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The numerical analysis of gas–liquid a-pinene hydrogenation

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ABSTRACT

The kinetic model of the process of α-pinene hydrogenation was suggested which takes into account the behavior of chemical reactions both in liquid phase and in gaseous phase. The two-phase mathematical model of the process in a tubular reactor was developed that considers a reaction mixture mole numbers due to hydrogen drawing on a hydrogenation reaction and also due to a phase transfers under the evaporation or the condensation of the components. The thermodynamic approach was proposed for a determination of the phase transfer velocity. The numerical analysis of the process in a tubular reactor was carried out under cocurrent or countercurrent flows of the reaction mixture and cooling water. The preference of the cocurrent reactor using was shown.

Key words: α-pinene hydrogenation, tubular reactor, chemical reactions, mathematical model.

INTRODUCTION

In modeling nonisothermal processes in reactors with the participation of a gas, a liquid, and a fixed solid catalyst, it is necessary to take into account that the change in the composition of the reaction mixture depends significantly not only on the chemical reaction itself but also on phase transitions in the catalyst bed. Account of these factors is virtually decisive in considering processes accompanied by the release of a large amount of heat in the reaction zone. Among such processes are the reactions of hydrogenation of unsaturated compounds [1, 2].

In this work, using a mathematical model, the α -pinene hydrogenation in a reactor with a fixed bed of a nickel silicate catalyst is studied with consideration of simultaneous chemical and phase transformations. The main purpose of this study is to determine the type of reactor and the operating conditions for which the yield of the desired product, cis-pinane, is maximal.The interest in this problem is caused by the great practical importance of the α-pinene hydrogenation product, cis-pinane, whose oxidation yields a stable hydroperoxide used as the initiator of low-temperature butadiene--styrene polymerization. Numerous studies determined [3] that the use of cis-pinane hydroperoxide as a polymerization initiator significantly improves the performance and specifications of butadiene--styrene rubbers, especially those produced at high monomer conversions.

Analysis of experimental data showed [3] that, on the chosen catalyst, chemical reactions can occur in both the liquid and the gas phases. A two-step scheme of α-pinene hydrogenation is proposed, which comprises an irreversible step of α-pinene interaction with hydrogen to form cis-pinane and a reversible step of α-pinene isomerization. As an α-pinene isomer, an analogue averaged between dipentene and α-terpinene is chosen.

Pinene + H_2 →Pinane or C1 + H2 → C2,
Pinene ↔ Isomers or C1 ↔ C3.

The kinetic equations for these steps have the form:
for the liquid phase:

$$W_1 = \bar{k}_1 C_1 P_H = k_1 x_1 y_H, \quad k_1 = \bar{k}_1 P C_L,$$

$$W_2 = \bar{k}_2 C_1 - \bar{k}_3 C_3 = k_2 x_1 - k_3 x_3,\ k_2 = \bar{k}_2 C_L,\ k_3 = \bar{k}_3 C_L .$$

for the gas phase:

$$w_1 = \bar{k}_4 C_1 C_H = k_4 y_1 y_H,\ k_4 = \bar{k}_4 C_G^2,$$

$$w_2 = \bar{k}_5 C_1 - \bar{k}_6 C_3 = k_5 x_1 - k_6 x_3,\ k_5 = \bar{k}_5 C_G,\ k_6 = \bar{k}_6 C_G .$$

Here, C_G and C_L are the molar densities (kmol/m^3) of the gas and the liquid phases, respectively; x_i and y_i are the mole fractions of the components in the liquid and the gas phases, respectively; and W_i and w_i are the rates of the reactions (kmol/(m^3 h)) in the gas and the liquid phases, respectively.

MATERIALS AND METHODS

To describe the α -pinene hydrogenation in the gas--liquid--solid catalyst system, a two-phase mathematical model is developed, which takes into account the change in the number of moles in the reaction system: first of all, the significant decrease in the number of moles in the gas phase because of the hydrogen consumption in the hydrogenation and also the change in the number of moles in both phases because of the evaporation or condensation of the components.

