

Elevation of performance of gas–liquid reactors on solid catalyst

E.F. Stefoglo^{a,*}, V.I. Drobyshevich^b, V.A. Semikolenov^c, I.V. Kuchin^a, O.P. Zhukova^a

^a Institute of Coal and Coal Chemistry, Rukavishnikov, 21, Kemerovo 650610, Russia

^b Institute of Computational Mathematics and Math. Geoph., Novosibirsk 630090, Russia

^c Boreskov Institute of Catalysis, Pr. Lavrentieva, 5, Novosibirsk 630090, Russia

Abstract

Different kinds of initial conditions for the gas–liquid process on a solid catalyst are discussed in the paper. The advantages of process with preliminary saturation of liquid with gas are considered. For the liquid batch reactor it is theoretically shown that preliminary saturation of the initial solution with gas prior to reaction profits more in comparison with “usual” mode. The experiments on hydrogenation of ethyl ether of *p*-nitrobenzoic acid to anesthesyne on suspended 5% Pd/C catalyst in a batch reactor were carried out for verification of the main results from the proposed model ($P_{H_2} = 40$ bar, $T = 20$ – 120 °C). As an example of a reactor, where the preliminary saturation effect can be used, the trickle-bed reactor operating without pumping was considered. Mathematical simulation of such type reactor is presented. © 2002 Elsevier Science B.V. All rights reserved.

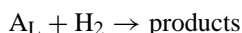
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1. Introduction

The gas–liquid process on a solid catalyst can be carried out using different modes of the reactor operation. The practical importance is to study the influence of the initial conditions on the performance of the reaction system: the preliminary saturation of a reaction solution have to be hydrogenated before the reactor (continuous) or before the reaction (in batch) in comparison with “usual” mode of operation. In the last case the solution (suspension) is saturated with the gas in the reactor and this process is simultaneously accompanied by the catalytic reaction. And the conversion changes are slower than when the solution is presaturated by gas. It should be noted that the concentration of gas reagent on the catalyst surface might influence the reaction direction. Thus, for example, the hydrogenation on hydrogen-“poor” instead of hydrogen-“rich” catalysts can involve hydrogenolysis and isomerization but not the reduction [1]. It is of interest to compare the conversion degrees X_L achieved at these different modes of operation.

2. Theory

In general the reaction equation of the liquid component hydrogenation can be written as



Let assume that the hydrogenation reaction rate equation is $r = kC_{\text{cat}}C_{\text{HL}}^1$. The process passes in a batch reactor at a constant temperature and pressure. Thus, the material balances for the gas dissolved in the suspension and the liquid reactant concentrations are

$$\frac{dC_{\text{HL}}}{d\tau} = \beta(C_{\text{H}}^* - C_{\text{HL}}) - kC_{\text{cat}}C_{\text{HL}} \quad (1)$$

$$\frac{dC_L}{d\tau} = -kC_{\text{cat}}C_{\text{HL}} \quad (2)$$

The process can take place at two different initial conditions:

- (1) $\tau = 0, C_{\text{HL}} = 0, C_L = C_{L_0}$
- (2) $\tau = 0, C_{\text{HL}} = C_{\text{H}}^*, C_L = C_{L_0}$

In the second case, gas before a reaction start performs a preliminary saturation of the solution or suspension of catalyst in the solvent up to the equilibrium value.

In order to simplify the equations we introduce the following dimensionless magnitudes:

$$\bar{C}_{\text{HL}} = \frac{C_{\text{HL}}}{C_{\text{H}}^*}, \quad \bar{C}_L = \frac{C_L}{C_{L_0}}, \quad Q = \frac{C_{\text{H}}^*}{C_{L_0}},$$

$$M = \frac{kC_{\text{cat}}}{\beta}, \quad t = \beta\tau$$

where t is dimensionless time.

