

## Prediction of Improved Performance of Catalytic Hydrogenation Reactor by Periodic Modulation of the Feed Rate

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Original scientific paper

Received: April 14, 2008

Accepted: February 16, 2009

A mathematical model of catalytic hydrogenation in a trickle bed reactor under forced modulation of the liquid feed rate has been formulated and the predicted results have been compared with the experiments on a pilot plant catalytic hydrogenation of styrene. Computed results have shown that the principal role in improving the reaction conversion under forced modulation of the liquid feed rate is the wetted surface of the catalyst. Improved reaction conversion has been predicted and observed experimentally at low splits of the periodic liquid feed bringing the regime temporarily close to the transition regime from the trickling to the natural pulsing regime. Computed transient profiles indicate that forced modulation of liquid velocity has much greater impact on the transient concentration profiles than on the transient temperature profiles.

*Key words:*

Trickle bed reactor, induced pulsing, hydrodynamics, mathematical model, hydrogenation, styrene

### Introduction

Trickle bed reactors have been employed in the industry mainly for hydrogenation and oxidation reactions; their primary importance being in petrochemistry and crude oil fractions refining or hydrocracking. The interest of research has turned to the transient operation of trickle bed reactors induced by forced periodic modulation of the inlet liquid feed about two decades ago.<sup>1</sup> This interest, however, has been continuing in recent years<sup>2–19</sup> and entails also mathematical modeling.<sup>17–20</sup>

Transient operation may be advantageous when the reactor exhibits an increased throughput in comparison with the steady state operation<sup>7</sup> and may be beneficial also for the reactor safety.<sup>6,9,14</sup> The purpose of this paper is to formulate a mathematical model of hydrogenation in a catalytic trickle bed reactor operated under forced periodic modulation of liquid feed in order to investigate the conditions that may lead to increased conversion of the reaction. The predictions will be compared with the experimental data obtained on a pilot plant trickle bed reactor for hydrogenation of styrene at elevated pressure.

### Transient model of trickle bed reactor

A mathematical model has been formulated of the catalytic trickle bed reactor under forced peri-

odic variation of the liquid feed rate. The reaction considered is the hydrogenation of a hydrocarbon A to B as:



Assuming constant mass density of liquid and the availability of liquid holdup as a function of gas and liquid superficial velocities for the given system<sup>16,21–23</sup> the mass balance on the mass of liquid in the reactor may be written as:

$$\frac{\partial h}{\partial t} + \frac{\partial L}{\partial z} = \frac{nM_{H_2}R_B}{\rho_L} \quad (1)$$

This type of liquid flow model equation has been used in the past by Lange.<sup>19</sup> In analogy, the mass balance on the number of moles of gas in the reactor with variable gas density is:

$$\frac{\partial}{\partial t}((\varepsilon - h)\rho_{MG}) + \frac{\partial}{\partial z}(\rho_{MG}G) = -nR_B \quad (2)$$

From eq. (2) we note that gas velocity in the bed will vary even in the absence of the reaction and even if the inlet gas velocity remains constant; gas velocity may then vary simply due to the liquid flow induced variations of holdup. Considering axial dispersion in the liquid the transient balance on the mass of the hydrogenation product B has the form:

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$$h \frac{\partial y_B}{\partial t} + L \frac{\partial y_B}{\partial z} = (M_B - nM_{H_2} y_B) \frac{R_B}{\rho_L} + D_L \frac{\partial^2 y_B}{\partial z^2} \quad (3)$$

From the adopted reaction scheme it follows that the sum of the moles of the reactant A plus the number of moles of the product B remains constant. For this reason, it is not necessary to formulate and solve the balance on A. Its concentration can be easily computed from the trivial solution  $y_A + y_B = y_{A0}$  where  $y_{A0}$  designates the inlet concentration of the reactant.

