Analysis of Rate Enhancement in a Periodically Operated Trickle-Bed Reactor

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When a trickle-bed reactor (TBR) is operated periodically, the bed is fed with liquid on and off, while the gas phase passes continuously. Rates and conversions could be higher than those corresponding to the steady-state operation. In the "dry cycles" the heat generated by the reaction can drive the vaporization of the liquid phase, and a much more rapid "gas phase" reaction may occur. There is a trade-off between the potential for hot-spot formation and the fact that overall rates are higher during cycling. A qualitative understanding of the phase transition in TBRs is obtained by a simple phenomenological model that takes into account different transport and reaction mechanisms occurring in a catalytic particle under different cycling conditions. A mathematical model is used to predict results.

Introduction

On–off cycling of the liquid flow to a trickle-bed reactor (TBR) can increase substantially the rate of reaction. In this mode of operation, the bed is flushed with liquid periodically while the gas phase is fed continuously.

In situations where the key reactant is in the gas phase, the liquid flowing through the bed adds a transport resistance that is often rate controlling when the gaseous reactant is sparingly soluble. When the liquid flow is cut off or drastically reduced, the bed partially drains. This thins out the liquid film surrounding the catalyst particles and raises the rate of reaction. The reaction proceeds between the liquid holdup and the flowing gas. There is a decrease in the transport resistances. If the reaction is exothermic, interruption of liquid flow reduces heat removal from the bed and elevates bed temperature. This increases the rate further.

The concept of periodic flow interruption for TBR was first described by Haure et al. (1989). The influence of periodic water flow on SO_2 oxidation in a trickle bed of activated carbon catalyst was investigated. An increase in the oxidation rate of about 30 to 45% was found within a range of cycle periods from 2 to 80 min. A temperature change of up to 7°C was observed in the bed during cycling. An explanation of the improved average oxidation rate under periodic operation was developed in terms of the steady-state rates with and without water flow for symmetrical and asymmetrical cycles. Periodic operation also leads to traveling thermal waves, as described by Haure et al. (1990). The on–off liquid flow causes a rising temperature front that is followed by a falling front in the direction of the liquid flow. These moving waves are predicted by a dynamic model that allows for gas–liquid mass transfer, product inhibition of reaction, and evaporation. In a recent work, Castellari and Haure (1995) described the hydrogenation of alpha methyl styrene (AMS) over commercial Pd catalyst in a laboratory TBR operated periodically. Significant improvements in the reaction rate and conversion were found, that is, an increase in the reaction rate of about 400% was reported for a cycle period of 10 min, split = 0.3. Rate enhancement is attributed to the reduction of mass-transfer resistances, the formation of controlled hot spots that results in higher catalyst temperatures, and the appearance of gas-phase reaction over a dry catalyst. The important issue is whether vaporization of the liquid phase within a multiphase fixed-bed reactor is to be avoided or exploited.

The occurrence of gas phase reaction over a dry catalyst is reported by several authors. Sedriks and Kenney (1971) studied the reduction of crotonaldehyde over a Pd catalyst in a laboratory TBR. They demonstrated that under incomplete wetting conditions, reaction on the dry catalyst may contribute significantly or even dominate the overall rate observed. The effect was attributed to the relatively higher rates of mass transfer and poorer heat transfer pertaining to the gas-phase reaction over a dry catalyst rather than to any difference in intrinsic kinetics.

Ruzicka and Hanicka (1994) used a model TBR, in which the trickle bed was simulated as a vertical string of commercial cylindrical pellets, to study the hydrogenation of cyclohexene. The experiments were carried out in order to achieve all three possible steady states in the reaction system: a gaseous-phase-reaction regime with externally fully dry catalyst pellets, a liquid-phase-reaction regime with a catalyst external surface totally covered with liquid-reaction mixture, and, eventually, a mixed-phase-reaction regime where part of the string was externally, completely wetted by the liquid-reaction mixture and the other part was externally, completely dry.