Eqs. (1) and (2) take the form:

$$\frac{d\bar{C}_{\text{HL}}}{dt} = 1 - \bar{C}_{\text{HL}} - M\bar{C}_{\text{HL}} \quad (3)$$

* Corresponding author. Tel.: +7-3842-365561; fax: +7-3842-281838.
E-mail address: chem@kemnet.ru (E.F. Stefoglo).

Nomenclature

C_{cat}	catalyst concentration in liquid (kg/m ³)
C_{HL}	gas dissolved concentration in liquid (kmol/m ³)
C_{H}^*	equilibrium gas dissolved concentration (kmol/m ³)
\bar{C}_{HL}	dimensionless gas dissolved concentration, $\bar{C}_{\text{HL}} = C_{\text{HL}}/C_{\text{H}}^*$
C_{L}	liquid component concentration (kmol/m ³)
\bar{C}_{L}	dimensionless liquid component concentration, $\bar{C}_{\text{L}} = C_{\text{L}}/C_{\text{L}0}$
$C_{\text{L}0}$	initial liquid component concentration (kmol/m ³)
D_{L}	diffusion coefficient (m ² /s)
H_i	high of i unit (m)
k	reaction rate constant (s ⁻¹)
M	dimensionless parameter, $M = kC_{\text{cat}}/\beta$
n	number of units
Q	dimensionless parameter, $Q = C_{\text{H}}^*/C_{\text{L}0}$
r	coordinate perpendicular to the liquid flow (m)
S_{ud}	specific gas–liquid and liquid–solid interface (m ² /m ³)
t	dimensionless time, $t = \beta\tau$
v	velocity of liquid (m/s)
X_{L}	conversion of liquid reactant
Y	weight fraction of gas dissolved in liquid
Y^*	equilibrium weight fraction of gas dissolved in liquid
z	vertical coordinate along the liquid downflow (m)

Greek letters

β	overall mass-transfer coefficient between gas and liquid, $\beta = k_{\text{L}} a$ (s ⁻¹)
δ	thickness of liquid film (m)
τ	time (s)

Subscripts/superscripts

1	reaction without preliminary saturation; unit or component number
2	reaction with preliminary saturation; unit or component number
in	inlet
max	maximal value

$$\frac{dX_{\text{L}}}{dt} = -\frac{d\bar{C}_{\text{L}}}{dt} = QM\bar{C}_{\text{HL}} \quad (4)$$

Initial conditions:

$$t = 0, \quad \bar{C}_{\text{HL}} = 0, \quad \bar{C}_{\text{L}} = 1 \quad (5)$$

$$t = 0, \quad \bar{C}_{\text{HL}} = 1, \quad \bar{C}_{\text{L}} = 1 \quad (6)$$

Solving (3) with two initial conditions and putting the derived expression for $\bar{C}_{\text{HL}} = f(t, M)$ to (4), then integrating

it enables us to find the conversion degrees $X_{\text{L}1}$ and $X_{\text{L}2}$ as functions of M , Q and t for two different process modes

$$\bar{C}_{\text{HL}1} = \frac{1}{1+M}(1 - e^{-(1+M)t}) \quad (7)$$

$$\bar{C}_{\text{HL}2} = \frac{1}{1+M}(1 + M e^{-(1+M)t}) \quad (8)$$

$$X_{\text{L}1} = \left(\frac{MQ}{1+M}\right)t - \frac{MQ}{(1+M)^2}(1 - e^{-(1+M)t}) \quad (9)$$

$$X_{\text{L}2} = \left(\frac{MQ}{1+M}\right)t + \frac{M^2Q}{(1+M)^2}(1 - e^{-(1+M)t}) \quad (10)$$

Then at a certain time t a gain in the conversion degree caused by preliminary saturation of liquid with gas is defined as

$$\Delta X_{\text{L}} = X_{\text{L}2} - X_{\text{L}1} = \left(\frac{MQ}{1+M}\right)(1 - e^{-(1+M)t}) \quad (11)$$