Similarly, the gas balance on the number of moles of hydrogen has the following form:

$$\begin{aligned} (\varepsilon - h) \frac{\partial x_{H_2}}{\partial t} + G \frac{\partial x_{H_2}}{\partial z} = & -(1 - x_{H_2}) \frac{nR_B}{\rho_{MG}} + \\ & + D_G \frac{\partial^2 x_{H_2}}{\partial z^2} + D_G \frac{\partial x_{H_2}}{\partial z} \frac{\partial \ln(\rho_{MG})}{\partial z} \end{aligned} \quad (4)$$

In this formulation we tacitly assumed that neither the reactant nor product evaporate into the gas phase.

Finally, the transient heat balance on the system, assuming that local temperatures of gas, liquid and catalyst are the same and providing for the heat losses through the reactor walls, takes the form:

$$\begin{aligned} \frac{\partial T}{\partial t} [h\rho_L c_{PL} + (\varepsilon - h)\rho_{MG} c_{PG}^M + (1 - \varepsilon)\rho_{cat} c_{Pcat}] + \\ + \frac{\partial T}{\partial z} [\rho_L L c_{PL} + \rho_{MG} G c_{PG}^M] = R_B \Delta H + \\ + k_{axial} \frac{\partial^2 T}{\partial z^2} - k_{heatloss} \frac{4}{d_{reactor}} (T - T_{ambient}) \end{aligned} \quad (5)$$

The above heat balance further assumes that the heat capacities of the catalyst, liquid and gas are constant.

The initial and boundary conditions are formulated on the assumption that the inlet concentrations are constant. The inlet temperature of the gas and liquid are the same and also constant. The constant inlet concentrations and temperature were applied in the well-know form due to Danckwerts. At the inlet end ( $z = 0$ ) for all times we thus have for the temperature:

$$\begin{aligned} (\rho_L L c_{PL} + \rho_{MG} c_{PG}^M G) T^{inlet} = \\ = (\rho_L L c_{PL} + \rho_{MG} c_{PG}^M G) T_{z=0+} - k_{axial} \frac{\partial T}{\partial z} \Big|_{z=0} \end{aligned} \quad (6)$$

and for the fractions of the product B and the reactant hydrogen:

$$L y_B^{inlet} = L y_B \Big|_{z=0+} - D_L \frac{\partial y_B}{\partial z} \Big|_{z=0} \quad (7a,b)$$

$$G x_{H_2}^{inlet} = G x_{H_2} \Big|_{z=0+} - D_G \frac{\partial x_{H_2}}{\partial z} \Big|_{z=0}$$

Across the outlet surface ( $z = Z$ ) we stipulate no heat dispersion flux:

$$\frac{\partial T}{\partial z} \Big|_{z=Z} = 0 \quad (8)$$

and analogously for the outlet mass flux of the product B and hydrogen.

Additional conditions stipulate that initially the reactor is at a uniform temperature and free of the reaction product B. Further we will concentrate on the reactor transients induced by time variations of the inlet liquid velocity while the inlet gas velocity is kept constant.

The formulated problem has been solved numerically considering periodic rectangular pulses of inlet superficial liquid velocity characterized by the time-period, the split and the base, and the mean superficial inlet liquid velocity. The split is defined as the fraction of the time-period during which the inlet velocity is increased above the value given by the base velocity. The peak velocity is computed from the split and the base velocity so as to maintain the same mean liquid velocity for different splits.

Numerical solution using the finite difference method was developed by forming iterative loops around the five transient balance equations that were solved repeatedly at each time instant until a predetermined accuracy was attained. Next the calculation advanced by an increment in time.

The fact that in the above outlined calculations we are using directly the experimental function for liquid holdup means that we assume that the kinetics of the liquid holdup formation is infinitely fast. Our unpublished measurements showed that the rates constants for liquid holdup formation are of the order of 0.1 s. Within the scope of the paper we thus believe that using the holdup function directly is justifiable.

