular variations in the θ direction. Axial symmetry is considered. The wetting efficiency, f , is introduced into the model with respect to a critical value of the angle, θ_f , as $2f = 1 - \cos(\theta_f)$ as proposed by Kouris et al. (1998). The relationship assumes that the wetting efficiency represents the fraction of the sphere area covered by liquid and corresponds to the area of the spherical cup.

Initial and boundary conditions postulated for the wet period of the cycling are:

$$\tau = 0, \quad \alpha_i = 1, \quad i = A, B, \quad (2a)$$

$$\rho = 0, \quad \frac{\partial}{\partial \rho} \alpha_i = \text{finite} \\ \text{if } 0 \leq \theta < \frac{\pi}{2} \text{ and } \frac{\pi}{2} < \theta \leq \pi, \quad i = A, B, \quad (2b)$$

$$\frac{\partial}{\partial \rho} \alpha_i = 0 \quad \text{if } \theta = \frac{\pi}{2}, \quad i = A, B, \quad (2c)$$

$$\rho = 1, \quad \frac{\partial}{\partial \rho} \alpha_A = Bi_{gl_s,A}(1 - \alpha_A),$$

$$\frac{\partial}{\partial \rho} \alpha_B = Bi_{ls,B}(1 - \alpha_B) \quad \text{if } \theta \leq \theta_f, \quad (2d)$$

$$\alpha_A = 1, \quad \frac{\partial}{\partial \rho} \alpha_B = 0 \quad \text{if } \theta > \theta_f, \quad (2e)$$

$$\theta = 0 \text{ or } \pi, \quad \frac{\partial}{\partial \theta} \alpha_i = 0, \quad i = A, B, \quad (2f)$$

where the dimensionless parameters are:

$$\rho = \frac{r}{R}, \quad \alpha_A = \frac{C_A}{C_A^*}, \quad \alpha_B = \frac{C_B}{C_{B0}}, \quad \tau = \frac{tD_A}{\varepsilon_p R^2},$$

$$\delta = \frac{D_B}{D_A}, \quad \xi = \frac{bC_A^*}{C_{B0}}, \quad \phi^2 = \frac{kR^2}{D_A},$$

$$Bi_{gl_s,A} = \frac{((1/kl_{Aa_{gl}}) + (1/ks_{Aa_p}))^{-1} R^2}{3D_A},$$

$$Bi_{ls,B} = \frac{ks_{Ba_p} R^2}{3D_B}.$$

For the dry period, the boundary conditions are the same, except Eqs. (2d) and (e), which become:

$$\rho = 1, \quad \alpha_A = 1, \quad \frac{\partial}{\partial \rho} \alpha_B = 0 \quad \forall \theta. \quad (2g)$$

Boundary conditions for solving the model under steady-state are Eqs. (2b)–(2f).

Model is solved by explicit finite differences. For each time step, solution was first evaluated along the radial direction at $\theta = \pi/2$ and a finite value was found for $\rho \cong 0$. This value was then assigned to $\rho = 0$ for every θ . Several discretization strategies were tested to verify convergence of the results. A network with 21 grid points in the angular position and 111 in the radial position was finally selected. Also, calculated limit values (complete wetting and steady-state with partial wetting) were contrasted against generally accepted approximations for three-phase systems.

At any time during a cycle, reactants radial and angular profiles can be evaluated with the model. Then, an instantaneous effectiveness factor can be obtained by integrating in the radial and angular directions:

$$\eta_i = \frac{3}{2} \int_0^\pi \int_0^1 \rho^2 \sin \theta \alpha_A(\rho, \theta) H(\alpha_B(\rho, \theta)) d\rho d\theta,$$

$$i = w, \text{nw}. \quad (3)$$

With the instantaneous overall efficiencies during the wet (η_w) and dry (η_{nw}) cycles, a global overall effectiveness factor for the cycle invariant state, η_{cyc} , can be calculated as

$$\eta_{cyc} = \frac{\int_0^{\tau_w} \eta_w d\tau + \int_0^{\tau_{nw}} \eta_{nw} d\tau}{\tau_w + \tau_{nw}}, \quad (4)$$

where τ_w and τ_{nw} are the times for which the liquid is ON and OFF, respectively.