Watson and Harold (1993) used a single-pellet catalytic reactor to study dynamic effects of vaporization with exothermic reaction in a porous catalytic pellet. The experiments allowed the simultaneous measurement of pellet weight (liquid holdup) and center temperature under conditions that mimic the unsteady local events within a fixed-bed multiphase reactor. In the liquid prefilled pellet experiments, the pellet (Pd/Al_2O_3-clay) was prefilled with AMS or cyclohexene and then exposed to the flowing hydrogen. The experiments demonstrate that without the heat removal from the flowing liquid, and with the direct contact of stagnant liquid and flowing gas, drying of the catalyst results. The rate of drying depends on the volatility of the liquid. However, if sufficient time elapses that a fraction of catalyst becomes exposed to the gas, a much more rapid gas-phase catalytic reaction occurs with an accompanying temperature excursion. A gas-phase reaction commences when the liquid film evaporates and gaseous reactants adsorb on formerly wetted active sites. While rates were not measured in this study, the authors conjecture that the higher temperatures offer higher rates.

Cini and Harold (1991) developed a new type of multiphase catalyst for transport-controlled, volatile-limited reactions: the tubular-supported ceramic membrane. The hydrogenation of AMS to cumene on Pd/Al_2O_3 was selected as test reaction. Apparent activation-energy analyses reveal that for catalyst temperatures below 40°C, the rate is kinetically controlled and catalyst utilization near complete. A reduction in the activation energy above 45°C (0–4 kJ/mol) indicates the onset of transport limitations or heat effects. That is, some pore emptying may have occurred because of the reaction heat effects. Harold (1988) has shown that a catalyst that is wetted on one side and unwetted on the other, and catalyzes an exothermic reaction, may not be completely filled by the imbibing liquid. The combination of an exothermic reaction heat, a volatile liquid phase, and ineffective heat removal by the gas increases the likelihood of pore emptying and a resultant gas-phase catalytic reaction. Under such conditions, transport within the gas-filled pores would likely be the slowest process.

It is clear that when an exothermic multiphase reaction is carried out in a fixed-bed of catalyst particles, the heat generated by the reaction can drive the vaporization of the liquid phase. This situation is problematic because of the potential for hot-spot formation, sintering of the catalyst and even a reactor runaway. However, overall rates on the nonwetted part are usually higher, allowing the use of smaller reactors to achieve the desired conversions.

The objective of this article is to compare the performance of a laboratory TBR operated in the periodic mode under different cycling conditions. A simple mathematical model based on experimental observations is used to predict results. The model takes into account the changes in the transport mechanisms occurring during periodic operation: mass-transfer-controlled reaction, evaporation of the liquid phase, gas-phase reaction, and depletion of the liquid reactant that allows operation under the semirunaway condition. The reaction under consideration is the hydrogenation of AMS over a commercial catalyst (Pd/Al_2O_3) that is representative of a large number of commercially important mass-transfer-controlled reactions and where reactants are present in both phases.

Table 1. Properties of the Reactor

Diameter	2.54 cm ID
Depth of prepacking	12 cm
Type of prepacking	Glass beads
Depth of catalytic bed	1.5 cm
Mass of catalyst	3.48 g
Depth of postpacking	50 cm
Type of postpacking	Glass beads
Catalytic-bed void fraction	0.48
Inert-bed void fraction	0.48

Experimental Details

The hydrogenation of AMS to cumene has been extensively studied by others (Morita and Smith, 1978; Herzkowitz et al., 1979; Cini and Harold, 1991). The reaction rate is rather fast under mild conditions (40°C, 1 atm) and cumene is the only measurable product. The reaction is mildly exothermic ($-\Delta H = 109$ kJ/mol). Under typical laboratory conditions, the liquid-phase catalytic reaction is mass-transfer controlled with respect to sparingly soluble hydrogen.

The AMS (Aldrich Chemical Co.) had a purity of 99%. Rectified hydrogen of a purity of at least 99.9% was used. The catalyst pellets used were of a form often employed commercially, where the active metal is deposited in a thin shell outside the pellet. Properties of the catalyst were reported by Castellari and Haure (1995).

The differential TBR operating procedure and analysis of data are given in detail by Castellari and Haure (1995). Operating conditions are given in Table 1. The bed consisted of an inert prepacking (12 cm), the catalytic bed (1.5 cm), and an inert postpacking (50 cm). A sheathed thermocouple was inserted axially in the middle of the catalytic bed. Local bed temperatures were recorded continuously by a data-acquisition device. A three-way solenoid valve (Jefferson model 365) activated by timers was used to generate liquid variations in the cycling experiments. More details are presented in Tables 2 and 3.