### Pilot plant experiments

The experiments were carried out on a pilot plant trickle bed reactor installed in the Research Centre of CHEMOPETROL Co., Litvinov, Czech Republic. A 0.1 m diameter, 2 m long stainless steel reactor was designed to sustain temperatures up to 200 °C and pressure 2.5 MPa. The unit was equipped with two pumps (maximum feed rate 120

and 600 dm<sup>3</sup> h<sup>-1</sup>), two 1.1 m<sup>3</sup> volume storage tanks, a 40 dm<sup>3</sup> phase-separator and a data logging and control system (ControlWeb 2000 SP9; Moravske pristroje, Zlin, Czech Republic). The function of the two pumps was controlled by a computer program forcing periodic rectangular-pulse modulation of the inlet liquid superficial velocity. The reactor was equipped with thermocouples located 0.1 m apart along the height of the catalyst bed and four pressure ports (BD sensors, Co.). The pressure probes (PX26, Omega, USA) measured the pressure difference across 0.3 – 0.5 m, 0.7 – 0.9 m and 1.0 – 1.2 m depth of the bed and the pressure drop across the entire packed bed.

Hydrogen was supplied via a mass flow meter (Brooks Co.) from the pressurized distribution network at constant feed rate 5 m<sup>3</sup> h<sup>-1</sup> in all experiments. This hydrogen rate provides its sufficient stoichiometric excess with respect to the concentration of the hydrogenated substrate.

The data were collected in the form of a time series of temperatures along the catalyst bed, gas pressure drop and liquid and superficial gas velocity. The temperature data series were logged at the frequency of 1 Hz and the pressures at 10 Hz on a computer hard disk.

The hydrogenation of styrene in the toluene solution (*w* = 10 %) was studied at 0.2 MPa pressure and 30 °C inlet temperature, using 1 m deep layer of palladium supported catalyst (Noblyst R 1505, 0.1 % Pd/Al<sub>2</sub>O<sub>3</sub>, 3 mm mean diameter particles, egg-shell type).

Each experiment started with the steady operation at constant liquid feed rate to reach the steady state to be followed subsequently by the regime of forced periodic modulation of the liquid feed rate and finished by returning to the steady state inlet regime. The mean liquid feed velocity was held always at 0.0044 m s<sup>-1</sup>. A comparison of the conversion under the steady regimes at the beginning and the final part of the continuous experiment provided the information about the extent of catalyst deactivation during the whole measurement.

The effluent reaction mixture was sampled periodically by collecting a sample during the whole period of the forced feed modulation for analysis. Samples were analyzed off-line by GC chromatography using a Shimadzu GC 17A and a capillary CP-SIL 8 CB chromatographic column.

The kinetics of the hydrogenation of styrene was evaluated in a 400 cm<sup>3</sup> laboratory autoclave (Parr, Co.) equipped with a stationary basket to hold the catalyst pellets. The temperature was kept within 1 °C by a two-loop controller. Prior to the hydrogenation tests the catalyst was pre-activated for three hours according to the earlier published

method and the resulting activation energy of 41100 kJ kmol<sup>-1</sup> was found in good agreement with the same resource.<sup>24</sup>

The experimental reaction rate expression involving liquid to catalyst volume ratio and the influence of catalyst internal diffusion resistance was found to have the following form:

$$R_B = A \exp \left[ -\frac{41100}{RT} \right] c_{\text{styrene}}^{0.65} P_{\text{H}_2}^{1.1} \quad (9)$$

The necessary values of liquid holdup were obtained experimentally in a glass laboratory column 0.05 m in diameter packed to 1 m height by the same catalyst pellets. The column was equipped with sensitive pressure transducers (Omega Co., USA) located 0.2 m apart measuring absolute pressure difference along the packing. Liquid was introduced by a gear pump, via flow meters and liquid distributor into the column; gas flow was controlled by a mass flow meter (Bronkhorst, Denmark). Liquid and gas supply was connected to the column by flexible plastic tubes.

The whole column, including liquid distributor was suspended on a strain gauge sensor (Single Point – D5075, Eilersen Electric, Denmark). The total mass of the actually weighted setup was about 18 kg that is just below the 20 kg maximum load of the strain gauge. Total liquid holdup in the column was in the order of 0.5 kg that favorably compares with the 1 g sensitivity of the load cell. The values of the dynamic liquid holdup were evaluated by subtraction from the mass of the column under operation, the mass of the column after liquid flow interruption and draining.