An enhancement factor (ε) due to periodic operation can thus be defined for the model, based on the steady-state overall effectiveness factor evaluated at the mean liquid velocity (η_{ss}) as:

$$\varepsilon = \eta_{cyc} / \eta_{ss}. \quad (5)$$

To compare results, the relationship between the liquid velocity for steady-state operation ($u_{L_{ss}}$) and during the ON cycle of periodic operation (u_{L_w}) is taken into account as

$$u_{L_w} = u_{L_{ss}}(1/s). \quad (6)$$

Mass transfer coefficients for the wet cycle would depend on the split as:

$$kl_w = kl_{ss}(1/s)^{\gamma_1}, \quad (7a)$$

$$ks_w = ks_{ss}(1/s)^{\gamma_2}, \quad (7b)$$

that will be reflected in the corresponding Biot values. The exponents, γ_1 and γ_2 , indicate the influence of the liquid velocity on each mass transfer coefficient and their value depend on the flow regime and on the correlation used to estimate them. Considering trickle flow around the particle, the correlation proposed by Goto and Smith (1975) can be used, with $\gamma_1 = 0.41$ and $\gamma_2 = 0.56$. In a similar way, the relationship between the wetting efficiency for steady-state and during the wet cycle must be established. According to Herskowitz (1981), the following correlation can be used:

$$f_w = f_{ss} + 0.0739 \ln(1/s). \quad (8)$$

Valid within the range $0.0002 < u_L < 0.01$ m/s. For larger liquid velocities, complete external wetting was assumed. Model parameters used for simulation were selected taking into account process conditions reported in the literature.

3. Results and discussion

We first analyze the situation in which the particle is completely wet at steady-state conditions and during the wet cycle ($f_w = f_{ss} = 1$). Gas and liquid reactant profiles inside the catalyst for the ON and OFF cycles develop with time, as surface conditions are changed. So, Fig. 1 represents typical gas and liquid reactant profiles for a given set of parameters. During the wet cycle, when both phases flow continuously, the gas reactant concentration at the catalyst surface is lower than the bulk value due to the gas–liquid mass transfer resistance. The internal profile of component A is established quickly in comparison to B, which is in large excess and can accumulate during this period. The liquid–solid mass transfer resistance considered in this case is small, leading to a liquid reactant concentration at the catalyst surface close to the liquid bulk concentration.

During the dry period of the cycle, the surface concentration of A equals the saturation value. The accumulated liquid reactant B, which is not fed during this period, starts to