Table 2. Catalyst Specifications

Palladium content (global)	0.5 wt. %
Active-layer thickness	250 μm
Activation method	Reduction on hydrogen atmosphere
Particle size	2–3.2 mm
Mean diameter	2.72 mm
Particle porosity	0.60
BET surface area	70 m^2/g
Pellet bulk density	1.322 g/cm^3

Table 3. Operating Conditions

Temperature	41°C
Pressure	1 atm
Gas flow rate	900 cm^3/min
Mean liquid flow rate	2.27 cm^3/s

Cycling Experiments

Since only a few seconds are needed to drain the bed and the shortest cycle period studied lasted 10 min, the on–off operation can be considered as square-wave cycling. Experiments were arranged randomly, alternating steady-state and cycling runs having short and long periods and different splits. Reproducibility was good and no deactivation of the catalyst was observed. Liquid samples were taken a minute before ending each wet cycle and analyzed in a GC (Hewlett-Packard 5890 A). Changes in the cumene concentration with time were used to evaluate the reaction rate according to Castellari and Haure (1995).

Periodic experiments were performed at a gas flow rate of 900 cm^3/min. Rates obtained under cycling were normalized with respect to the corresponding steady-state rate at the mean liquid flow rate. If periodic operation did not affect TBR performance, the normalized rate would be unity. These normalized rates are plotted against cycle periods for splits 0.1, 0.3, 0.5 and 0.7, as shown in Figure 1. Cycling can increase the reaction rate up to a factor of 4. The normalized rates present a maximum with the cycle period: for split 0.3, the optimum period is 10 min, while for split 0.5, the optimum period is 16 min, approximately. The split effect is not significant (Castellari and Haure (1995)). Temperature profiles for different splits and periods are shown in Figure 2. Figure 2c represents results for split 0.5, period 40 min. In the wet cycle the bed is isothermal at 41°C. When the liquid is halted, the temperature reaches a maximum at 75°C after approximately 8 min of exposure to the gas phase only.

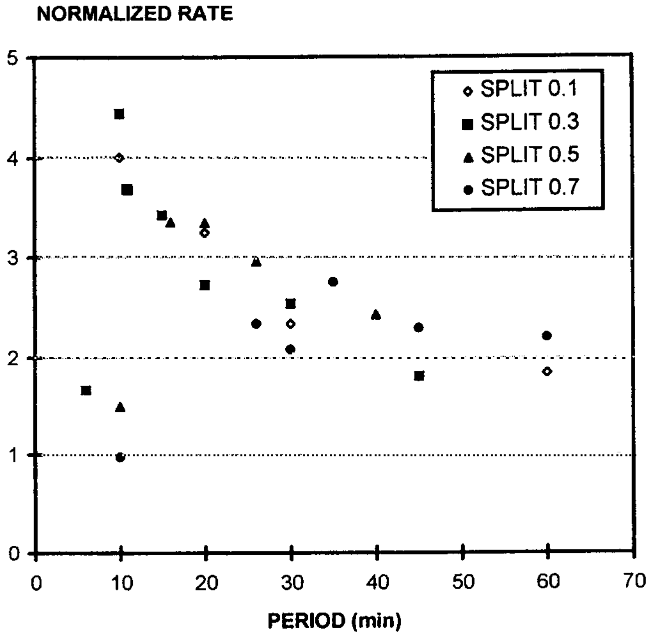

Figure 1. Normalized rates against cycle period for different splits.

Q_g = 900 cm^3/min; L_{ave} = 2.27 cm^3/s; for split 0.1 L_{ave} = 0.1 cm^3/s.