It can be seen from Eq. (11) that we have the limiting maximal value of the ΔX_{L} gain, but it does not exceed the Q value equal to $C_{\text{H}}^*/C_{\text{L}0}$. This phenomenon is presented in Figs. 1 and 2. The mathematical analysis of the proposed model shows that this gain (ΔX_{L}) is greater when the reaction rate is higher M ($k \rightarrow \infty$). Thus, if the reaction rate is high or there is a significant mass transfer limitation $\beta \rightarrow 0$ and thus ($M \rightarrow \infty$), the greater the pressure (Q) the higher the ΔX_{L} value.

Let us consider the region, where $X_{\text{L}1}$ and $X_{\text{L}2}$ are practically linear functions of time to be a steady-state region. Then $X_{\text{L}1}$ reaches the same value as $X_{\text{L}2}$ with the constant time lag Δt at any M and Q values (Fig. 2):

$$\Delta t = t_1 - t_2 = 1 \quad (12)$$

The time lag in a dimension form:

$$\Delta \tau = \tau_1 - \tau_2 = \frac{1}{\beta} \quad (\text{s}) \quad (13)$$

Thus, in a steady-state region (including the moment when the reaction is over) the time gain for the process presaturated

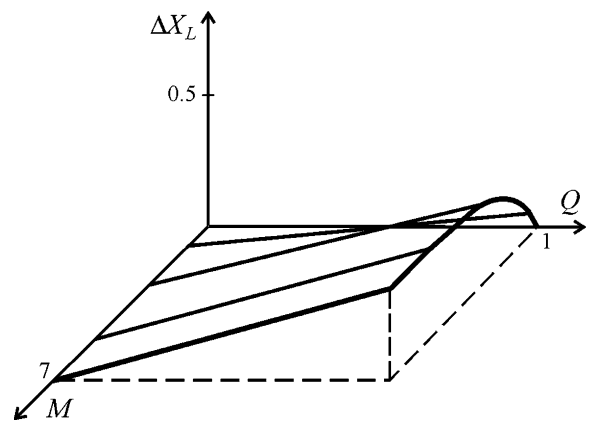


Fig. 1. The general view of $\Delta X_{\text{L}} = f(Q, M)$ at $t \rightarrow \infty$ for the reaction of $r = -kC_{\text{cat}}C_{\text{HL}}$.

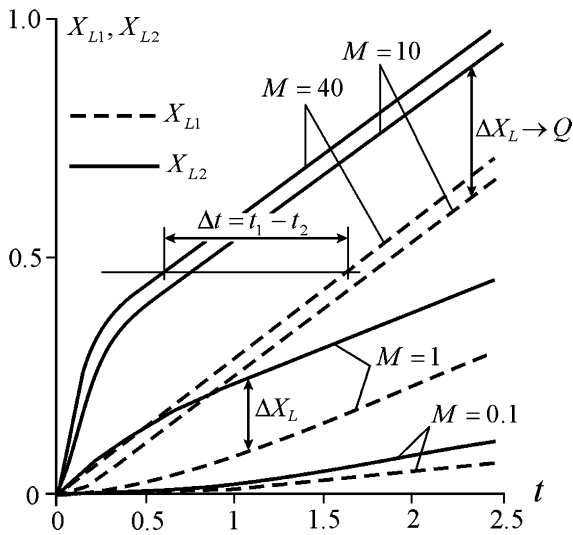


Fig. 2. Unsteady-state conversion behavior at a high pressure ($Q = 0.25$) for the reaction $r = kC_{cat}C_{HL}$ at different initial conditions for a liquid batch reactor.

with gas is a value, depending on neither pressure (parameter Q) nor on a reaction rate (parameter M). It is defined only by the intensity of a mass transfer rate between gas and liquid phases.

