Analysis of the CSTR with two-phase flow under phase equilibrium conditions

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Abstract

A mathematical model of the flow gas–liquid continuous stirred tank reactor (CSTR) is presented under the assumption of thermodynamic equilibrium of the two-phase flow. Phase equilibrium was calculated using the Redlich–Kwong–Soave (RKS) equation of state. An efficient algorithm based on homotopy method was used to obtain a numerical solution of the system of nonlinear algebraic equations of the model. By an example of the liquid-phase hydrogenation of benzene, steadystates were analyzed in isothermal and adiabatic regimes and at partial removal of heat released as a result of exothermic reaction. It was shown that under certain conditions, a multiplicity of stationary solutions is possible due to nonlinearity of the kinetic reaction, on the one hand, and deviation of the reaction mixture properties from the ideal state, on the other hand.

Keywords: Mathematical modeling; Multiphase reactions; Phase equilibria; Thermodynamics process

1. Introduction

In a continuous stirred tank reactor (CSTR) with two-phase gas–liquid flow, a stationary composition of the phases involved in the reaction at specified kinetic laws forms as a result of chemical transformations and two phases seeking a thermodynamic equilibrium. Phase equilibrium is often calculated as a rough approximation, assuming, e.g., that the solubility of gas components in the liquid phase obeys Henry’s law and does not depend on the solution composition, and fugacity of liquid components in the reaction is negligible or described by Raoults law. In our opinion, these phase equilibrium problems of multicomponent mixtures must be solved more accurately using the modern methods of applied thermodynamics. In numerous publications, thermodynamic methods for calculation of phase and chemical equilibrium successfully supplement the traditional methods of mathematical modeling of chemical reactors and flow charts (Yablonsky et al., 1983; Shinnar, 1988; Sophos et al., 1980; Morachevsky, 1989; Bertucco et al., 1997).

For the gas–liquid systems where chemical reactions occur, conditions of phase equilibrium remain the same as for the phase equilibrium without a chemical reaction (Morachevsky, 1989). The main distinction in the description of such systems relates to the equations of balance limitations, expressing the laws of conservation of matter. For example, if no chemical reaction proceeds in the system, the laws of conservation provide for a constant total number of moles of each component distributed over the equilibrium phases. With a chemical reaction, the total number of moles of each component will follow the laws of chemical kinetics and stoichiometry, depending on the reaction step. Phase equilibrium between gas and liquid forms stationary concentrations of the reactants in the liquid phase, and thus the rate of chemical reaction in this phase. Phase equilibrium also determines the amount and composition of gas and liquid flows at the reactor outlet. For example, the flow of “dry” gas fed to the reactor is saturated with vapor components of the liquid phase in the gas–liquid system, while
the liquid phase dissolves components of the gas phase; as a result, the liquid-phase components are removed from the reactor. In some cases, this removal may be so significant that it prevents the occurrence of the stationary regime in a two-phase flow reactor in the region of actual process parameters.

The present work is aimed at analyzing the stationary states in an ideal backmixed reactor with liquid and gas flows under the assumption that the stationary regime provides thermodynamic equilibrium of the phases at the reactor outlet.

The subject of our study is the reaction of liquid-phase hydrogenation of benzene, which is currently one of the most thoroughly investigated reactions, its kinetics being presented as complex nonlinear equations (Temkin and Murzin, 1989; Van Meerten et al., 1977; Van Meerten and Coenen, 1977; Toppinen et al., 1996). These kinetic equations were written out using detailed experimental data on the mechanism of elementary reactions in the liquid phase proceeding on the slurry catalyst surface.