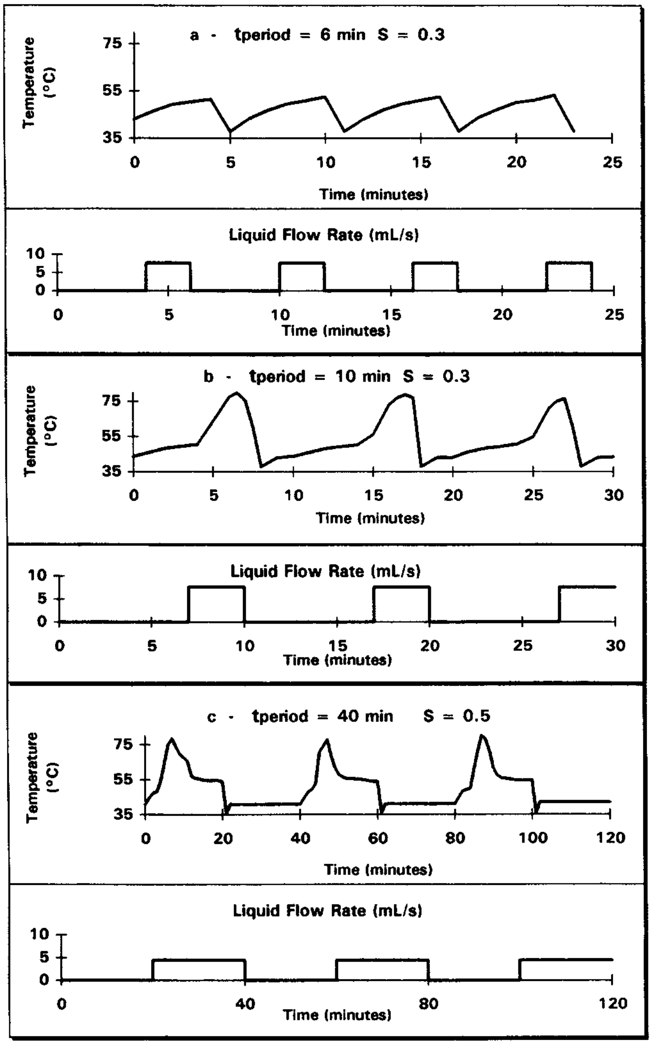

Figure 2. Temperature profiles for different cycling conditions.

A typical temperature profile for period 40 min and split 0.5, gas flow rate 900 cm^3/min is shown in Figure 3. Three different zones can be distinguished. During the flushing cycle (zone **A**), the bed is kept isothermal at 41°C. Wetting is complete and the reaction proceeds between the hydrogen dissolved and the AMS. The heat generated is easily dissipated by the flowing liquid (4.5 mL/s).

When the liquid flow is cut off, the reaction takes place between the liquid holdup and the flowing hydrogen (zone **B**). Hydrogenation reactions are characterized by a relatively large heat of reaction, and interruption of the liquid flow reduces heat removal from the reactor and elevates bed temperatures (Watson and Harold, 1993) (zone **B1**). Under these conditions evaporation of the liquid phase followed by gas phase reaction may occur. This represents a change in the reaction mechanism from a mass-transfer-limited reaction to a gas-phase reaction, with different activation energies (Cini and Harold, 1991). Once the gas-phase catalytic reaction

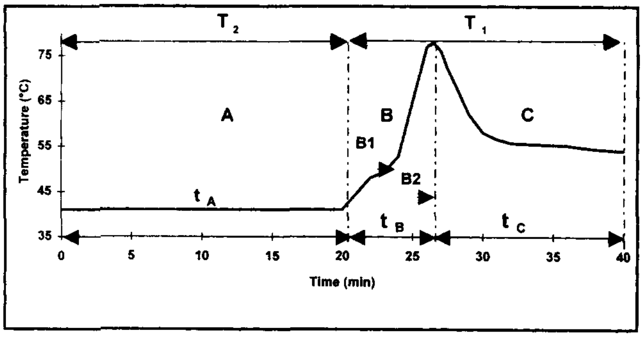

Figure 3. Typical temperature cycle for split 0.5, period 40 min.

$t_{\text{period}} = T_1 + T_2$; $T_D = t_B$; $T_1 = T_D \Rightarrow T_{\text{opt}} - T_2 = T_D$; $(T_{\text{opt}} - T_2)/T_{\text{opt}} = T_D/T_{\text{opt}}$; $1 - S = T_D/T_{\text{opt}}$; and $T_{\text{opt}} = T_D/(1 - S)$

commences, the drying process accelerates (Watson and Harold, 1993). Reaction rate and temperature increase (zone **B2**). Partial drying out of the bed was observed after minutes of exposure to the gas phase. When the holdup is depleted, the temperature reaches a maximum. It is obvious from Figure 1 that for a constant split, there is an optimum period in which the reaction rate is at its highest value. In the case of reactants present in both phases, the optimum period (T_{opt}) is the one in which the time of exposure to the gas reactant only (T_1) equals the depletion time of the less volatile reactant (T_D) in Figure 3, after Castellari and Haure (1995). For these particular experimental conditions, the depletion time was approximately 8 min, as shown in Figures 2b and 2c. Therefore, we assume that the optimum period depends on experimental conditions such as liquid holdup and composition, gas velocity, evaporation, reaction rates, and so forth. This should be further tested.