The holdups were measured using toluene as liquid and air as gas under the atmospheric pressure and a room temperature of 25 °C. The measurements covered the range between 0.002 and 0.018 m s<sup>-1</sup> of superficial liquid velocity and between 0.014 and 1.2 m s<sup>-1</sup> superficial gas velocity.

## Results

The primary goal of our effort was to compare the performance of the reactor operated at constant feed rate with that experienced during forced periodic liquid feed rate modulation and otherwise the same mean liquid superficial velocity and operating conditions.

The initially obtained results of the model solution were very encouraging since the model predicted clearly higher output conversions under modulation of inlet liquid superficial velocities. Unfortunately, the higher conversions exhibited the output concentrations time-averaged over the

time-period of the modulation. However, the evaluations of cup-mixing averages, defined as:

$$y_B^{\text{cup-mixing}} = \frac{\int_t^{t+\text{period}} y_B^{\text{outlet}} L^{\text{outlet}} dt}{\int_t^{t+\text{period}} L^{\text{outlet}} dt} \quad (10)$$

showed actually worse reaction conversion. The evaluation of the cup-mixing means is very important because under liquid feed rate modulation the effluent stream varies not only its concentration but also its flow rate.

For the improved conversion and the throughput of the reactor under forced liquid feed modulation, of course, the time-averaged values are irrelevant and only cup-mixing values count. Thus, the above pseudo-homogeneous reaction model, eq. 9, did not help us explain the observed improvement of the conversion under modulated feed.

Next the model was solved with the reaction term showing explicitly the role of external diffusion<sup>25,26</sup> but the effort was again in vain.

Finally, we implemented a function that expresses the wetted fraction of the catalyst surface reflecting the fact that on transition from the trickling to the natural pulsing flow regime<sup>27</sup> the catalyst wetting is known to strongly increase.<sup>28,29</sup>

The newly computed cup-mixing mean conversion of the reactor under forced modulation of the liquid feed is plotted in Fig. 1 as a function of the split. The computed points now do predict the improvement of the reactor mean conversion at low values of the split.

Fig. 2 compares the predicted (line) and experimental (points) conversion of the reactor expressed as a fraction of the conversion under the steady-state operation. The reactor was started operating at steady inlet liquid velocity in the morning

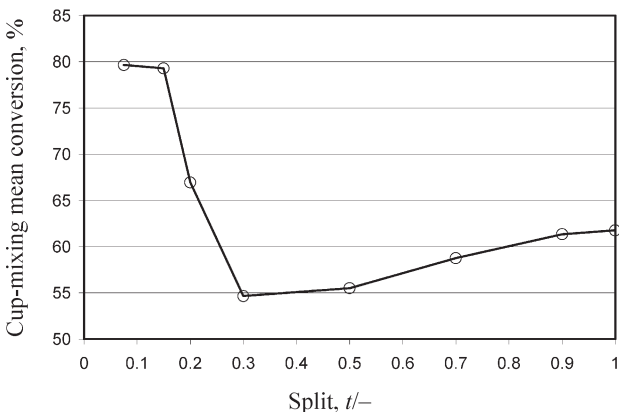


Fig. 1 – Predicted values of cup-mixing mean conversion as a function of the split under periodic modulation of liquid feed. Period = 60 s; gas velocity = 0.098 m s<sup>-1</sup>; base liquid velocity = 0.0021 m s<sup>-1</sup>; mean liquid velocity = 0.0044 m s<sup>-1</sup>.