2. Kinetic model

The equation of benzene hydrogenation in the liquid phase can be presented as follows:

\[
C_6H_6 + 3H_2 \rightarrow C_6H_{12}.
\]

(1)

According to Toppinen et al. (1996), the reaction rate of benzene hydrogenation in the liquid phase on nickel catalyst in the temperature range of 368–398 K at pressure 2.0–4.0 MPa is described by the kinetic equation

\[
r = \frac{k_1 K_A K_H c_A c_H}{[3K_A c_A + (K_H c_H)]^{1/2} + 1} \quad \text{(mol/s/gcat.)},
\]

(2)

where

\[
k_1 = 0.0013 \exp \left[ \frac{-E}{R \left( \frac{1}{T} - \frac{1}{T_0} \right)} \right] \quad \text{(mol/s/gcat.)},
\]

(3)

\[
T_0 = 373 \text{ K}, \quad K_A = 1.831/\text{mol}, \quad K_H = 7074.51/\text{mol},
\]

(4)

\[
E = 53900 \text{ J/mol}.
\]

(5)

Here, \(c_A\) is the benzene concentration and \(c_H\) is the concentration of hydrogen dissolved in the liquid phase, mol/l.

3. Mathematical model of the reactor

3.1. Isothermal regime

Consider the isothermal regime in the benzene hydrogenation reactor at a constant pressure. Flows of liquid benzene and gaseous hydrogen are fed to the reactor. Changes in the total flow of components at the reactor outlet are caused by the chemical reaction. This flow is split into two equilibrium phases, gas and liquid. The total change of molar flows in the reactor is described by the material balance equations

\[
F_i = n_i^0 - n_i + q_i(x, T) \times m_{cat} = 0.
\]

(6)

Here \(n_i^0 = n_{iG}^0 + n_{iL}^0\) is the molar flow of the \(i\)th component fed to the reactor (g mol/s); \(n_i = n_{iG} + n_{iL}\) is the same flow at the reactor outlet; \(i = 1, 2, 3\) relates to benzene, cyclohexane and hydrogen. Indexes \(G\) and \(L\) indicate, respectively, the gas and liquid flows. Weight of the catalyst loaded to the reactor is denoted as \(m_{cat}\).

\[
q_i(x, T) = \frac{q_i}{m_{cat}}.
\]

(7)

Here \(q_i = q_{1i}(x, T)\) is the rate of the \(i\)th component consumption/formation. It is apparent for reaction (1) that \(q_1 = -r, q_2 = r\) and \(q_3 = -3r\); \(x\) stands for the vector of molar fractions of the liquid-phase components. Concentrations of benzene (\(c_A\)) and hydrogen (\(c_H\)), presented in kinetic expression (2) in units of mol/l, are converted to corresponding molar fractions \(x_1\) and \(x_3\) using relations

\[
x_1 = c_A v_{ml} \quad \text{and} \quad x_3 = c_H v_{ml}.
\]

(7)

where \(v_{ml}\) is the molar volume of the liquid phase.

Normalization of Eqs. (6) to the total molar flow at the reactor inlet

\[
S^0 = \sum_{i=1}^{N_S} \left( n_{iG}^0 + n_{iL}^0 \right)
\]

converts Eqs. (6) to the dimensionless form

\[
F_i = x_i^0 - x_i + q_i(x, T) \times \tau = 0.
\]

(8)

Here \(x_i^0 = n_{iG}^0/S^0 = x_{iG}^0 + x_{iL}^0\); \(x_i = n_i/S^0 = x_{iG} + x_{iL}\); \(\tau = m_{cat}/S^0\) (g/s/mol).

\[
\sum_{i=1}^{N_S} x_i^0 = 1, \quad \sum_{i=1}^{N_S} x_i = 1
\]

(9)

Here \(\Phi_i(x, T, P)\) and \(\Phi_i(x, T, P)\) stand for the fugacity coefficients of the \(i\)th component in liquid and gas phases as functions of molar composition of phase \(x, y\), temperature and pressure. Fugacity coefficients are calculated using the equation of state. \(S_L\) and \(S_G\) in Eqs. (9) denote the sums

\[
S_L = \sum_{i=1}^{N_S} x_{iL} = \frac{1}{S^0} \sum_{i=1}^{N_S} n_{iL},
\]