Dividing Eq. (3) on (4) we find

$$\frac{d\bar{C}_{HL}}{dX_L} = \frac{1 - \bar{C}_{HL} - M\bar{C}_{HL}}{MQ\bar{C}_{HL}} \quad (14)$$

Solving obtained equation with the same two initial conditions we find that \bar{C}_{HL} reaches its constant value (in coordinates $\bar{C}_{HL} - X_L$) at different values of X_{L1}^{st} and X_{L2}^{st} (Fig. 3). The difference $\Delta X_L^{st} = X_{L2}^{st} - X_{L1}^{st}$ is the complex

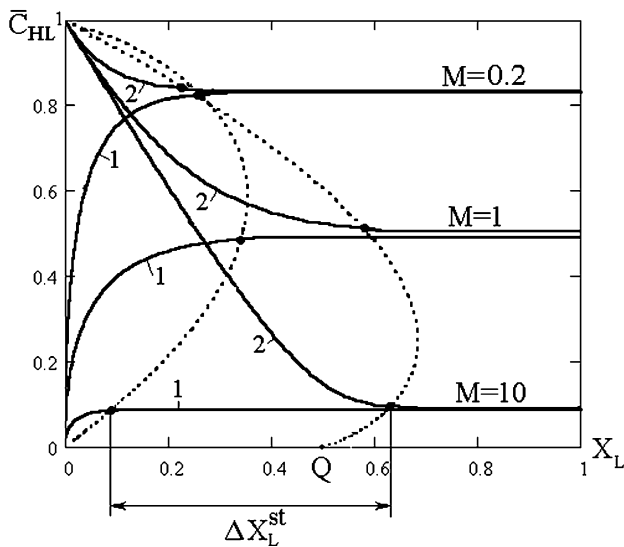


Fig. 3. Steady-state region's achievement for a gas concentration in the suspension during the reaction.

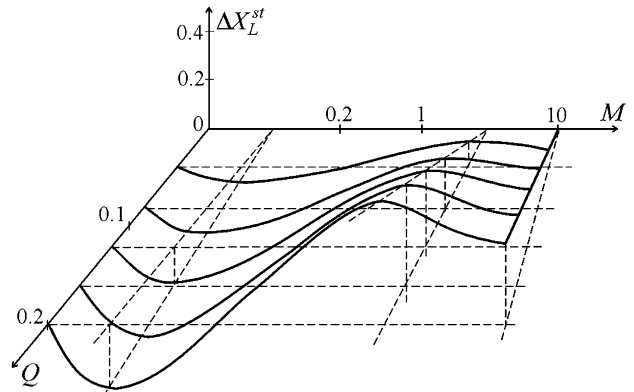


Fig. 4. The conversion gain ΔX_L^{st} as the function of M and Q parameters.

function of M and Q (Fig. 4):

$$\Delta X_L^{st} = \frac{MQ}{(1+M)^2} \ln M + \frac{MQ}{1+M} \quad (15)$$

3. Experimental results

The influence of preliminary saturation effect on process rate was verified experimentally for reaction having more complex kinetics. In Figs. 5 and 6 the experimental and calculated data on ethyl ether of *para*-nitrobenzoic acid (EEpNBA) hydrogenation are presented. The process carried out on Pd/C catalyst in a batch stirred reactor with different initial conditions. It can be seen from Figs. 5 and 6 that a good agreement between experimental and theoretical results takes place. The reaction of EEpNBA hydrogenation has Langmuir–Hinshelwood mechanism with respect

