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The influences of the gas rate dissolution and mass-transfer limitation at the interfaces on selectivity of gas–liquid processes in stirred reactors with a suspended catalyst

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Abstract

A complex mathematical model accounting for the hydrogen dissolution process in suspensions and mass-transfer steps at the liquid–solid interface for the gas and liquid components is given. The calculated data according to the model for the reaction A → B → C shows, that the yield of an intermediate product B is very much affected by the relation of the gas component mass-transfer coefficient on the gas–liquid interface to that on the liquid–solid one. The hydrogenation of chlornitroaromatic compounds was analysed. The kinetics of the catalytic reduction of *p*-chlornitrobenzene to *p*-chloraniline via corresponding arylhydroxilamine on the Ir/C catalyst experimentally in a batch reactor has been studied. In this process the first reactions depend on the hydrogen concentration but the second ones are not dependent — this is a disproportion of the intermediate product to the final product — amine. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Slurry reactor; Kinetic simulation; Selectivity of gas–liquid reactions

1. Introduction

The gas component concentration in liquid (suspension) is 2–4 orders of magnitude lower than that of the liquid reagents and, as a rule, it mainly determines the rate and direction of gas–liquid reactions. Hence, the gas dissolved amount in the suspension and its concentration calculation procedure appears to be very important.

In a complex catalytic process involving reactions with different mechanisms with respect to gas component, its concentration in suspension may affect considerably intermediate selectivity [1].

The dissolved gas content is depended on pressure, temperature, catalyst concentration, physical–chemical properties of gas and liquid, reaction mechanism and mass-transfer at gas–liquid–solid interfaces [2]. It should be noted that the concentration of gas reagent on the catalyst surface might influence the reaction direction. Thus, e.g., the hydrogenation on hydrogen-“poor” instead of hydrogen-“rich” catalysts can involve hydrogenolysis and isomerisation but not the reduction [3].

This paper presents the mathematical model of a gas–liquid process on a suspended catalyst, which allows to simulate the influence of mass-transfer resistance of all reaction components at the interfaces, and to determine the effect of pressure and gas component mass-transfer limitations on the gas–liquid and liquid–solid interfaces on the intermediate product selectivity.

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Nomenclature

a_S, a_L	specific surface of the catalyst particles and gas hole, respectively (m^{-1})
C_{AL}, C_{BL}, C_L	liquid reagent concentration in a suspension ($kmol/m^3$)
C_{AS}, C_{BS}, C_{HS}	reagent concentration on the catalyst surface ($kmol/m^3$)
C_{A_0}, C_{C_0}	initial concentration of a educt reagent ($kmol/m^3$)
C_{cat}	catalyst concentration (kg/m^3)
C^*_H, C_{HL}, C_{HG}	equilibrium concentration, gas concentration in the suspension and a gas concentration in gas phase ($kmol/m^3$)
$\bar{C}_i$	dimensionless concentration of liquid reagents, $\bar{C}_i = C_i/C_{A_0}$
$\bar{C}_{HL}$	dimensionless concentration of hydrogen, $\bar{C}_{HL} = C_{HL}/C^*_H$
k_{AS}, k_{BS}, k_{HS}	coefficient of reagent mass-transfer between liquid and catalyst (m/s)
k_{HL}	coefficient of mass-transfer between gas and liquid (m/s)
k_1, k_2	reaction rate constants ($m^6/(kmol\,kg\,s)$)
M, Q	dimensionless parameters, $M = kC_{cat}C^{*^{n-1}}_H C^m_L/\beta_{G–L}$, $Q = C^*_H/C_{A_0}$
S	selectivity of an intermediate B, $S = C_{BL}/X_A$
t	dimensionless time, $t = \beta_{G–L}\tau$

Greek symbols

$\beta_{G–L}$	gas–liquid mass-transfer coefficient, $\beta_{G–L} = k_{HL}a_L$ (s^{-1})
τ	time (s)

1.1. Development of the mathematical model for a gas–liquid consecutive reaction on a suspended catalyst accounting for mass-transfer limitations at interfaces

The derived model equations will be based on the following assumptions:

- the catalyst is homogeneously suspended in the liquid phase;
- the catalytic $A \xrightarrow[H_2]{r_1} B \xrightarrow[H_2]{r_2} C$ reactions take place;
- there is complete mixing on a micro scale in the liquid and gas phases;
- there are no pressure and temperature gradients in the gas and the liquid phase in the reactor;
- the solutes are not volatile;
- the ideal gas law can be applied;
- the reactor is isothermal;
- Henry's law can be applied to calculate the hydrogen concentration at the gas–liquid interface.