(10)

\[
S_G = \sum_{i=1}^{N_S} x_{iG} = \frac{1}{S^0} \sum_{i=1}^{N_S} n_{iG},
\]

while \(x\) and \(y\) are the \(N_S\)-dimensional vectors of the molar fractions of components in liquid and gas phases, respectively: \(x_i = x_{iL}/S_L, y_i = x_{iG}/S_G\); \(N_S = 3\) is the number of components.
The system of Eqs. (8) and (9) in isothermal isobaric regime at specified inlet flows \( z_i^0 \) and \( z_i^0 \) and parameter \( \tau \) define the problem completely. Unknown are flows \( z_i^L \) and \( z_i^G \). Solution of the problem allows determination of each component flow and the equilibrium composition of phases at the reactor outlet, \( x, y \); the fractions of gas and liquid in the total outlet flow are \( W_G = S_G/(S_L + S_G) \). \( W_L = 1 - W_G \); the coefficient of variation in the total number of moles due to chemical reaction is \( \gamma = (S_L + S_G) \). Conversions for benzene and hydrogen are determined as follows:

\[
X_C6H6 = \frac{z_0^0 - z_1^0}{z_1^0}, \quad X_H2 = 3\frac{z_0^0}{z_3}X_C6H6.
\] (11)

### 3.2. Nonisothermal regime

In the case of the nonisothermal regime of the reactor operation, the system of Eqs. (8) and (9) is supplemented by the heat balance equation:

\[
F_{2N_5+1} = Q_{\text{Heat}} - (Q_{\text{React}} - Q_{\text{Cooler}} + Q_{\text{Evap}}) = 0 \quad \text{(J/mol initial mix)},
\] (12)

where \( Q_{\text{Heat}} \) is the heat necessary for heating the initial mixture from temperature \( T^0 \) to the reaction temperature \( T \); \( Q_{\text{React}} \) is the heat evolved as a result of chemical transformations; \( Q_{\text{Cooler}} \) is the average integral heat removed from the reaction volume by a cooler; \( Q_{\text{Evap}} \) is the heat of the liquid ⇔ gas phase transitions, a negative value for evaporation of liquid components, and positive value for condensation. These heats can be calculated from the following relations:

\[
Q_{\text{Heat}} = \sum_{i=1}^{N_S} z_i^0 \bar{H}_L(T, x^0) - \bar{H}_L(T^0, x^0) + \sum_{i=1}^{N_S} z_i^0 \bar{H}_G(T, y^0) - \bar{H}_G(T^0, y^0).
\] (13)

\[
Q_{\text{React}} = -\Delta H_{\text{React}} \times r \times \tau = -\tau \times \sum_{i=1}^{N_S} q_i \bar{H}_L(T, x),
\] (14)

where \( \Delta H_{\text{React}} \) is the change in enthalpy of reaction (1) occurring in the liquid phase,

\[
Q_{\text{Evap}} = -\sum_{i=1}^{N_S} (z_i^G - z_i^G) \times \Delta \bar{H}_{L, \text{Evap}},
\] (15)

where \( \Delta \bar{H}_{L, \text{Evap}} \) is the change in enthalpy at the gas–liquid interface (J/mol).

Here \( \bar{H}_L \) and \( \bar{H}_G \) denote partial molar enthalpies of the \( i \)th component of liquid and gas, respectively, calculated at appropriate temperature and pressure with regard to their dependence on the mixture composition. By definition of partial molar values, they have dimensionality of J/mol of the \( i \)th component.

All quantities in Eq. (12), due to the normalization made above, are related to 1 mol of the initial mixture fed to the reactor. The value \( Q_{\text{Cooler}} \) is calculated as a fraction of \( Q_{\text{React}} + Q_{\text{Evap}} \), that is

\[
Q_{\text{Cooler}} = \alpha (Q_{\text{React}} + Q_{\text{Evap}}),
\] (16)

with the coefficient of proportionality \( \alpha \geq 1 \). Apparently, in isothermal regime, \( \alpha = 1 \), while in adiabatic regime, \( \alpha = 0 \).