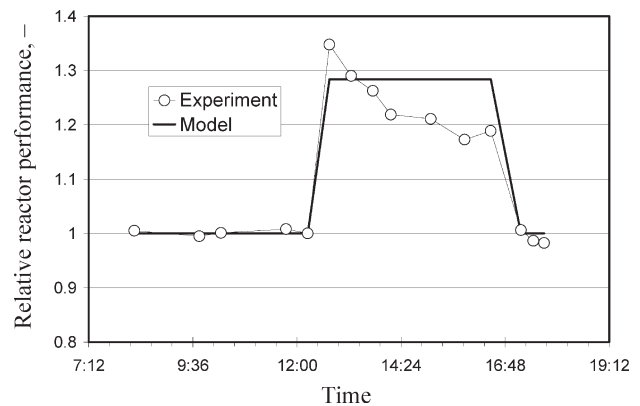


Fig. 2 – Predicted (circles) and experimental (line) performance of the reactor relative to steady-state operation operated under periodic modulation of liquid feed between 12:45 and 16:28 hours. Split = 0.15; Period = 60 s; gas velocity = 0.098 m s<sup>-1</sup>; base liquid velocity = 0.0021 m s<sup>-1</sup>; mean liquid velocity = 0.0044 m s<sup>-1</sup>.

but between 12:45 and 16:28 h of time the operation switched to the forced periodic modulation of the liquid feed rate with the following characteristics: Split = 0.15; period = 60 s; superficial gas velocity = 0.098 m s<sup>-1</sup>; base liquid velocity = 0.0021 m s<sup>-1</sup>; mean superficial liquid velocity = 0.0044 m s<sup>-1</sup>.

The figure shows that the relative performance of the reactor is predicted reasonably well but the experimental values show that the performance deteriorates with time. This deterioration is clearly ascribed to the observed fairly rapid deactivation of the used catalyst primarily due to the polymerization of styrene.

Additional experiments were aimed at investigating which split of the inlet velocity modulation provides for the best reactor performance. The experiments have shown that at 60 seconds time-period the best performance was attained in some cases with the split 0.15, in others with the split equal 0.075.

In judging these results one has to realize that for the split 0.075 the peak value of the liquid velocity is more than 14 times that of the base liquid superficial velocity and the peak has to be maintained for only 4.5 s. Practical realization of these conditions may not be therefore perfectly accurate.

The experimentally observed most effective splits are also in fair agreement with the model results in Fig. 1 showing the best performance for the splits 0.15 and 0.075 and actually very little difference between them. It may thus be concluded that the model predicts the best reactor performance for the least values of the split that can be practically realized.

Finally, Fig. 3 compares the predicted time course of the temperature in different depths within

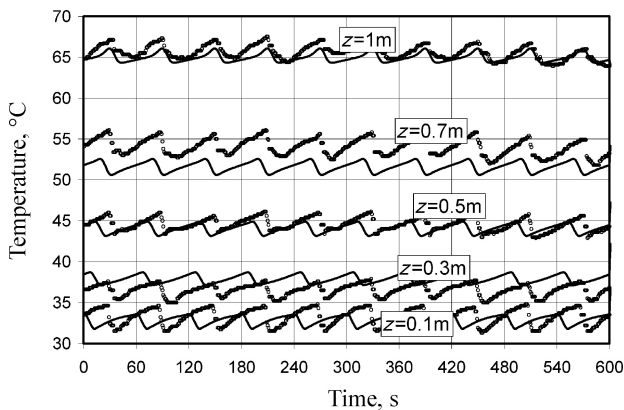


Fig. 3 – Predicted (lines) and experimental (circles) transient course of the temperature in the reactor under periodic modulation of liquid feed. Split = 0.15; period = 60 s; gas velocity =  $0.098 \text{ m s}^{-1}$ ; base liquid velocity =  $0.0021 \text{ m s}^{-1}$ ; mean liquid velocity =  $0.0044 \text{ m s}^{-1}$ .

the catalyst bed with the experimental results obtained for the 60 s time-period of the forced superficial liquid velocity modulation and the split 0.15. The plotted data correspond to the later stages of the experiment when the effect of the initial conditions in the bed has died down. The zero time in the figure thus does not coincide with the beginning of the experiment.

Fig. 3 shows a fair agreement of the predictions of the shapes of the temperature waves and the mean temperatures at the various depths measured from the top with the experiment. A systematic deviation is observed in that the experimental data seem to exhibit the peak temperature on a given level of the depth more or less at the same time instant while the model predicts the peaks at different depths mutually shifted in time. The explanation of this observation is difficult. A possible cause is that the model assumes the same temperature of all the three phases involved while the thermocouples react probably fastest to the temperature of the gas for which the time shift indeed may be small.