After the maximum is reached, temperature decreases sharply (zone C). One possible explanation is that, in the absence of any liquid flow, depletion of the AMS reduces the overall reaction rate and allows the zone to cool down by convection only. Another possibility is that the reaction proceeds between the flowing hydrogen and AMS supplied by the gas phase, since hydrogen is contacted with AMS that remains in the prepacking section. This reaction rate depends on AMS concentration in the gas phase, since hydrogen is in great excess, and is lower than the previous rates. The heat evolved is dissipated by the flowing hydrogen. Once the liquid flow is restored, the reaction proceeds as mentioned previously (zone **A**).

Model Formulation

A one-dimensional pseudohomogeneous model is developed to describe the behavior of the catalytic bed during periodic operation. Consider a catalytic pellet, as shown in Figure 4. The pellet pore volume is assumed to be liquid filled due to strong capillary forces. The reaction occurs in a thin surface shell. The pellet is surrounded by an atmosphere containing the gaseous reactant.

During the wet cycle (zone **A** in Figures 3 and 4), the pellet is completely wet, the dissolved gas species is the limiting reactant, and the overall rate is external mass-transfer controlled, as in conventional TBR operation.

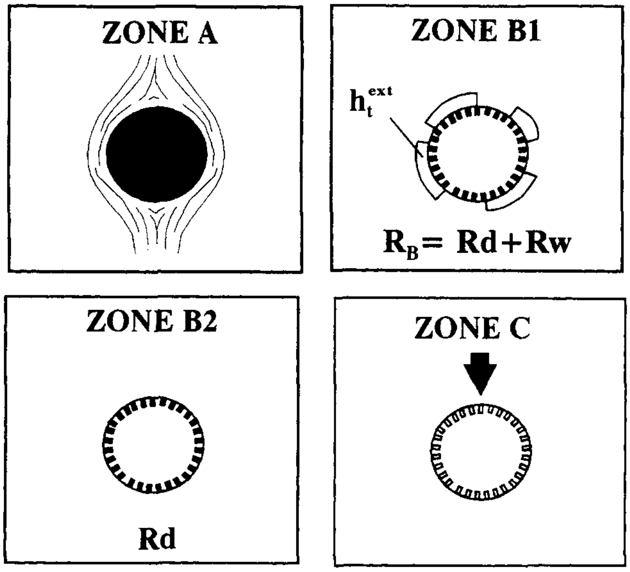

Figure 4. Phenomenological model.

When the liquid flow is cut off, the bed partially drains and the catalytic reaction proceeds between the flowing hydrogen and the external liquid holdup. The holdup diminishes with time, due to evaporation of the liquid phase. Dry zones appear because of poor heat removal and a gas-phase catalytic reaction may occur. The overall reaction rate in this zone has then two contributions: one from the wetted areas, the other from the nonwetted surfaces. The contributions have different activation energies, as pointed out by Cini and Harold (1991). In the wetted part, mass transfer of the dissolved hydrogen controls the rate. The gas-reactant mass-transfer rate is higher on the nonwetted part of the pellet, because the liquid that wets part of the surface constitutes an additional resistance. In the dry areas, a much more rapid gas-phase catalytic reaction may occur, with an accompanying temperature excursion that accelerates the external drying process (zone **B1**). When the external liquid holdup is depleted, the reaction takes place between the evaporated internal holdup and the flowing hydrogen, both adsorbed on the catalytic surface (zone **B2**). Here, we assume that the reaction proceeds via gas-phase catalysis. The temperature increases up to a maximum that depends on the liquid holdup and composition, and the gas flow rate. Once the internal holdup is depleted (zone **C**), the temperature decreases. This could be due to two different processes: cooldown of the bed by the flowing hydrogen without chemical reaction, or cooldown and gas-phase reaction, where the AMS is provided by the flowing hydrogen.

Model Equations

Although the speculative explanations in the previous paragraph could be tested by further experiments, a more useful approach is to model the on–off TBR operation and test the possible explanations using the model. This approach has the added merit that if the model represents the TBR behavior, it could be applied to other reactor systems to assess the advantages of periodic operation.