In adiabatic regime, Eq. (12) is transformed to equality of enthalpies of the inlet flow at temperature \( T^0 \) and of the outlet flow at temperature \( T^0 \):

\[
F_{2N_5+1} = 
\begin{align*}
&\left( \sum_{i=1}^{N_S} z_i^G \bar{H}_i(T^0, P, y) + \sum_{i=1}^{N_S} z_i^G \bar{H}_i(T^0, P, y) \right) \\
&- \left( \sum_{i=1}^{N_S} z_i^G \bar{H}_i(T^0, P, y) + \sum_{i=1}^{N_S} z_i^G \bar{H}_i(T^0, P, x) \right) \\
&= 0.
\end{align*}
\] (17)

Partial molar enthalpies of components in Eqs. (13)–(17) are calculated using the thermodynamic model presented below.

### 4. Thermodynamic model

Fugacity coefficients in Eq. (9) were calculated using the Redlich–Kwong–Soave (RKS) equation of state (Soave, 1972):

\[
P = RT/(v_m - b_m) - a_m(T)/(v_m(v_m + b_m)),
\] (18)

where \( a_m, b_m \) are the mixture coefficients, and \( v_m \) is its molar volume.

Fugacity function \( f_i \) based on this model has the form

\[
\ln f_i(\eta) = \ln[m_i RT/(v_m - b_m)] + b_i/(v_m - b_m) + \frac{a_m}{RT b_m^2} \frac{\bar{z}_i}{\bar{z}_i} \ln \left( \frac{v_m + b_m}{v_m} \right) - \frac{b_m}{(v_m + b_m)},
\] (19)

where

\[
\bar{z}_i = 2 \sum_j \eta_j a_{ij}, \quad \bar{z}_i = 2 \sum_j \eta_j b_{ij} - b_m.
\]

Coefficients \( a_m \) and \( b_m \) for a mixture with specified molar composition \( \eta \) are determined as follows:

\[
a_m = \sum_{j=1}^{N_i} \sum_{i=1}^{N_s} \eta_j \eta_j a_{ij}, \quad b_m = \sum_{j=1}^{N_i} \sum_{i=1}^{N_s} \eta_j \eta_j b_{ij},
\] (20)

\[
a_{ij} = a_i(T)(0.42748R^2T_e^2/P_e),
\] (21)

\[
b_{ij} = 0.08664RT_e/P_e,
\] (22)

\[
a_{ij} = (1 - k_{ij}) \sqrt{a_{ii} a_{jj}},
\] (23)
\[ b_{ij} = (1 - c_{ij})(b_{ii} + b_{jj})/2, \]
\[ \alpha_i(T) = \left[ 1 + d_i \left( 1 - \sqrt{T/T_{ci}} \right) \right]^2, \]
\[ d_i = 0.480 + 1.574 \alpha_i - 0.176 \alpha_i^2. \]

Here \( P_{ci} \) and \( T_{ci} \) are the critical pressure and temperature of the \( i \)th component of the mixture; \( \alpha_i \) is the acentric factor.

In the above equations, \( \eta \equiv x \) for the liquid phase, and \( \eta \equiv y \) for the gas phase. Molar volumes \( v_m \) for gas and liquid phases are calculated directly from Eq. (18) as roots of cubic polynomial. Fugacity coefficients of the components of gas and liquid phases are determined as

\[ \phi_iL(x, T, P) = f_i(x, T, P)/x_i/P \quad \text{and} \quad \phi_iG(y, T, P) = f_i(y, T, P)/y_i/P. \]  