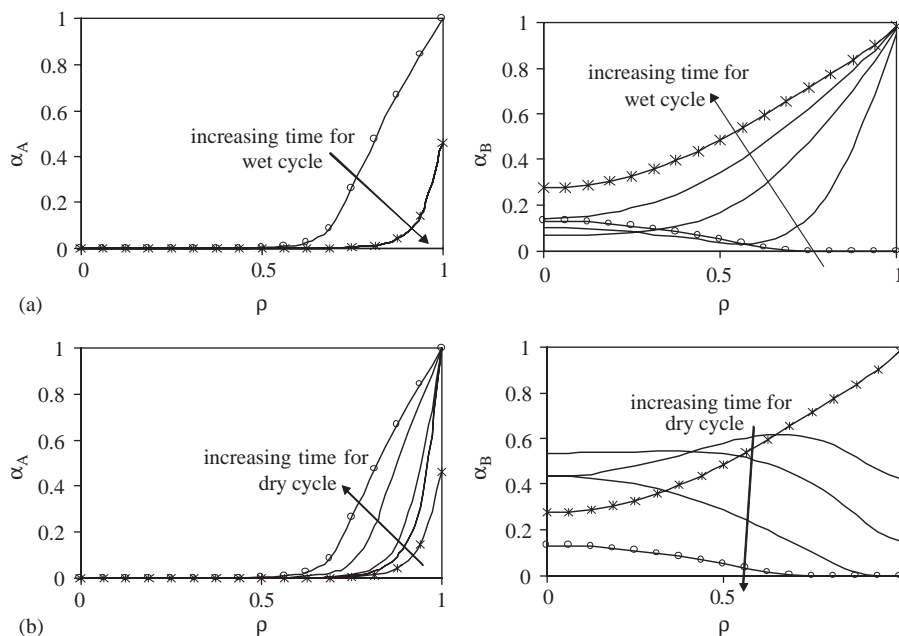


Fig. 1. Time evolution of reactant concentrations inside the catalytic pellet during the (a) wet and (b) dry cycles. Cycle period=0.64; $s = 0.3$, $\phi = 20$; $Bi_{glA,ss} = 10$; $Bi_{lsB,ss} = 100$; $\delta = 0.5$; $\zeta = 0.05$; $f_{ss} = f_w = 1$. (—○—) end of dry cycle, (—×—) end of wet cycle.

be thoroughly consumed at a higher rate in the outer layer of the catalyst. An inversion in the radial profile of B occurs. If the dry period is long, a risk of complete consumption of B at certain regions of the catalyst exists. This situation is appreciated in Fig. 1b, where concentration of B has reached values close to zero for $\rho > 0.8$ at the end of the dry period. When B is completely consumed in the outer layer, A can penetrate further inside the catalyst. For an even lower split, B could be totally consumed in the whole particle and the reaction will stop during the dry period. The gaseous reactant will then reach high concentrations even in the center of the catalyst at the end of the dry cycle.

Calculated dynamic concentration profiles are less steep for smaller values of ϕ (not shown).

From reactant profiles, instantaneous overall effectiveness factors were calculated as indicated in Eq. (3). In a similar way, mean liquid reactant concentrations were obtained. Their cyclic time evolutions during two complete cycles are shown in Fig. 2, for different cycling parameters.

For intermediate cycle periods, in the order of a hundred seconds, variations of the mean liquid reactant concentration inside the catalyst are mild (Fig. 2a and b). Its concentration is quite larger than the concentration of A , and a pseudo-first-order approach successfully represents the situation. For the conditions examined in Fig. 2a, the overall effectiveness factors tend to asymptotic values both during the wet and dry cycles. There is a transient at the beginning of each cycle that lasts less than 30% of τ_w for the wet period. During the dry period, the asymptotic value of η_{nw} is approached faster, in less than 15% of τ_{nw} . For a lower split (Fig. 2b), the wet period is not long enough to attain a plateau. Also, the mean

liquid reactant concentration inside the catalyst is lower due to a very short feeding time of B . However, starvation of B is still prevented since τ_{nw} is not long enough to consume all B .

As mentioned before, depletion of the liquid reactant is an important issue that arises specially for the case of strong internal mass transport limitations and prolonged dry periods. Therefore, Fig. 2c and d illustrates the time evolution of effectiveness factor and mean liquid reactant concentration inside the catalyst for a prolonged cycle period. Partial consumption of B can be attained (Fig. 2c) and complete depletion is observed for split 0.1 (Fig. 2d).

As liquid reactant depletion starts at the outer surface of the catalyst and proceeds toward the catalyst interior, two particular times can be observed:

- (1) The instant at which the liquid reactant concentration at the catalyst surface becomes zero; i.e., partial depletion of B .
- (2) The instant when the liquid reactant concentration becomes zero in the whole particle; i.e., complete depletion of B .

The fractions of the dry cycle required to attain both times will be called F_1 and F_2 hereafter. Their values depend on the system and cycling parameters.

The mean concentration of B largely depends on the extension of the wet period. When the dry cycle starts, the mean concentration of B decreases fast, especially until F_1 . Afterwards, the rate of decrease is lower due to a smaller effective volume for reaction. The overall effectiveness factor