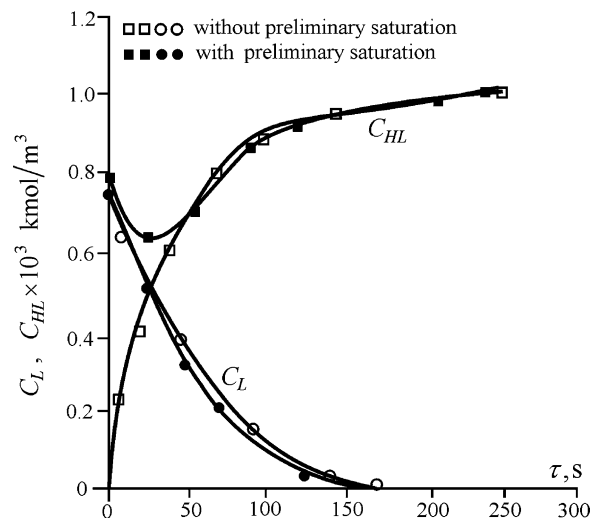


Fig. 5. Hydrogenation of EEpNBA (ethyl ether of *p*-nitrobenzoic acid) with different initial conditions ($T = 100^\circ\text{C}$, $P = 2.5 \text{ bar}$, $C_{cat} = 0.383 \text{ kg}_{Pd}/\text{m}^3$, $C_{L0} = 0.76 \text{ kmol}/\text{m}^3$).

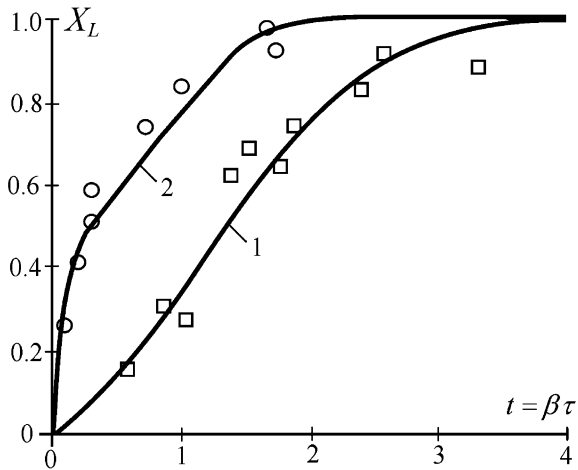


Fig. 6. High pressure ($P_{H_2} = 40$ bar) hydrogenation of EEpNBA, $T = 100^\circ\text{C}$, $C_{\text{cat}} = 0.383 \text{ kg}_{\text{pd}}/\text{m}^3$, $C_{L_0} = 0.53 \text{ kmol}/\text{m}^3$, $\beta = 4 \times 10^{-2} \text{ s}^{-1}$, (1) reaction without presaturation, (2) reaction with presaturation.

to both gas and liquid components, so the rate equation is

$$r = k C_{\text{cat}} \frac{K_H C_{\text{HL}}}{1 + K_H C_{\text{HL}}} \frac{K_L C_L}{1 + K_L C_L} \quad (\text{kmol}/(\text{m}^3 \text{ s}))$$

The kinetics of given reaction was investigated earlier [2]. The values of kinetic constants k , K_H , K_L are

$$k = 1.544 \times 10^{11} \exp\left(-\frac{9833.33}{T}\right) \quad (\text{kmol}/(\text{kg}_{\text{pd}} \text{ s}))$$

$$K_H = 5.38 \times 10^{-9} \exp\left(\frac{8000}{T}\right) \quad (\text{m}^3/\text{kmol})$$

$$K_L = 8.186 \times 10^{-4} \exp\left(\frac{3032.5}{T}\right) \quad (\text{m}^3/\text{kmol})$$

$$K_P = 0.025 \exp\left(\frac{2400}{T}\right) \quad (\text{m}^3/\text{kmol})$$

$$T = 100 \quad (^\circ\text{C})$$

$$C_{\text{cat}} = 0.383 \quad (\text{kg}_{\text{pd}} \text{ m}^3)$$

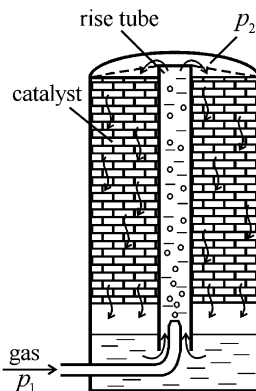


Fig. 7. Scheme of trickle-bed reactor operating without pumping.