The mathematical description of the nonisothermal α-pinene hydrogenation in a tubular reactor with a fixed catalyst bed is given by the set of material and heat balances:

$$\begin{gathered}
\frac{1}{S}\left(C_P^L L + C_P^G G\right)\frac{dT}{dl} = \sum_{j=1}^{2} Q_j\left[(1-\varphi)W_j + \varphi w_j\right] - \frac{V_{vap}}{V_p}\sum_{i=1}^{3}\Delta H_i^V Y_i + \alpha_{ð} S_{ð}\left(T_{ð} - T\right),\\
\mp \frac{G_x C_x}{S}\frac{dT_x}{dl} = \alpha_{ð} S_x\left(T - T_x\right),\\
\frac{1}{S}\frac{dL}{dl} = -\frac{V_{vap}}{V_{ð}} = F_L,\\
\frac{1}{S}\frac{dx_i}{dl} = \frac{F_i - x_i F_L}{L},\quad F_i = \sum_{j=1}^{2}(1-\varphi)\nu_{ij}W_j - \frac{V_{vap}}{V_{ð}}Y_i,\qquad i = 1,2,3,\\
\frac{1}{S}\frac{dG}{dl} = -(1-\varphi)W_1 - \varphi w_1 + \frac{V_{vap}}{V_p} = \hat{O}_G,\\
\frac{1}{S}\frac{dy_i}{dl} = \frac{\hat{O}_i - y_i\hat{O}_G}{G},\quad \hat{O}_i = \sum_{j=1}^{2}\varphi\nu_{ij}w_j + \frac{V_{vap}}{V_p}Y_i,\\
\frac{1}{S}\frac{dy_H}{dl} = \frac{-(1-\varphi)W_1 - \varphi w_1 - y_H\hat{O}_G}{G},
\end{gathered} \tag{1}$$

under the boundary conditions at $l = 0$:

$$x_i = x_i^o,\ y_i = y_i^o,\ L = L_0,\ G = G_0,\ T = T_0, \tag{2}$$

Here, Q_j are the heats of reactions, kcal/kmol; ΔH_i^V are the heats of evaporation of the components, kcal/kmol; C_P^G and C_P^L are the molar specific heats of the gas and the liquid phases, respectively, kcal/(kmol K); C_x is the mass heat capacity of the coolant, kcal/(kg K); G_x is the mass flow rate of the coolant, kg/h; S_x is the external specific heat-transfer surface area, m^2/m^3; α_x is the heat-transfer coefficient, kcal/(m^2 h K); L and G are the molar flow rates of the liquid and the gas phases, respectively, kmol/h; l is the axial coordinate along the reactor length, m; S is the cross-sectional area of tubes, m^2; V_{vap} is the molar evaporation rate, kmol/h; ν_{ij} are the stoichiometric coefficients; and φ is the mole fraction of the gas phase.

RESULTS

Of fundamental importance for developing the model is an approach to determining the phase transition rate. There are two main approaches there to: thermodynamic equilibrium between the two phases is assumed [4] and V_{vap} is calculated using a certain equation [5]. In the model advanced, it is suggested that V_{vap} in set (1) be determined as the difference between the equilibrium value G* and the actual value G. G* is calculated from the total composition of the reaction mixture and current values of the phase variables P and T, and G is the solution of set (1). Then, the evaporation rate $V_{vap}=G^{*}-G$. In evaporation, this value is positive, and in condensation, it is negative. If the equilibrium value of the mole fraction of the gas phase should be 1, then the evaporation rate is taken to be maximal and equal to L.

All the kinetic and thermophysical parameters are available in the literature [3]. The thermophysical parameters (phase equilibrium constants, enthalpies of the components, their molar specific heats in the gas phase, and heats of evaporation of the components) are calculated according to published procedures [6].

At an inlet temperature of about 30^{o}C under adiabatic conditions because of the high exothermicity of α-pinene hydrogenation, the temperature in the reactor exceeds 300^{o}C [3]. This temperature is much higher than the experimentally recommended limiting temperature $140\ldots150^{o}$C [3] (above the latter temperature, there are thermal decomposition of the components, coking, and catalyst deactivation). Therefore, the process should be performed in reactors with sufficiently good heat removal, e.g., in tubular reactors, which can be designed in two variants: with cocurrent and countercurrent flows of the reaction mixture and the coolant.

Depending on the variant of reactor design, the sign of the left-hand side of the equation for the coolant in set (1) can be either plus or minus for a cocurrent or countercurrent reactor, respectively.

Then, set (1) is closed by the following boundary conditions:

$$T_x\Big|_{l=0} = T_x^{0} \text{ for the cocurrent reactor and } T_x\Big|_{l=L_{mp}} = T_x^{0} \text{ for the cocurrent reactor.} \qquad (3)$$

Using set (1) under boundary conditions (2) and (3), a computational experiment was performed for a tubular reactor with tubes 3.5 m^3 in volume, 50 mm in diameter, and 2 m in length at an average constant pressure of 5 atm with water as a coolant. The volume of the intertubular space is approximately 1.5 times larger than that of the reaction space. The initial conditions are $T_0 = 30^{0}$C, L_0 = 1.95 kmol/h, and G_0 = 2.45 kmol/h. The coolant flow rate G_c is a parameter being varied.

Some of the calculation results are presented in Figs. 1--4 (the solid and dashed lines show the data for the cocurrent and countercurrent reactors, respectively).