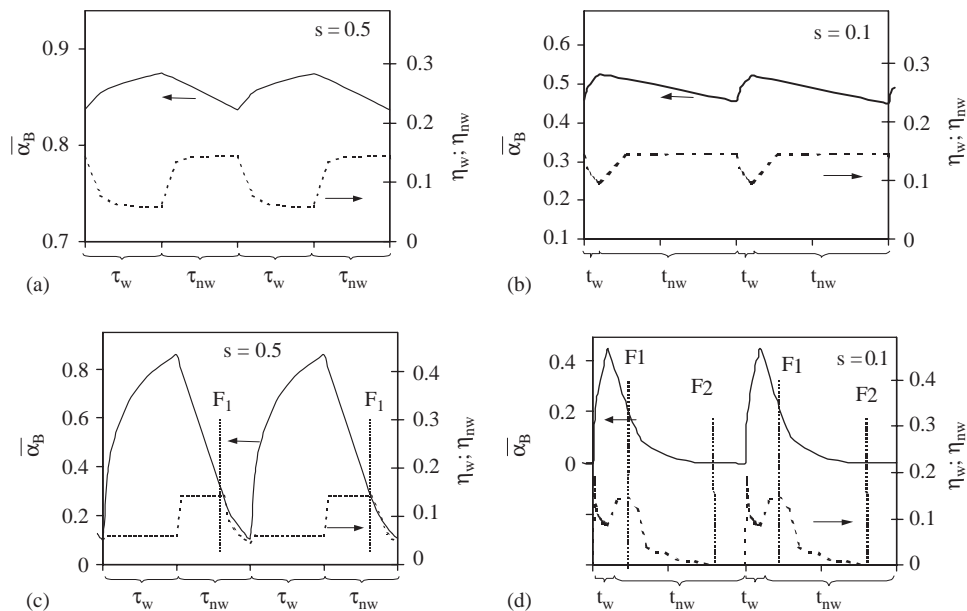


Fig. 2. Time evolution of the mean liquid reactant concentration within the catalyst and of the overall effectiveness factor during the wet and dry cycles. $\phi = 20$; $Bi_{glA,ss} = 10$; $Bi_{lsB,ss} = 100$; $\delta = 0.5$; $\zeta = 0.05$; $f_{ss} = f_w = 1$: (a) cycle period = 0.064, $s = 0.5$; (b) cycle period = 0.064, $s = 0.1$; (c) cycle period = 0.64, $s = 0.5$; and (d) cycle period = 0.64, $s = 0.1$.

increases due to reduction in external mass transfer resistance until another pseudo-steady state, which ends in F_1 , as shown in Fig. 2c and d. Then, as B is consumed, a progressive decrease of the effectiveness factor is observed, until it finally becomes zero after F_2 (Fig. 2d). For the fraction of the dry cycle after F_2 , no reaction takes place. With prolonged cycle periods, experimental enhancement factors lower than one can be obtained, as reported by Skala and Hanika (2002) and Muzen et al. (2005).

Comparison of initial η_w (Fig. 2c and d) indicate that, for the smaller split, a transient state is observed in which η_w increases up to a maximum, related to the high initial loading of A inside the particle after a period without reaction. Then, η_w decreases towards the asymptotic value, but it cannot attain it due to the very short τ_w .

From these results, it is obvious that proper selection of cycling variables is critical to achieve performance enhancement when liquid reactant depletion is an issue.

The influence of the ratio of reactants concentrations, ζ , on F_1 and F_2 should be emphasized, since it is particularly relevant for an integral reactor. The value of ζ increases along the reactor due to conversion of the liquid reactant, and larger values of ζ remarkably decrease the length of the dry cycle required to attain partial or complete depletion of B , as seen in Fig. 3. Therefore, if high conversion of the liquid reactant is required, for example in the case of catalytic wet oxidation of contaminated water, these characteristic times would be important limits to consider for a cyclic operation strategy. Fig. 3 also shows that ε decreases as the ratio of reactant concentrations increases due to the reactant depletion effect. An important conclusion can be inferred