The solubility of hydrogen in isopropyl alcohol was also studied [2]. Henry's constant is equal to $H_e = 1.706 \times 10^6 \exp(860.41/T)$ ($\text{Pa m}^3/\text{kmol}$). Then the hydrogen equilibrium concentration at 2.5 and 40 bar is equal to 0.014 and $0.227 \text{ kmol}/\text{m}^3$, respectively.

The developed mathematical simulation has showed that for a continuous reactor the advantages of preliminary saturation also take place and the analytical expressions for ΔX_L calculation can be found for different kinds of a rate equation. Thus, it is obvious experimental fact that the higher is the pressure, the bigger is the profit in the conversion and the profit is the greatest, when the gas absorption controls the reaction but is a negligible one in a kinetic regime.

4. Practical use of preliminary saturation

4.1. Reactor description

One of the reactor constructions, where the preliminary saturation effect can be used, is a trickle-bed reactor (Fig. 7). Gas from the bottle under pressure feeds the reactor and enters into the rise tube. Liquid in the tube is lifted by gas bubbles on the principle of air lift. Movement of gas is caused by a pressure drop $\Delta p = p_1 - p_2$ (p_2 lower than p_1 due to gas consumption on reaction). During the lifting the

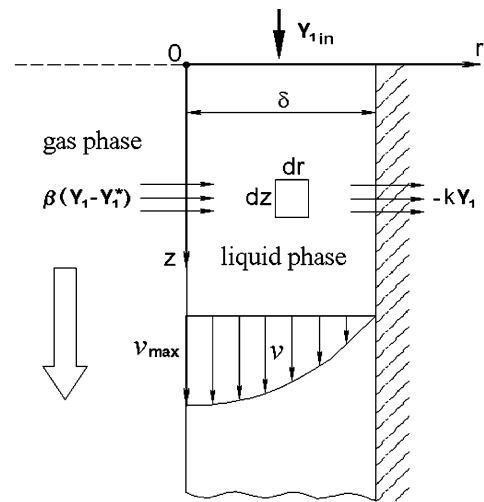


Fig. 8. Simplified presentation of gas and liquid flows and distribution of velocities in liquid film.

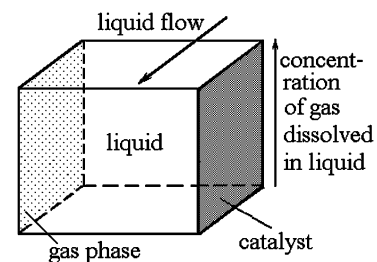


Fig. 9. Scheme of gas, liquid and solid phases location in Fig. 10.

gas dissolves in liquid in the tube. Liquid saturated with gas reaches the top of reactor and flows down over the catalyst particles in a thin film where a chemical conversion takes place. Further the liquid flows down to the bottom of the reactor and again enters the rise tube. So the reactor operates cyclically and does not need any pumping.

4.2. Model description

Mathematical model describing the behavior of gas dissolved in liquid flowing down through the catalyst bed was developed. Reaction has the first order with respect to gas and a zero order with respect to the liquid component. Direc-

tion of gas and liquid flows as well as distribution of liquid velocities are shown in Fig. 8.

It is assumed that the flow geometry of the model is represented by series of zero volume mixing points separated by relative short lengths of vertical flat plates (e.g. dumped or structured packing) over which the liquid flows [3]. These small sections (units) can be regarded as very short falling film contactors. Their expected number per unit bed length is dependent on the type, shape and size of packing used.