Zone A

Global reaction rate for a first-order kinetics is given by Ramachandran and Chaudari (1983):

$$R_A = C_A \left(\frac{1}{K_L a_B} + \frac{1}{k_s a_p} + \frac{1}{\omega k \eta} \right)^{-1} \frac{V_L}{m_c}.$$

Zone B

Global reaction rate is obtained considering the contribution of both wet and dry zones as follows:

$$R_B = R_w + R_d$$

$$R_B = W_R(t) C_A \left(\frac{1}{K_L a_B} + \frac{1}{k_s a_p} + \frac{1}{\omega k \eta} \right)^{-1} \frac{V_L}{m_c} + [1 - W_R(t)] k_0 e^{-Eag/RT} C_B(T).$$

The relative wetting, W_R, is a measure of the wetting efficiency variation with time and is defined as:

$$W_R(t) = \left(\frac{h_t^{\text{ext}}}{h_0^{\text{ext}}} \right)$$

and

$$h_t^{\text{ext}} = h_0^{\text{ext}} - \int_0^t N_B \, dt$$

$$N_B = W_R(t) \frac{V_R}{m_c} K_{Lg} a_p [C_B(T) - C_B^0],$$

where N_B is the mass-transfer rate of liquid from the wetted surface, and $C_B(T)$ is evaluated with the ideal gas law.

Total liquid balance is given by

$$\frac{V_R \rho_l}{M m_c} \frac{dh_{\text{tot}}}{dt} = -(N_B + R_d).$$

Energy balance:

$$m_c c_p \frac{dT}{dt} = m_c R_B(-\lambda_r) - \frac{V_R \rho_l}{M} \frac{dh_{\text{tot}}}{dt} (\lambda_v) - V_R h_f a_p (T - T_G).$$

Zone C

Reaction rate is controlled by AMS transfer from the gas phase:

$$R_C = \frac{K_g a_p C_B}{m_c / V_R}.$$

Table 4. Model Conditions

C_A	2.85 10^{-6} mol/cm^3
C_p	Perry and Chilton (1975)
Eag	2,000 J/mol
$h_f a_p$	Froment and Bischoff (1979)
h_o^{ext}	0.0045 mol liq
h_{tot}	0.0145 mol liq
$\omega k \eta$	0.0046 s^{-1}
$k_s a_p$	Goto and Smith (1975)
$K_L a_B$	Goto and Smith (1975)
k_o	50 cm^3/g cat s
$K_{Lg} a_p$	Froment and Bischoff (1979)
M	118.18 g/mol
ρ_l	0.893 g/cm^3
T_G	41°C
V_L	600 mL

Energy balance

$$m_c c_p \frac{dT}{dt} = m_c R_c(-\lambda_r) - V_R h_f a_p (T - T_G),$$

and the predicted overall normalized rate is defined as

$$R_{Nm} = \frac{\Sigma R_i t_i}{R_{CSS} t_{\text{period}}} \qquad i = A, B, C,$$

where R_{CSS} was determined using the model at steady state with the average liquid flow rate.

Parameters of the model shown in Table 4 are either based on values measured by Gabarain (1994) or were estimated from correlations of TBR data. Fitting of the data shown in Figure 1 was not done. As an approximation, the value of $K_g a_p$ was considered equal to $K_{Lg} a_p$ (Beaudry et al., 1987).

Results

Normalized overall rates obtained at different periods are compared with experimental values in Figure 5 at split 0.1. When $C_B = 0$, that is, $R_C = 0$, the model predicts the maximum rate at the optimum period, but shows differences with experimental data when the period is higher than the optimum, that is, when the time of exposure to the gas phase is increased beyond the depletion time. To explain this, additional experiments were performed in a column filled with glass spheres only, which simulated the prepacking section. The bed was preflooded with AMS and exposed to flowing H_2 at 900 cm^3/min and elution curves were recorded. Concentration of AMS in the gas effluent varies with time, being 30% of the saturation a conservative value of the concentration in the dry cycle. When C_B has a finite value 30% of the saturation quantity), R_C is not zero and the results agree better. Gas phase could be enriched in AMS by mass transfer in the prepacking section as mentioned previously.

Model predictions for split 0.5, are shown in Figure 6. Fitting, as mentioned for split 0.1, is better if the reaction in zone C is taken into account. Similar results were found for splits 0.3 and 0.7.