With an increase in the coolant flow rate G_c, the temperature T_{max} in the reactor naturally decreases, but at equal coolant flow rates, the temperature in the countercurrent reactor is always higher than that in the cocurrent reactor (Fig. 1). However, to reach the same temperature in the reactor, the coolant flow rate in the countercurrent reactor should be significantly higher than that in the cocurrent reactor.

A convenient characteristic for estimating the operating conditions is the average temperature T_{av} in the reactor. The maximal temperature T_{max} in the reactor and the α-pinene conversion X as functions of T_{av} are presented in Figs. 2 and 3, respectively.

Figure 2 shows that, lest T_{max} exceed a limiting value of 150^{0}C, T_{av} should be 96^{0}C in the cocurrent reactor and 70^{0}C in the countercurrent reactor. In this case, X exceeds 99% and is about 96%, respectively (Fig. 3). The coolant flow rates G_c for these reactors are 550 and 2600 kg/h, respectively. The latter value is technologically unrealistic and economically unacceptable. Characteristic profiles of the temperature in the reactors under such operating conditions are presented in Fig. 4.

The determining process parameter is T_{max}. Comparison of Figs. 1--4 shows that, at the same T_{max}, in the cocurrent reactor, the average temperature T_{av} in the reactor, the coolant temperature, and the average coolant temperature are higher. In the countercurrent reactor, only G_c is higher. This is because the temperature of the water cooling the reaction zone through the tube walls in the cocurrent reactor is lower than that in the countercurrent reactor, in which much of the heat should be removed in the tail part of the reactor, where the reaction rate and, hence, the heat release are insignificant. Therefore, in the countercurrent reactor, the coolant begins to contact the reaction zone at a higher temperature, which leads to the necessity of increasing the coolant flow rate. It is seen that the presence of a heat source---chemical reaction---makes cocurrent tubular reactors more efficient, in contrast to ordinary heat exchangers.