Two types of mathematical models were developed. In the first one (equilibrium model) it is assumed that equilibrium exists between gas and liquid at the interface. In this case

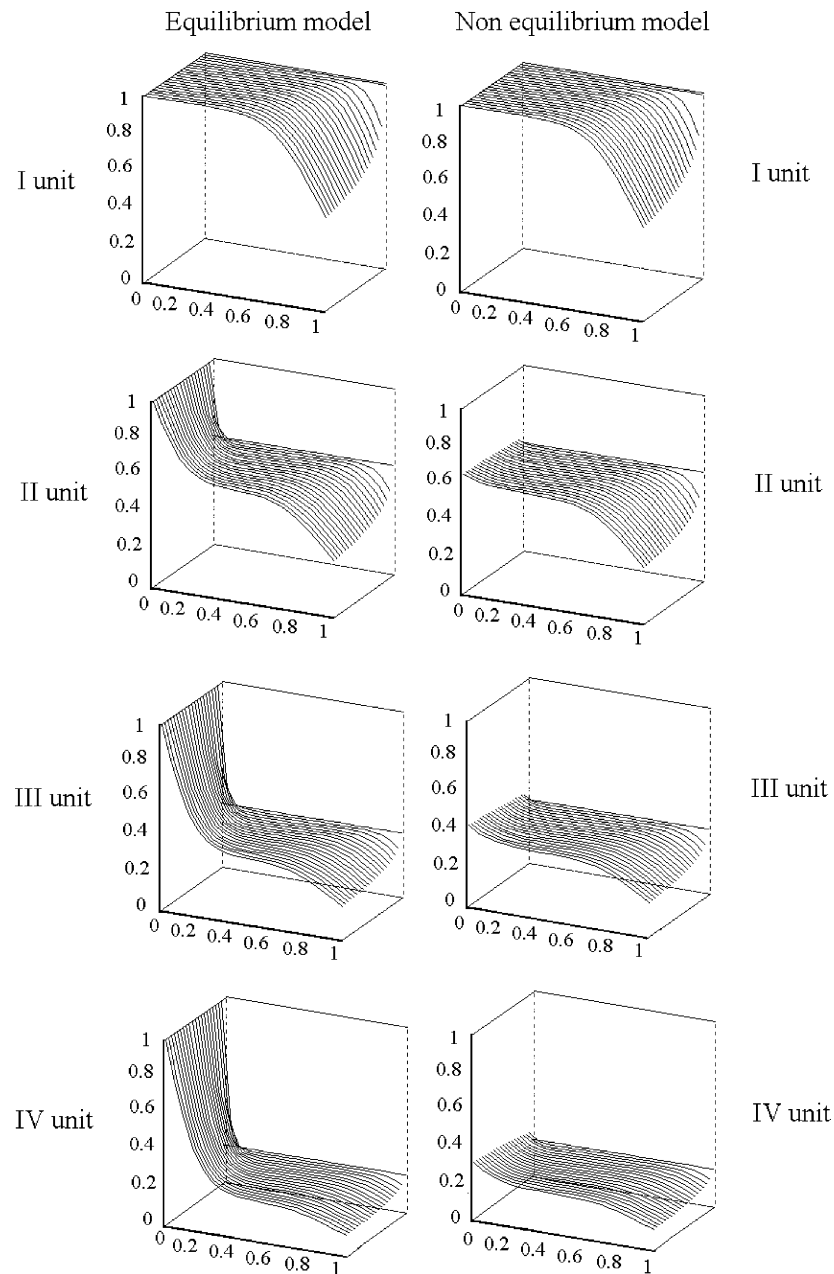


Fig. 10. Results of numeric solution of equilibrium and non-equilibrium models.