In order to present the power of the model to predict the reactor transients, Figs. 4a–c plot each the computed profile of conversion of the reactant A scaled by its inlet concentration, the liquid superficial velocity scaled by the peak inlet velocity, and the temperature in three successive time instants under the forced periodic regime after the effect of initial conditions had died down.

In Fig. 4a the peak of liquid velocity is just entering the reactor; in Fig. 4b the peak is approximately in the middle of the reactor while in Fig. 4c it is just leaving the reactor.

On the profiles of the conversion of the reactant one can see that the initially (Fig. 4a) high conversion at the downstream end of the reactor de-

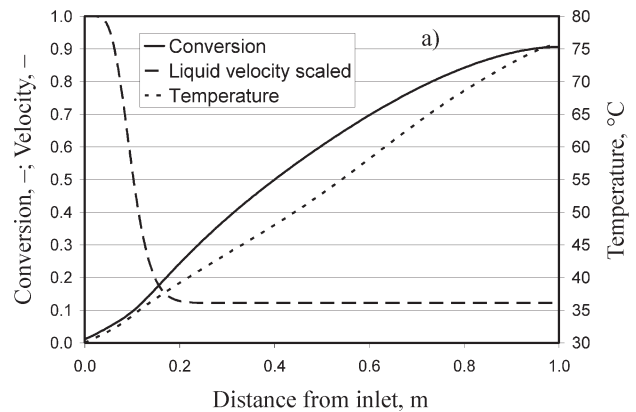


Fig. 4a – Computed profiles of conversion of the reactant, liquid velocity scaled by the peak inlet value and temperature within the reactor at time  $t = t_0$  for period 60 s and split 0.15

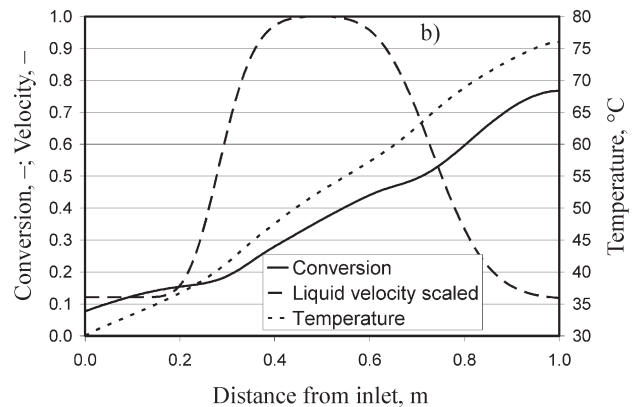


Fig. 4b – Computed profiles of conversion of the reactant, liquid velocity scaled by the peak inlet value and temperature within the reactor at time  $t = t_0 + 12.8 \text{ s}$  for period 60 s and split 0.15

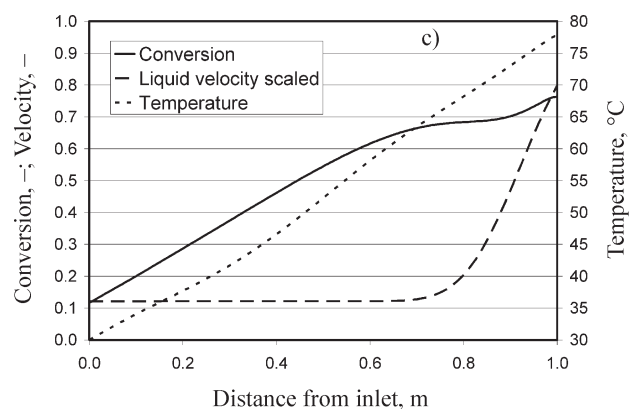


Fig. 4c – Computed profiles of conversion of the reactant, liquid velocity scaled by the peak inlet value and temperature within the reactor at time  $t = t_0 + 25.6 \text{ s}$  for period 60 s and split 0.15

creases as the peak of the wave moves through the reactor (Figs. 4b and 4c). At the same time one can see, however, that past the wave the conversion quickly recovers (Fig. 4c).