If the first-order power law reaction for both gas and liquid components occurs, the material balance equations for hydrogen under steady state condition takes the form:

$$\beta(C^*_H - C_{HL}) = k_{HS}a_S(C_{HL} - C_{HS}) = k_1C_{cat}C_{AL}C_{HS} + k_2C_{cat}C_{BL}C_{HS} \quad (1)$$

If the mass-transfer resistance of the liquid components at the liquid–solid interface is significant, so the following assumptions based on the material balance equations for A and B under the steady state conditions are valid:

$$k_{AS}a_S(C_{AL} - C_{BL}) = k_1C_{cat}C_{AS}C_{HS} \quad (2)$$

$$k_{BS}a_S(C_{BS} - C_{BL}) = k_1C_{cat}C_{AS}C_{HS} - k_2C_{cat}C_{BS}C_{HS} \quad (3)$$

Then, the mathematical model, describing simultaneous processes of mass-transfer of all components at the interfaces and catalytic reactions under a constant pressure and temperature are written as

$$\frac{d\bar{C}_{HL}}{dt} = 1 - \bar{C}_{HL} - \frac{k_{HS}a_S}{\beta_{G–L}}(\bar{C}_{HL} - \bar{C}_{HS}) \quad (4)$$

$$\frac{d\bar{C}_{HS}}{dt} = -\frac{k_{HS}a_S}{\beta_{G–L}}(\bar{C}_{HL} - \bar{C}_{HS}) - M_1\bar{C}_{AS}\bar{C}_{HS} - M_2\bar{C}_{BS}\bar{C}_{HS} \quad (5)$$

$$\frac{d\bar{C}_{AL}}{dt} = -M_1Q\bar{C}_{AS}\bar{C}_{HS} \quad (6)$$

$$\frac{d\bar{C}_{BL}}{dt} = M_1Q\bar{C}_{AS}\bar{C}_{HS} - M_2Q\bar{C}_{BS}\bar{C}_{HS} \quad (7)$$

$$\frac{d\bar{C}_{\mathrm{CL}}}{dt} = M_2 Q \bar{C}_{\mathrm{BS}} \bar{C}_{\mathrm{HS}} \tag{8}$$

where

$$\bar{C}_{\mathrm{AS}} = \frac{\bar{C}_{\mathrm{AL}}}{(k_1 C_{\mathrm{A_0}} C_{\mathrm{cat}} / k_{\mathrm{AS}} a_{\mathrm{S}}) Q \bar{C}_{\mathrm{HS}} + 1} \tag{9}$$

$$\bar{C}_{\mathrm{BS}} = \frac{(k_1 C_{\mathrm{A_0}} C_{\mathrm{cat}} / k_{\mathrm{BS}} a_{\mathrm{S}}) Q \bar{C}_{\mathrm{AS}} \bar{C}_{\mathrm{HS}} + \bar{C}_{\mathrm{BL}}}{(k_2 C_{\mathrm{A_0}} C_{\mathrm{cat}} / k_{\mathrm{BS}} a_{\mathrm{S}}) Q \bar{C}_{\mathrm{HS}} + 1} \tag{10}$$

and the initial conditions are: $t = 0$, $\bar{C}_{\mathrm{AL}} = 1$, $\bar{C}_{\mathrm{BL}} = 1$, $\bar{C}_{\mathrm{CL}} = 1$, $\bar{C}_{\mathrm{HL}} = 0$. Let the selectivity of an intermediate B, S_{B} be the ratio of the dimensionless concentration B to the initial substance conversion degree: $S_{\mathrm{B}} = C_{\mathrm{BL}} X_{\mathrm{A}}$.

Now the model (4)–(10) for some particular cases is analysed.