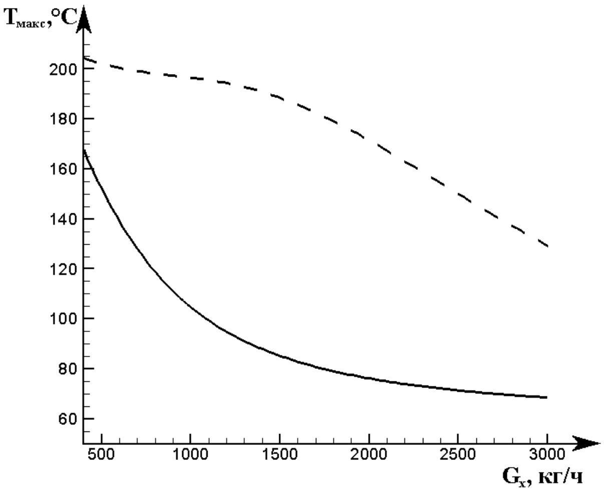

Fig. 1. Maximal temperature in the reactor vs. coolant flow rate

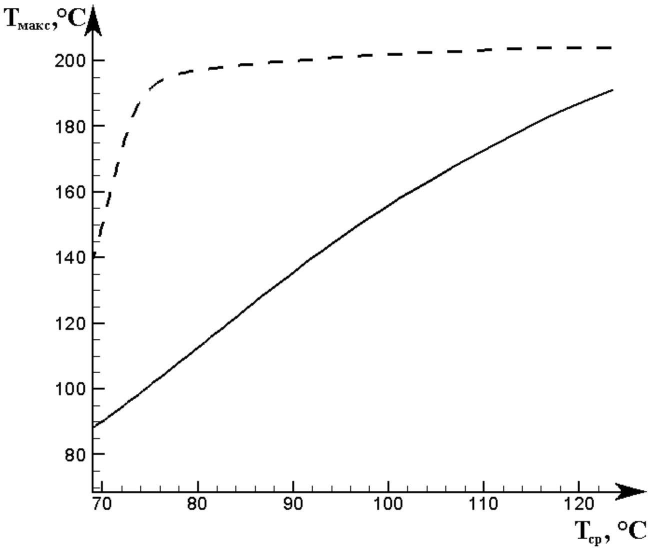

Fig. 2. Maximal temperature in the reactor vs. average temperature

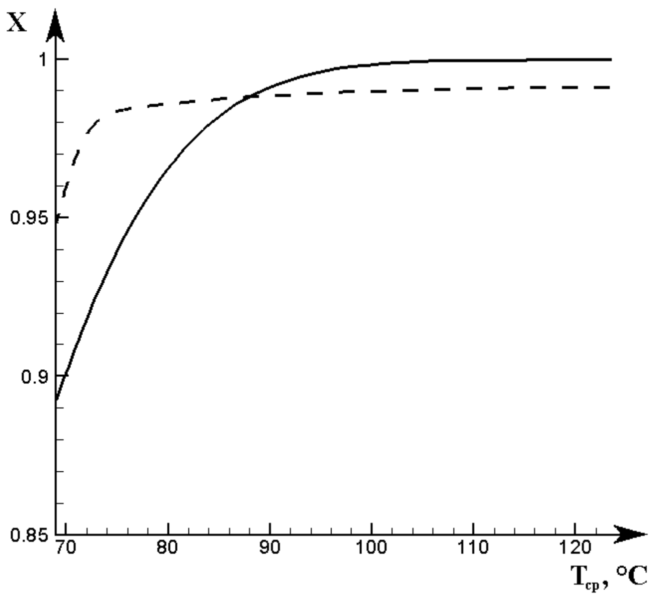

Fig. 3. **α-Pinene conversion in the reactor vs. average temperature.**

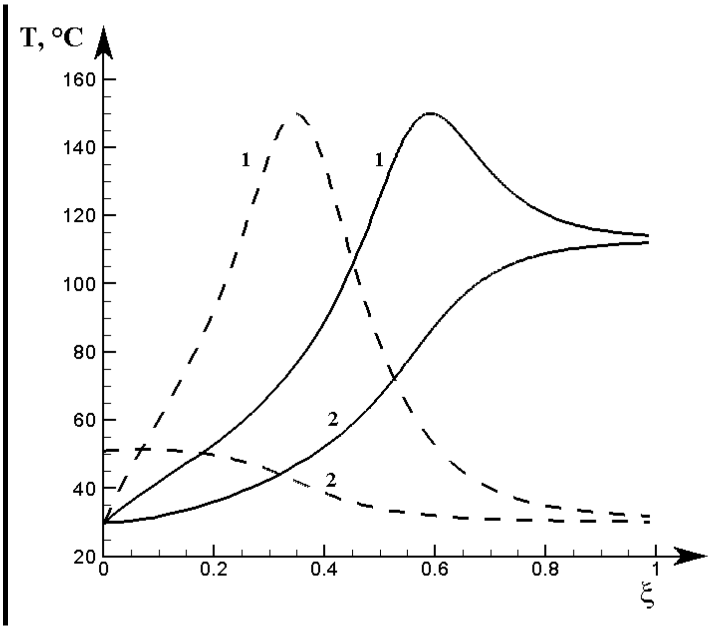

Fig. 4. **(1) Catalyst and (2) coolant temperature profiles along the relative reactor length.**

If, to increase the reactor operation reliability, T_{max} is decreased to 140^0C, then X will be 98.6% for the cocurrent reactor and below 95% for the countercurrent reactor. In this case, G_c should be increased to 600 and 2800 kg/h, respectively. It is clear that such conditions in the countercurrent reactor are impossible to implement.

The numerical analysis demonstrated that the α-pinene hydrogenation to form cis-pinane can be efficiently performed in a tubular reactor with a fixed bed of a nickel silicate catalyst with cocurrent flows of the reaction mixture and the coolant. Figures 1--3 show that such a reactor has quite a high technological flexibility. Even with a decrease in T_{max} to 130^0C, the operating conditions remain suitable: X = 97% at G_c = 720 kg/h.

CONCLUSION

Thus, a fundamental novelty of the results of this study consists in using a thermodynamic approach for determining the phase transition rate and also in obtaining evidence that gas--liquid hydrogenation in tubular reactors can be efficient only in the case of cocurrent flows of the reaction mixture and the coolant.

REFERENCES

[1] V.V. Molchanov, R.A. Buyanov, *Khim. Prom-st.*, **1999**, 4, 61-65.
[2] L.B. Datsevich, A. Iess, M.P. Kambur, D.A. Mukhortov, *Katal. Prom-st.*, **2004**, Special Issue, 18--26.
[3] S.A. Mustafina, A.V. Balaev, R.S. Davletshin, S.I. Spivak, U.M. Dzhemilev, *Doklady Chemistry*, **2006**, 406, 2, 26-29
[4] V.A. Kirillov, V.I. Drobyshevich, *Teor. Osn. Khim. Technol.*, **1998**, 32, 1, 72-81.
[5] V.A. Kirillov, V.A. Kuzmin, N.A. Kuzin, *Teor. Osn. Khim. Technol.*, **1993**, 27, 5, 508--513.
[6] R.C. Reid, J.M. Prausnitzand, T.K. Sherwood, *The Properties of Gases and Liquids*, 3rd ed., New York: McGraw Hill, **1977**.
[7] Kasyanova, L.Z., Extended Abstract of Cand. Sci. (Chem.) Dissertation, Ufa, **2002**