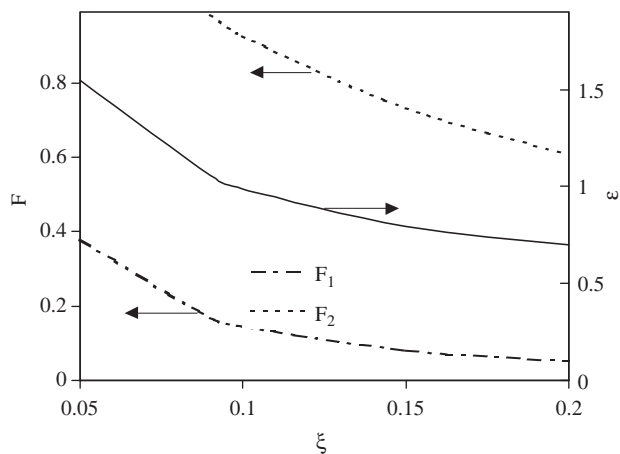


Fig. 3. Effect of the ratio of reactants on the length of the dry cycle required for partial or complete depletion of the liquid reactant inside the catalyst. Influence of ζ on the enhancement. Cycle period = 0.64; $s = 0.5$; $\phi = 20$; $Bi_{glA,ss} = 10$; $Bi_{lsB,ss} = 100$; $\delta = 0.5$; $f_{ss} = f_w = 1$.

from this result. For hydrogenation or oxidation processes, where α_A is almost constant along the reactor, an increase in ζ can be assimilated to an increase in conversion of B . Fig. 3 shows that, for a given liquid flow modulation strategy, the enhancement varies along the reactor, as the liquid reactant concentration decreases in the liquid bulk. Hence, to compare different modulation strategies used in an integral TBR, initial concentration and conversion levels should be similar. For the same reason, enhancements obtained in a differential reactor will be completely different from those achieved in an integral reactor.

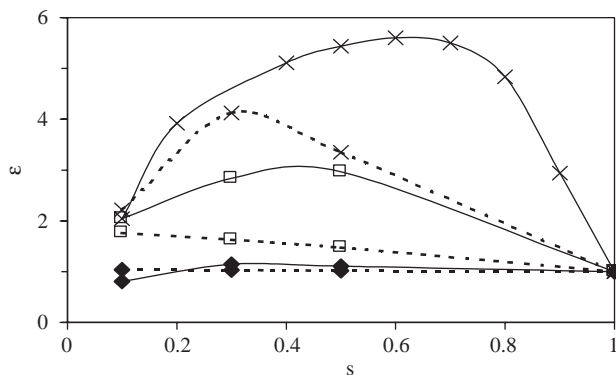


Fig. 4. Influence of different levels of external mass transfer resistance on the enhancement predicted by the model for different Thiele modulus: (—) $\phi = 20$ and (---) $\phi = 5$. (◆) $Bi_{glA,ss} = 100$; $Bi_{lsB,ss} = 100$; (□) $Bi_{glA,ss} = 5$; $Bi_{lsB,ss} = 50$; (×) $Bi_{glA,ss} = 1$; $Bi_{lsB,ss} = 1$; cycle period = 0.64; $\delta = 0.5$; $\zeta = 0.05$; $f_{ss} = f_w = 1$.

The influence of mass transport resistances on cycling performance is also addressed. Fig. 4 represent the enhancement vs. split obtained varying the magnitudes of the Biot numbers for different Thiele modulus. Cycling effectively enhances reactor performance when internal and external mass transport resistances at steady-state operation are considerable. With strong external mass transport resistances, a maximum is observed in the enhancement vs. split curves. This finding is in agreement with numerous experimental results (Lange et al., 1994; Skala and Hanika, 2002; Banchero et al., 2004). This maximum arises from the progressively longer dry cycles for smaller splits. On one side, a longer OFF period improves gaseous reactant access to the particle, increasing reaction rate. However, if the split is too small, total consumption of the liquid reactant will occur. Since reactants consumption is larger for higher Thiele modulus and given Biot numbers, the maximum is shifted to larger split values for larger values of ϕ . Likewise, the maximum will also appear at different splits if the Biot is modified for a given Thiele modulus. When the external mass transport resistance is negligible, cycling will have a poor influence on the enhancement.

Many experimental studies of periodic operation of TBRs have been carried out at laboratory or pilot plant scale units under conditions of incomplete wetting of the catalyst. Reactor enhancement against split is presented in Fig. 5 for different Thiele modulus and external wetting conditions. When the catalyst is completely wet ($f_w = f_{ss} = 1$), the enhancement achieved while cycling can be considerable, especially at high Thiele modulus. Under steady-state operation, the effectiveness factor will be relatively small. During the ON cycle, the higher Biots will result in higher effectiveness factors. In addition, when the liquid is OFF, the effectiveness factor will also increase. Therefore, provided that B is not consumed during the dry cycle, the enhancement achieved during cycling for the complete wetting situation is the highest possible.