the simple equilibrium model is written as [4]

$$v_{\max} \left(1 - \left(\frac{r}{\delta}\right)^2\right) \frac{\partial Y_1}{\partial z} = D_L \frac{\partial^2 Y_1}{\partial r^2}$$

$$z = 0 \text{ and } r \geq 0 : Y_1 = Y_{1\text{in}};$$

$$z \geq 0 \text{ and } r = 0 : Y_1 = Y_1^*;$$

$$z \geq 0 \text{ and } r = \delta : S_{\text{ud}} D_L \frac{\partial Y_1}{\partial r} = -kY_1$$

$$z = 0, \quad z = H_i, \quad i = 1, \dots, n;$$

$$i = 1 : z = 0 \text{ and } r \geq 0 : Y_1 = Y_{1\text{in}}$$

$$i = 2, \dots, n : z = 0 \text{ and } r \geq 0 : Y_1 = \frac{1}{\delta} \int_0^\delta Y_1(H_{i-1}, r) \partial r$$

At not very high values of gas–liquid mass-transfer coefficient and at high velocity of liquid, concentration of gas dissolved in liquid near the interface is lower than its equilibrium value. Then the simple non-equilibrium model is written as:

$$v_{\max} \left(1 - \left(\frac{r}{\delta}\right)^2\right) \frac{\partial Y_1}{\partial z} = D_L \frac{\partial^2 Y_1}{\partial r^2}$$

$$z = 0 \text{ and } r \geq 0 : Y_1 = Y_{1\text{in}}$$

$$z \geq 0 \text{ and } r = 0 : S_{\text{ud}} D_L \frac{\partial Y_1}{\partial r} = \beta(Y_1 - Y_1^*)$$

$$z \geq 0 \text{ and } r = \delta : S_{\text{ud}} D_L \frac{\partial Y_1}{\partial r} = -kY_1$$

$$z = 0, \quad z = H_i, \quad i = 1, \dots, n$$

$$i = 1 : z = 0 \text{ and } r \geq 0 : Y_1 = Y_{1\text{in}}$$

$$i = 2, \dots, n : z = 0 \text{ and } r \geq 0 : Y_1 = \frac{1}{\delta} \int_0^\delta Y_1(H_{i-1}, r) \partial r$$

4.3. Numerical solution of models

The results of numeric solution of given models are presented in Fig. 10. It can be seen from Figs. 9 and 10 that conditions of equilibrium between gas and liquid at the in-

terface have a significant influence on the distribution of gas dissolved concentration in the liquid film.

In real process gas dissolved concentration diminishes along the catalyst bed not only due to a chemical conversion, but due to a gas pressure decrease as well.

5. Conclusions

The analysis of the mathematical model for a liquid batch stirred reactor with a suspended catalyst according to different initial conditions showed that in the case, when the educt solution (or suspension of the fine catalyst in solvent) was preliminarily saturated, we have a gain that reaches a certain degree of a liquid component conversion. This gain is the greatest when strong mass-transfer limitations occur but not in excess of the maximal value equal to a $C_{\text{H}}^*/C_{\text{L}0}$ ratio. In the kinetic regime this gain is negligible and approaches to zero.

One of the reactors, where the preliminary saturation effect can be used is a trickle-bed reactor which operates without the liquid pumping due to a pressure drop between a gas supply pressure and pressure in the top of the reactor. Mathematical model describing the behavior of gas dissolved in liquid flowing down through the catalyst bed was developed. In comparison with the model taken from published papers the developed model describes a more general case when the equilibrium does not exist between gas and liquid at the interface. The results of a numerical solution of the models testify that the conditions of equilibrium between gas and liquid have a significant influence on the distribution of gas dissolved concentration in the liquid film.

References

- [1] P.N. Rylander, Catalytic Hydrogenation in Organic Synthesis, Academic Press, New York, pp. 138–152.
- [2] O.P. Zhukova, Study of process of anesthesin production by liquid phase hydrogenation of ethyl ether of *p*-nitrobenzoic acid on Pd/C catalyst, PhD Thesis, 1995.
- [3] G. Astarita, W.J. Beek, Chem. Eng. Sci. 17 (1962) 665–674.
- [4] G.F. Versteeg, et al., Absorption accompanied with chemical reaction in trickle-bed reactors, Chem. Eng. Sci. 52 (1997) 4057–4067.