First consider the kinetic regime. The gas solubility and mass-transfer of all components to the catalyst surface do not limit the catalytic reaction. In this case the rate equations are

$$r_1 = k_1 C_{\mathrm{cat}} C_{\mathrm{AL}} C^*_{\mathrm{H}}, \qquad r_2 = k_2 C_{\mathrm{cat}} C_{\mathrm{BL}} C^*_{\mathrm{H}} \tag{11}$$

Solving the system for $C_{\mathrm{HS}} = C_{\mathrm{HL}} = C^*_{\mathrm{H}}$, $C_{\mathrm{AL}} = C_{\mathrm{AS}}$, $C_{\mathrm{BL}} = C_{\mathrm{BS}}$, $C_{\mathrm{CL}} = C_{\mathrm{CS}}$ (i.e. k_{H}, k_{AS}, k_{BS}, $k_{\mathrm{CS}} \to \infty$), we obtain that the selectivity of B does not depend on the pressure (parameter Q). But on the ratio of reaction rate constants k_1 and k_2 (parameters M_1 and M_2) as well as in a classical case of such reaction with the same kind of both reaction rates' equations.

Another example. Let us consider the situation when the gas absorption rate only can limit the process. Now in the rate equation (11) the hydrogen concentration values become C_{HL} and the liquid component concentration is the same as in the previous case. Solving the set, Eqs. (4)–(10), we obtained that the gas rate absorption limitations do not influence the selectivity.

Suppose that there is an additional mass-transfer resistance at the liquid–solid interface for the gas component. The reaction rate equations can be written as

$$r_1 = k_1 C_{\mathrm{cat}} C_{\mathrm{AL}} C_{\mathrm{HS}}, \qquad r_2 = k_2 C_{\mathrm{cat}} C_{\mathrm{BL}} C_{\mathrm{HS}} \tag{12}$$

Numerical calculations have shown that at the variation of $k_{\mathrm{HS}} a_{\mathrm{S}}$ the S_{B} depend neither on the conversion degree of substances A and Q nor on the parameter $k_{\mathrm{HS}} a_{\mathrm{S}} / \beta_{\mathrm{G–L}}$. The equations have been solved for the following parameters: $C_{\mathrm{A_0}} = 0.1\,\mathrm{kmol/m^3}$, $C_{\mathrm{cat}} = 5.0\,\mathrm{kg/m^3}$, $\beta_{\mathrm{G–L}} = 0.1\,\mathrm{s^{-1}}$, $k_1 = k_2 = 0.2$.

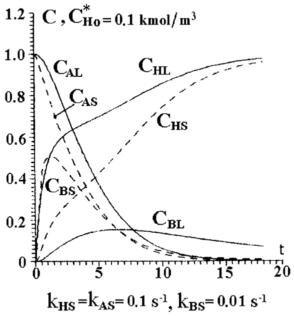

Fig. 1. Concentration of reaction components in suspension (in the bulk liquid and on the surface of catalyst).

The changes of the reaction liquid component concentrations and the hydrogen-dissolved content in the suspension in a liquid batch reactor are shown in Fig. 1.

The gas concentration influence on the intermediate B selectivity at the mass-transfer limitations of all components to the catalyst external surface is given in Fig. 2. Here, the suspension saturation with hydrogen decreases the B yield (all other factors are equal).

The calculations show how the absolute values of the reaction constants k_1 and k_2 affect the reaction component concentration. As k_1 grows, the yield of B drastically increases and the value of C_{HL} decreases since the gas is more and more consumed on the reaction. Similarly, with increasing k_2 the yield of B decreases, the change of the dissolved gas concentration is the same as in the previous case. The result of the relation between coefficients of hydrogen mass-transfer at the interfaces of the intermediate yield is of interest. A maximum concentration of B

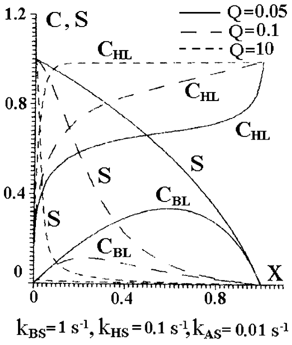

Fig. 2. Concentration and selectivity of reaction components vs conversion degree at varying Q parameter.

increases with k_{HS} rising and its maximum value moves to the reaction end. Thus, it has been shown, that if the liquid and gas components mass-transfer limitations occurs, a non-linear function appears with respect to the liquid components and hydrogen concentrations at the model equations, which show more complicated dependence of selectivity on the process conditions at the presence of mass-transfer all reagents resistance.