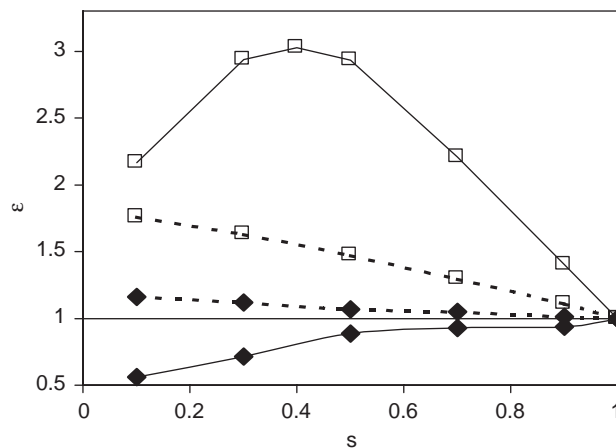


Fig. 5. Effect of wetting conditions on the enhancement predicted by the model for different Thiele modulus: (—) $\phi = 20$ and (---) $\phi = 5$. (□) $f_{ss} = 1$; (◆) $f_{ss} = 0.4$. Cycle period = 0.64; $\delta = 0.5$; $\zeta = 0.05$; $Bi_{glA,ss} = 5$; $Bi_{lsB,ss} = 50$.

Let us analyze the incomplete wetting situation, i.e., $f_{ss} = 0.4$ and f_w given by Eq. (7). At the reference steady-state, a large fraction of the particle is exposed directly to the gas environment, resulting in a relatively high effectiveness factor. During the ON cycle, wetting is larger and the effectiveness factor is lower than the steady-state values, despite the increase in Biot numbers. Once the liquid is OFF, the effectiveness factor will increase. However, the enhancement during the OFF cycle will not be as relevant as in the complete wetting situation. Thus, for low values of the wetting efficiency, liquid flow modulation could actually be deleterious, as in the case of $\phi = 20$ (Fig. 5). As expected, when the internal mass transport resistances are reduced, $\phi = 5$, the influence of cycling is tempered for both values of f_{ss} .

Finally, the effect of the cycle period on the predicted enhancement is illustrated in Fig. 6 for conditions typically found in laboratory and bench scale units (Muzen et al., 2005). For large internal limitations, three regions may be appreciated, particularly for the lower split. At intermediate to low cycle periods (below 150 s; i.e., below 0.08 in dimensionless units), the enhancement decreases as the cycle period increases. This trend is related to the relatively slow dynamics inside the particle. As shown in Fig. 2a, the transients before attaining asymptotic values for η_w and η_{nw} are not symmetrical. They are longer during the wet period of the cycle. Their effect is more important as the cycle period is reduced and leads η_{cyc} to values closer to the asymptote of the dry cycle as the cycle period tends to zero. Since the wet period is longer for higher splits, the influence of cycle period is larger for this situation. When cycle periods are of the order of 150–750 s (0.1–0.4 in dimensionless units), the influence of the internal dynamics diminishes and the enhancement factor tends to level off at a constant value. For longer cycle periods, the influence of partial and complete depletion of the liquid reactant usually becomes the