The profiles of the temperature in the reactor demonstrate that the effect of the passage of the liquid wave on the temperature was much less dramatic than that on the reaction conversion. This is so clearly due to the fact that the heat, unlike the reacting species, accumulated to a large extent also in the solid phase that does not move.

## Conclusion

Lange *et al.*<sup>19</sup> reviewed eight principal factors influencing the performance of the trickle bed reactor. The model solutions presented in this paper have shown that of these factors the transient hydrodynamics alone, such as the development of liquid holdup, cannot account for the improved reactor conversion under the forced modulation of liquid feed.

Model modifications accounting for the variations of the wetted surface confirmed the currently adopted explanation that the major phenomenon responsible for the improved conversion under modulated liquid feed is the improved wetting of the catalyst surface. The improvement of the reactor conversion appears at low end of the split of the forced modulation of liquid feed when the reactor is brought temporarily to the transition zone to the natural pulsing flow.

The investigated technique of improving reactor performance by periodic modulation of the feed rate appears very promising. The extra investment and operating cost compared to the steady state operation are only minor. The periodic process further contributes to the stability and safety of the operation because repeated increases of liquid rate replenish the liquid on the catalyst surface where dangerous spots might develop due to overheating that is particularly important for exothermic hydrogenation reactions.

## ACKNOWLEDGEMENT

The authors gratefully acknowledge financial support of the project by the Ministry of Industry and Trade of the Czech Republic under the grant number FT-TA039.

## List of symbols

$A$  – frequency factor,  $\text{kmol}^{0.35} \text{m}^{-1.05} \text{s}^{-1} \text{MPa}^{-1.1}$   
 $c_{\text{styrene}}$  – styrene molar concentration,  $\text{kmol m}^{-3}$   
 $c_{\text{Pcat}}, c_{\text{PL}}$  – specific heat capacity of catalyst and liquid,  $\text{kJ kg}^{-1} \text{K}^{-1}$   
 $c_{\text{PG}}^M$  – specific heat capacity of gas,  $\text{kJ kmol}^{-1} \text{K}^{-1}$   
 $D_G, D_L$  – axial dispersion in gas and liquid,  $\text{m}^2 \text{s}^{-1}$

$d_{\text{reactor}}$  – diameter of reactor, m  
 $G$  – superficial gas velocity,  $\text{m s}^{-1}$   
 $h$  – liquid holdup, –  
 $k_{\text{axial}}$  – effective axial thermal conductivity of bed,  $\text{kJ m}^{-1} \text{s}^{-1} \text{K}^{-1}$   
 $k_{\text{heatloss}}$  – bed to surroundings heat loss coefficient,  $\text{kJ m}^{-2} \text{s}^{-1} \text{K}^{-1}$   
 $L$  – superficial velocity of liquid,  $\text{m s}^{-1}$   
 $M_B, M_{\text{H}_2}$  – molecular mass of species given by subscript,  $\text{kg kmol}^{-1}$   
 $n$  – stoichiometric number, –  
 $P_{\text{H}_2}$  – hydrogen partial pressure, MPa  
 $R$  – gas constant,  $8.314 \text{ kJ kmol}^{-1} \text{K}^{-1}$   
 $R_B$  – rate of production of B,  $\text{kmol m}^{-3} \text{s}^{-1}$   
 $T, T_{\text{ambient}}$  – temperature in reactor and ambient temperature, K  
 $t$  – time coordinate, s  
 $x_{\text{H}_2}$  – mole fraction of hydrogen in gas, –  
 $y_B$  – mass fraction of product B in liquid, –  
 $z$  – axial coordinate, m  
 $Z$  – depth of catalyst bed, m  
 $\Delta H$  – heat of reaction,  $\text{kJ kmol}^{-1}$   
 $\rho_{\text{cat}}, \rho_L$  – mass density of catalyst and liquid,  $\text{kg m}^{-3}$   
 $\rho_{\text{MG}}$  – molar density of gas,  $\text{kmol m}^{-3}$   
 $\varepsilon$  – void fraction of bed, –

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