2. Practical example

The scheme of the liquid-phase catalytic reduction of nitroaromatic compounds supplemented by a new reaction route involving the catalytic disproportion of intermediate *N*-aryl hydroxylamine to corresponding amine is

$$\mathrm{ArNO_2(A)} \rightarrow \mathrm{ArNHOH(B)} \rightarrow \mathrm{ArNH_2(C)}$$

The catalytic surface is assumed to be non-homogenous and it contains centre I activating the molecular hydrogen, $\mathrm{ArNO_2}$ hydrogenation on them is performed. Thus, the reaction rate for $\mathrm{ArNO_2}$ hydrogenation is

$$\frac{\mathrm{d}C_{\mathrm{A}}}{\mathrm{d}\tau} = k_{\mathrm{A}}^{*}\frac{K_{\mathrm{H}}C_{\mathrm{HL}}}{1+K_{\mathrm{H}}C_{\mathrm{HL}}}\frac{K_{\mathrm{A}}C_{\mathrm{A}}}{K_{\mathrm{A}}C_{\mathrm{A}}+K_{\mathrm{B}}C_{\mathrm{B}}+K_{\mathrm{C}}C_{\mathrm{C}}} \tag{13}$$

where C_{A}, C_{B}, C_{C}, C_{HL} are the concentrations of $\mathrm{ArNO_2}$, ArNHOH, $\mathrm{ArNH_2}$ and hydrogen, respectively, K_{A}, K_{B}, K_{C}, K_{H} are their adsorption coefficients. At the given hydrogen pressure, this equation takes the form:

$$R_{\mathrm{A}} = -k_{\mathrm{A}}\frac{K_{\mathrm{A}}C_{\mathrm{A}}}{K_{\mathrm{A}}C_{\mathrm{A}}+K_{\mathrm{B}}C_{\mathrm{B}}+K_{\mathrm{C}}C_{\mathrm{C}}} \tag{14}$$

where R_{A} is the $\mathrm{ArNO_2}$ hydrogenation rate, k_{A} is an effective constant.

The equation for ArNHOH conversion rate is based on the assumption that disproportion partially occurs on the centre I and partially on the centre II, not activating hydrogen, the reaction is carried out via Langmuir–Hinshelwood mechanism and $\mathrm{ArNO_2}$ adsorption on centre II is negligible.

$$R_{\mathrm{B}} = -k_{\mathrm{B}}\frac{K_{\mathrm{B}}C_{\mathrm{B}}}{K_{\mathrm{B}}C_{\mathrm{B}}+K_{\mathrm{C}}C_{\mathrm{C}}} - k'_{\mathrm{B}}\frac{K'_{\mathrm{B}}C'_{\mathrm{B}}}{K'_{\mathrm{A}}C_{\mathrm{A}}+K'_{\mathrm{B}}C_{\mathrm{B}}+K'_{\mathrm{C}}C_{\mathrm{C}}} \tag{15}$$

where R_{B} is the disproportion rate, k_{A} the effective constant of disproportion. Index ($'$) characterises the disproportion rate on the centre I.

The experiments on *p*-chlornitrobenzene (A) reduction to *p*-chlornitrobenzenhydroxylamine (B) after to chloraniline (C) were carried out in a non-gradient flow installation at $T = 20°\mathrm{C}$ and $P = 0.1$–$0.9\,\mathrm{MPa}$. The rate of nitrocompound hydrogenation depends almost linear on the hydrogen pressure. At the initial stage, ArNHOH concentration increases with hydrogen pressure because of the linear dependence of $\mathrm{ArNO_2}$ hydrogenation rate. After the nitrocompound is exhausted, the rate of ArNHOH conversion does not depend on the hydrogen pressure.

The mathematical model of the nitrocompound catalytic reduction at the constant temperature and the hydrogen pressure for the hydrogen dissolved in the liquid is

$$\frac{\mathrm{d}C_{\mathrm{A}}}{\mathrm{d}\tau} = \beta(C_{\mathrm{H}}^{*}-C_{\mathrm{HL}}) - k_{\mathrm{A}}^{*}\frac{K_{\mathrm{H}}C_{\mathrm{HL}}}{1+K_{\mathrm{H}}C_{\mathrm{HL}}} \times \frac{K_{\mathrm{A}}C_{\mathrm{A}}C_{\mathrm{cat}}}{K_{\mathrm{A}}C_{\mathrm{A}}+K_{\mathrm{B}}C_{\mathrm{B}}+K_{\mathrm{C}}C_{\mathrm{C}}} \tag{16}$$