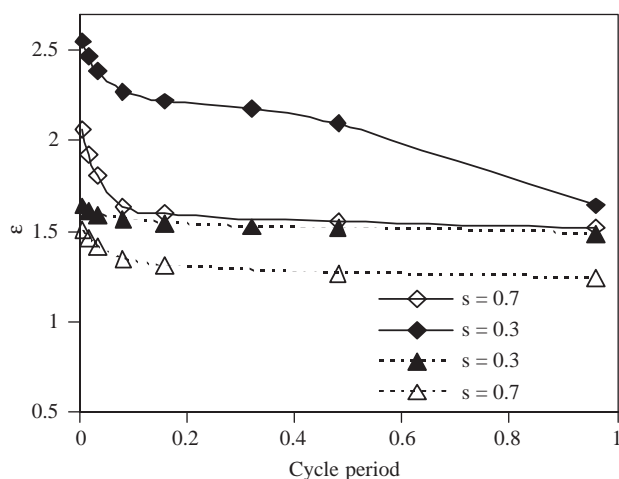


Fig. 6. Influence of the cycle period on the enhancement predicted by the model for different values of splits and incomplete wetting. $f_{ss} = 0.7$; $\delta = 0.5$; $\zeta = 0.05$; $Bi_{glA,ss} = 5$; $Bi_{lsB,ss} = 50$; Thiele modulus: (—) $\phi = 20$ and (---) $\phi = 5$.

predominant factor and the enhancement markedly decreases. For a higher split, the effect of liquid reactant depletion appears for longer cycle periods, not shown in the figure. Again, for low values of the Thiele modulus, the influence of the cycle period is less significant.

Many experimental contributions have found a maximum in the enhancement-period curve, even in isothermal or nearly isothermal explorations (Muzen et al., 2005; Tukac et al., 2003; Khadilkar et al., 1999). Khadilkar et al. (1999) showed that reactor performance enhancement due to periodic operation for hydrogenation of diluted α -methyl styrene presented the highest value at cycle periods around a 100 s. However, the present model does not predict a maximum in the enhancement vs. period curve in that region. At very short periods, the time required to drain the particle would be certainly greater than the extent of the dry cycle and the square-wave assumption used to estimate the liquid velocity and all the key parameters will not be efficient any more to represent the actual situation. Under such conditions, hydrodynamics and its interaction with external mass transport will affect markedly reactor performance.

4. Conclusions

A model to describe the behavior of an isothermal porous catalyst particle inside a TBR operated with liquid flow modulation is presented. A single first-order reaction between a gaseous reactant and a non-volatile liquid reactant is considered. Instantaneous and global overall effectiveness factor for the cycle invariant state were obtained. The enhancement achieved during cycling was evaluated taking into account the influence of internal and external mass transfer, wetting

conditions, cycle period and split on reactant profiles inside the particle.

The model successfully predicts experimental trends obtained by several authors at intermediate to long cycle periods, characteristic of “slow” cycling. In this case, the dynamics inside the catalyst particle and the accumulation of reactants largely determines reaction rate and should not be neglected in modeling the process. Model fails to predict experimental results for low cycle periods, characteristics of “fast” cycling, where the square-wave assumption considered to describe hydrodynamic and mass transport coefficient variations is not longer valid.

Present model contributes to define liquid flow modulation strategies that lead to improvements in reactor performance. Liquid flow modulation will not improve significantly reactor performance if mass transfer limitations are negligible or if the external wetting efficiency is low, for the reference steady-state. In addition, the ratio of reactant concentrations remarkably affects the possibility of enhancement. Therefore, experimental comparison among different cycling strategies should consider this parameter. Hence, great care should be taken while extrapolating results obtained in a differential reactor.

In brief, model results indicate that cycling will effectively enhance performance if the system has the following steady-state characteristics:

- important internal and external mass transport resistances;
- complete external wetting of the particle.

In addition, a suitable cycling strategy must be chosen to avoid depletion of the liquid reactant.

Notation

a_{gl}	gas–liquid interfacial area per unit volume of catalyst particle, m^{-1}
a_p	external surface area per unit volume of catalyst particle, m^{-1}
b	stoichiometric coefficient for B
C	fluid phase concentration in the catalyst, M
D	effective diffusivity, m^2/s
f	wetting efficiency
F	fraction of dry period of the cycle
k	reaction rate constant, s^{-1}
kl	overall gas liquid mass transfer coefficient, m/s
ks	liquid to particle mass transfer coefficient, m/s
r	radial variable in the catalyst, m
R	radius of the catalyst particle, m
s	split
t	time, s
u	velocity, m/s