Temperature profiles at different cycling conditions are also predicted by the model. Results for $C_B = 0$ are presented in

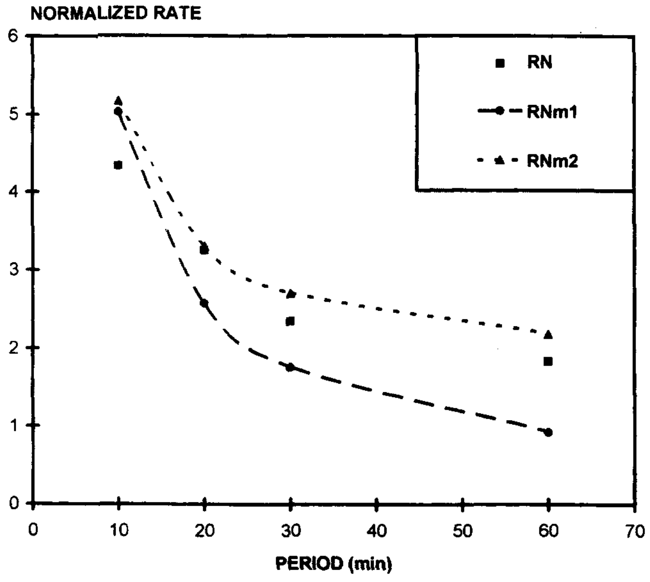

Figure 5. Comparison between experimental and model results.

Split 0.1. R_{Nm1} with $C_B = 0$ and R_{Nm2} with $C_B = 0.3C_B^{sat}$.

Figure 7A for split 0.5 and period of 40 min. The maximum is predicted satisfactorily. When the concentration of AMS in the entering gas is 30% of the saturation value, the predicted profiles are in better agreement with the experimental data, as shown in Figure 7B. In both cases, theoretical profiles are sharper than the experimental ones. Differences are likely due to the uncertainty in estimating model parameters.

Variations of the liquid holdup and relative wetting with time are predicted by the model according to Figure 8. Both decrease as the pellet is exposed to the gas phase and the temperature increases.

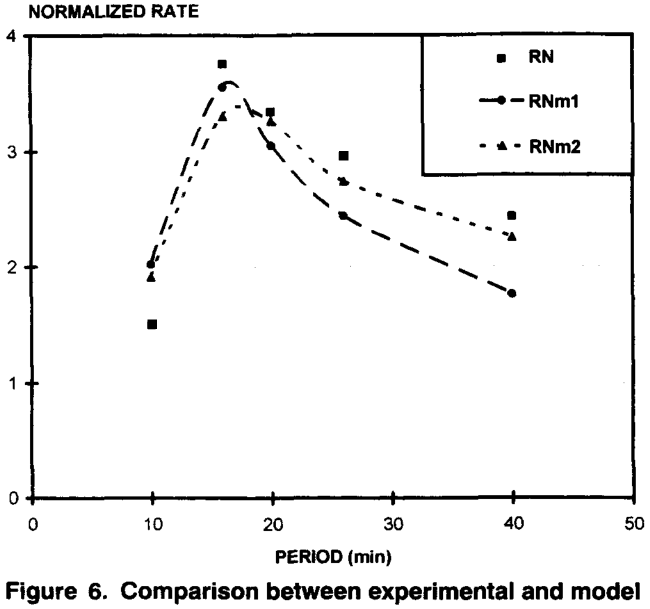

Figure 6. Comparison between experimental and model results.

Split 0.5. R_{Nm1} with $C_B = 0$ and R_{Nm2} with $C_B = 0.3C_B^{sat}$.

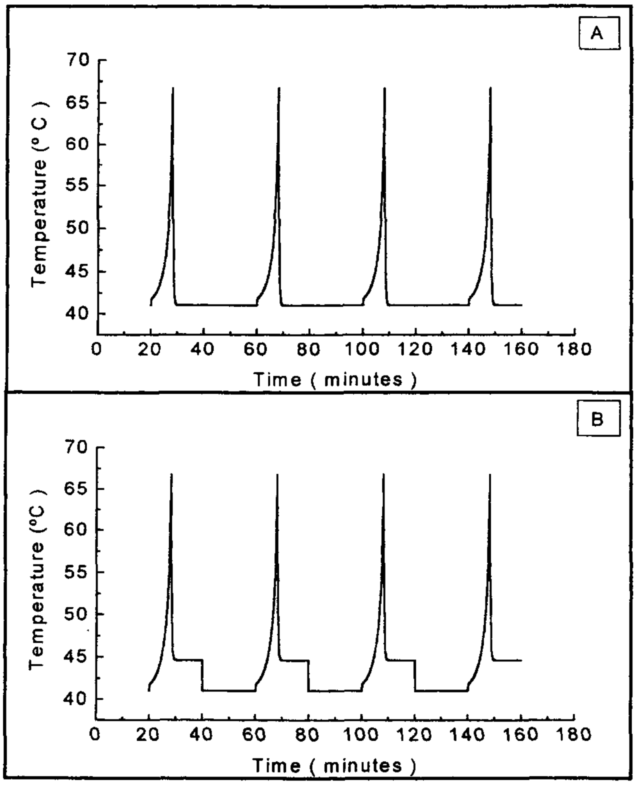

Figure 7. Temperature profiles obtained with the model.