for a hydrogenated nitrocompound

$$\frac{\mathrm{d}C_{\mathrm{A}}}{\mathrm{d}\tau} = -k_{\mathrm{A}}^{*}\frac{K_{\mathrm{H}}C_{\mathrm{HL}}}{1+K_{\mathrm{H}}C_{\mathrm{HL}}}\frac{K_{\mathrm{A}}C_{\mathrm{A}}C_{\mathrm{cat}}}{K_{\mathrm{A}}C_{\mathrm{A}}+K_{\mathrm{B}}C_{\mathrm{B}}+K_{\mathrm{C}}C_{\mathrm{C}}} \tag{17}$$

for disproportionition of intermediate arylhydroxylamine

$$\frac{\mathrm{d}C_{\mathrm{B}}}{\mathrm{d}\tau} = -k_{\mathrm{A}}^{*}\frac{K_{\mathrm{H}}C_{\mathrm{HL}}}{1+K_{\mathrm{H}}C_{\mathrm{HL}}}\frac{K_{\mathrm{A}}C_{\mathrm{A}}C_{\mathrm{cat}}}{K_{\mathrm{A}}C_{\mathrm{A}}+K_{\mathrm{B}}C_{\mathrm{B}}+K_{\mathrm{C}}C_{\mathrm{C}}} - k_{\mathrm{B}}^{*}\frac{K_{\mathrm{B}}C_{\mathrm{B}}C_{\mathrm{cat}}}{K_{\mathrm{B}}C_{\mathrm{B}}+K_{\mathrm{C}}C_{\mathrm{C}}} - k'_{\mathrm{B}}\frac{K'_{\mathrm{B}}C_{\mathrm{B}}C_{\mathrm{cat}}}{K'_{\mathrm{A}}C_{\mathrm{A}}+K'_{\mathrm{B}}C_{\mathrm{B}}+K'_{\mathrm{C}}C_{\mathrm{C}}} \tag{18}$$

for the product — amine-compound

$$\frac{\mathrm{d}C_{\mathrm{B}}}{\mathrm{d}\tau} = k_{\mathrm{B}}\frac{K_{\mathrm{B}}C_{\mathrm{C}}C_{\mathrm{cat}}}{K_{\mathrm{B}}C_{\mathrm{B}}+K_{\mathrm{C}}C_{\mathrm{C}}} + K'_{\mathrm{B}}\frac{K'_{\mathrm{B}}C_{\mathrm{B}}C_{\mathrm{cat}}}{K'_{\mathrm{A}}C_{\mathrm{A}}+K'_{\mathrm{B}}C_{\mathrm{B}}+K'_{\mathrm{C}}C_{\mathrm{C}}} \tag{19}$$

Chemical conversion of *p*-chlornitrobenzene into *n*-chloraniline was numerically described by Rozenbrok the second-order equations with the following parameters:

$$k_A(3\,\text{at}) = 1.528 \times 10^{-5}, \quad k_A = 2.7810 \times 10^{-5},$$
$$k_A = 4.48 \times 10^{-5}\,\text{kmol/m}^3\,\text{s}$$

$$k_H = 3.848\,\text{m}^3/\text{kmol}, \quad C_H^* = 21.29\times10^{-3}\,\text{kmol/m}^3,$$
$$k_B = 0.1\times10^{-5}\,\text{kmol/kg s}, \quad k_B' = 0.5810\,\text{kmol/kg s},$$
$$K_B/K_A = 0.138, \quad K_C/K_A = 0.0417, \quad K_C/K_B = 0.3, \quad T = 20°\text{C}, \quad C_{cat} = 3.87\,\text{kg/m}^3, \quad K_A'/K_B' \gg 1, \quad K_C'/K_B' \ll 1.$$