Greek letters

α	dimensionless reactant concentration
δ	model parameter ($=D_B/D_A$)
ε_p	porosity in the catalyst particle
η	overall effectiveness factor (defined by Eqs. (3) and (4))
ξ	model parameter ($=bC_A^*/C_{B0}$)
ρ	dimensionless radial variable in the catalyst
τ	dimensionless time ($=tD_A/(R^2\varepsilon_p)$)
ϕ	Thiele modulus ($=R\sqrt{k/D_A}$)

Subscripts

0	initial value
A	gaseous reactant
B	non-volatile reactant
cyc	cycling
L	liquid
nw	non-wet cycle
ss	steady-state
w	wet cycle

Superscript

*	saturation value
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References

- Banchero, M., Manna, L., Sicardi, S., Ferri, A., 2004. Experimental investigation of fast-mode liquid modulation in a trickle-bed reactor. *Chemical Engineering Science* 59, 4149–4154.
- Boelhouwer, J.G., 2001. Nonsteady operation of trickle-bed reactors: hydrodynamics, mass and heat transfer. Ph.D. Thesis, Technische Universiteit Eindhoven, The Netherlands.
- Dudukovic, M.P., Larachi, F., Mills, P.L., 2002. Multiphase catalytic reactors: a perspective on current knowledge and future trends. *Catalysis Reviews* 44, 123–246.
- Goto, S., Smith, J.M., 1975. Trickle bed reactor performance: 1. Hold-up and mass transfer effects. *A.I.Ch.E. Journal* 21 (6), 706–713.
- Gupta, R., 1985. Pulsed flow vapour–liquid reactor. US Patent 4, 526, 757.
- Harold, M.P., Ng, K.M., 1987. Effectiveness enhancement and reactant depletion in a partially wetted catalyst. *A.I.Ch.E. Journal* 33 (9), 1448–1465.
- Haure, P., Hudgins, R.R., Silveston, P.L., 1989. Periodic operation of a trickle bed. *A.I.Ch.E. Journal* 35, 1437–1444.
- Herskowitz, M., 1981. Wetting efficiency in trickle-bed reactors: its effect on the reactor performance. *Chemical Engineering Journal* 22, 167–175.
- Khadilkar, M., Al-Dahhan, M.H., Dudukovic, M.P., 1999. Parametric study of unsteady-state flow modulation in trickle-bed reactors. *Chemical Engineering Science* 54, 2585–2595.
- Kouris, Ch., Neophytides, St., Vayenas, C.G., Tsamopoulos, J., 1998. Unsteady state operation of catalytic particles with constant and periodically changing degree of external wetting. *Chemical Engineering Science* 53, 3129–3142.
- Lange, R., Hanika, J., Stradiotto, D., Hudgins, R.R., Silveston, P.L., 1994. Investigations of periodically operated trickle-bed reactors. *Chemical Engineering Science* 49, 5615–5622.
- Lange, R., Gutsche, R., Hanika, J., 1999. Forced periodic operation of a trickle-bed reactor. *Chemical Engineering Science* 54, 2569–2573.
- Lee, C.K., Bailey, J.E., 1974. Diffusion waves and selectivity modifications in cyclic operation of porous catalyst. *Chemical Engineering Science* 29, 1157–1163.
- Muzen, A., Fragufo, M.S., Cassanello, M., Ayude, M.A., Haure, P.M., Martínez, O.M., 2005. Clean oxidation of alcohols in a trickle-bed reactor with liquid flow modulation. *Industrial and Engineering Chemistry Research*, to be published. Web release date: 05 February 2005. Submitted for publication in the special issue: In honor of Milorad P. Dudukovic.
- Skala, D., Hanika, J., 2002. Periodic operations of trickle-bed reactor. In: *Proceedings of the CHISA 2002—15th International Congress of Chemical and Process Engineering*, Praga, Zchec Republic, August 2002.
- Stegasov, A.N., Kirillov, V.A., Silveston, P.L., 1994. Modeling of catalytic SO₂ oxidation for continuous and periodic liquid flow through a trickle bed. *Chemical Engineering Science* 49, 3699–3710.
- Tukac, V., Hanika, J., Chyba, V., 2003. Periodic state of wet oxidation in trickle-bed reactor. *Catalysis Today* 79–80, 427–431.