(A) Split = 0.5, period 40 min, and (B) split = 0.5, period 40 min and $C_B = 0.3C_B^{sat}$.

Conclusions

The behavior of a TBR under cycling operation is extremely complex. It is a strong function of the switching between wet and dry operation. In the non-wet cycles, the occurrence of vaporization followed by a gas-phase reaction results in higher rates and temperatures.

A qualitative understanding of the phase transition in TBRs is obtained by a simple phenomenological model that takes into account the different transport and reaction mechanisms

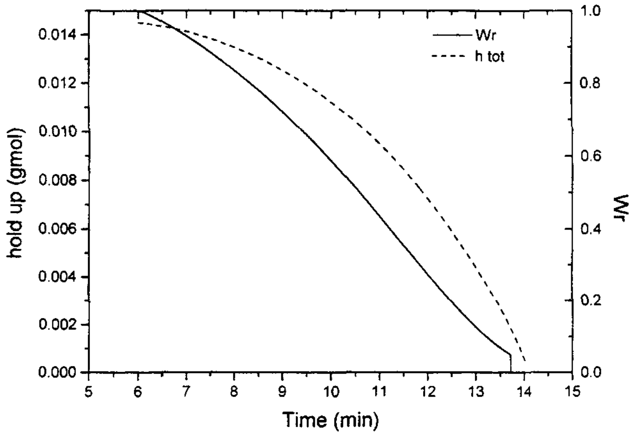

Figure 8. Variations of the liquid holdup and relative wetting with time.

occurring in a catalytic particle under different wetting conditions.

The mathematical model gives a satisfactory representation of the experimental data, predicting the rates and temperature profiles at different cycling conditions. It allows evaluation of the period and split influence. Experimental and theoretical results show that the time of exposure to the gas phase is an important variable. Differences between experimental and theoretical values are likely because of the uncertainty in estimating model parameters.

It is expected that the phenomenological model could be used as a tool to understand and predict the behavior of similar reaction systems in which reactants are present in both phases and the reaction is exothermic. Scaleup of this new technology should also be addressed with special emphasis in predicting the hot spot.

Efforts are currently under way to develop a criterion able to determine the conditions at which cycling would improve the performance of a TBR. The effect of several variables, such as gas and liquid composition and flow rate, liquid holdup, temperature, reaction, and evaporation rates, will be studied.

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Notation

C_A = equilibrium concentration of hydrogen in liquid bulk
C_B = concentration of alpha methyl styrene in the gas phase
C_B^{sat} = equilibrium concentration of alpha methyl styrene in the gas phase
Cp = catalyst specific heat
Eag = apparent activation energy
$h_f a_p$ = heat-transfer coefficient
h_t^{ext} = external holdup evaluated at different times
h_o^{ext} = initial external holdup
h_{tot} = total liquid holdup
i = different zones **A**, **B**, **C**
k = kinetic constant
$K_g a_p$ = overall mass-transfer coefficient from gas to solid
$K_L a_B$ = overall mass-transfer coefficient from gas to liquid
$K_{Lg} a_p$ = mass-transfer coefficient from liquid to gas
$k_s a_p$ = mass-transfer coefficient from liquid to solid
ko = preexponential factor for gas-phase reaction
L_{ave} = average liquid flow rate
m_c = mass of catalyst
M = molecular weight
R = ideal gas constant
R_{CSS} = corresponding steady-state rate
R_d = reaction rate in gas-phase catalysis
R_N = normalized rate
R_w = reaction rate in liquid-phase catalysis
S = split (T_2/t_{period})
t = time
t_i = time correspondent to zone i
t_{period} = period
T = temperature
T_2 = time of duration of the wet cycle
T_G = gas temperature
V_L = total volume of liquid
V_R = volume of catalytic bed
λ_r = heat of reaction
λ_v = heat of vaporization
η = enhancement factor
ρ_l = liquid density
$\omega = m_c/V_L$

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