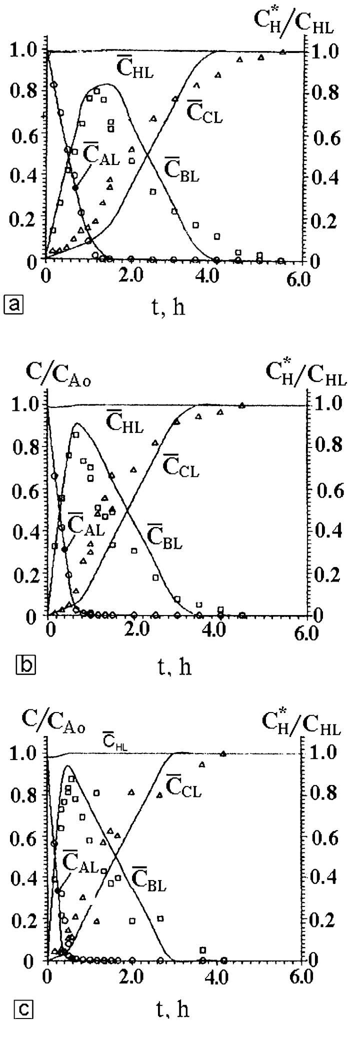

Fig. 3. Reagents concentrations of *n*-chlornitrobenzene conversion as the functions of pressure: (a) $P = 3 \times 10^5$ Pa; (b) $P = 5\times10^5$ Pa; (c) $P = 7\times10^5$ Pa, $T = 20°\text{C}$, $C_{cat} = 3.87\,\text{kg/m}^3$, $C_{A_0} = 0.204\,\text{kmol/m}^3$.

The calculated and experimental data for the chemical conversion of $ArNO_2$ to $ArNH_2$ through ArNHOH disproportion at different pressure are shown in Fig. 3a–c. As hydrogen pressure grows, ArNHOH selectivity increases and the process time decreases. At the given experimental conditions, the reaction converts to a kinetic region and the measured concentration of the hydrogen dissolved in the suspension is close to equilibrium. The method of the experimental determination of the gas dissolved in the suspension during the reaction is described early [4,5].

We can say that the suggested model adequately describes hydrogenation process of a nitrocompound and disproportion of an intermediate to a final product.

Now, we can use the model (4)–(10) to simulate the process at the lack of the hydrogen (high catalyst concentration). The selectivity as the function of the coefficients of mass-transfer at the gas–liquid interface, $\beta_{G\text{–}L}$, is presented in Fig. 4. Intensification of the process (increase of $\beta_{G\text{–}L}$) leads to increase of only the hydrogenation rates and hence the selectivity of the component B increases also.

When $\beta_{G\text{–}L}$ is within 0.001–0.1 s^{-1}, the concentration of the hydrogen dissolved in the suspension changes insufficiently, the rate of A → B reaction remains unchangeable. As the mass-transfer coefficient decreases, the process passes to a diffusion region: hydrogen concentration in A → B reaction approaches zero and reaches high (equilibrium)

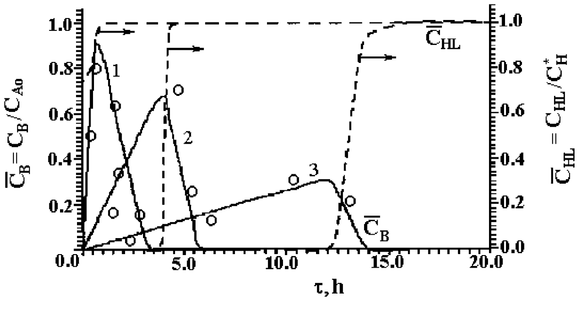

Fig. 4. Numerical and experimental data on the influence of mass-transfer coefficient, $\beta_{G\text{–}L}$ of the selectivity of *p*-chlopnitrobenzene hydrogenation ($T = 20°\text{C}$, $P = 5 \times 10^5$ Pa, $C_{cat} = 3.87\,\text{kg/m}^3$, 1 : $\beta_{G\text{–}L} = 0.1\,\text{s}^{-1}$, 2 : $\beta_{G\text{–}L} = 0.003\,\text{s}^{-1}$, 3 : $\beta_{G\text{–}L} = 0.001\,\text{s}^{-1}$).

value only when the process is over and selectivity decreases considerably [6,7].

The complex process involving the reactions with different mechanisms with respect to the gas component concentration increases the chosen component selectivity by varying not only the pressure but also the gas absorption rate [8,9].

3. Conclusion

A mathematical model involving the influence of the mass-transfer resistance of the gas and liquid components at the interfaces in a gas–liquid batch reactor with a suspended catalyst on the intermediate selectivity in various reactions A → B → C type was described in this paper. Rate equations for both reactions are the same, and as it was shown the selectivity does not depend on the pressure when the mass-transfer limitation is at interfaces. However, when the simultaneous resistance of liquid and gas components to the solid surface of catalyst particles, selectivity essentially depends not only on the pressure but also on the ratio of gas component coefficients mass-transfer at the interfaces too.

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