Coefficient \( k_{i,j} \) and \( c_{ij} \) in relations (23) and (24), allowing for the binary interactions of molecules, are determined from the experimental data by the equilibrium in binary systems \( C_6H_6 - C_6H_{12}, \) \( H_2 - C_6H_6 \) and \( H_2 - C_6H_{12} \) (Anikeev and Yermakova, 1998). Because of this, the RKS model adequately describes the P–V–T properties of the mixture under study. This is illustrated in Fig. 1, which shows the calculated curve of boiling temperature for benzene–cyclohexane binary mixtures at \( k_{i,j} = 0.2854 \) and \( c_{i,j} = 0.3059 \) versus benzene content in comparison with the experimental data (Sangster et al., 1988). One may see from Fig. 1 that the RKS equation describes the experimental data with high accuracy.

Partial molar enthalpies of individual components of liquid and gas mixtures are determined with the use of the known thermodynamic relations (Sandler, 1999) as

\[ H_{iL}(T, P, x) = H_i^0(T, P_0) - RT^2 \frac{\partial \ln \phi_iL(T, P, x)}{\partial T}, \]
\[ H_{iG}(T, P, y) = H_i^0(T, P_0) - \frac{1}{RT^2} \ln \phi_iG(T, P, y). \]

5. Numerical analysis of the model

The system of Eqs. (8), (9) and (12) was calculated with respect to unknown values \( z_{iL}, z_{iG} \) and \( T \) at specified pressure and values of inlet flows. Solutions were searched in parametric form depending on parameter \( \tau \).

5.1. The homotopy algorithm

It is known that the homotopy continuation methods find roots of systems of nonlinear equations by tracking the homotopy path from one or multiple starting points. Given a known point on or near a homotopy path, a path tracking algorithm follows the path by determining new points near the path (Choi et al., 1996; Allgower and Georg, 1980). The algorithm presented below is based on the method of arc length continuation. \( \tau \) was used as a homotopy parameter. The method employs the two-step “predictor–corrector” algorithm with linear step predictor according to Euler and step correction by Newton’s method (Choi et al., 1996).

Determine the \( N \)-dimensional vector of unknown quantities with dimensionality \( N = 2N_S + 1 \): \( \mathbf{u} \equiv [z_{1L}, z_{2L}, z_{3L}, z_{1G}, z_{2G}, z_{3G}, T]^T \), the composite vector with dimensionality \( N + 1 \): \( \mathbf{w} = [\mathbf{u}, \tau] \) and the vector-function \( \mathbf{F} \equiv [F_1, F_2, \ldots, F_{2N_S+1}]^T \). Then the system of Eqs. (8), (9) and (12) is presented as

\[ \mathbf{F}(\mathbf{u}, \tau) = 0. \]  

The essence of the applied method consists in parametric representation of solution (30): \( \mathbf{u} = \mathbf{u}(s), \tau = \tau(s) \), where \( s \) is the arc length of a smooth spatial curve plotted from the starting point \( s = 0 \) to the current point. As a starting solution we use point \( T = T_0, \tau = 0 \) (at \( m_{ext} = 0, S^0 \neq 0 \)). Under these conditions, the contacting gas and liquid flows come to phase equilibrium without chemical transformation. The algorithm for solving this problem at such a statement (system of equations (9)) is well known (Michelsen, 1982). Consecutive steps of the predictor in iterations are found by solving the system of linear equations:

\[ \left[ \begin{array}{c} \frac{\partial \mathbf{F}}{\partial \mathbf{w}}(s^k) \\ \frac{\partial \mathbf{F}}{\partial s}(s^k) \end{array} \right] \times \mathbf{v}^k = e_{N+1} \]  

and

\[ \frac{\partial \mathbf{w}}{\partial s}(s^k) = 0 \mathbf{v}^k \| \mathbf{v}^k \|_2. \]  

Fig. 1. Boiling temperature of benzene–cyclohexane binary mixtures vs. benzene content. Solid line—the calculation by RKS EOS, dots—experimental data (Sangster et al., 1988).
where \( k \) is the iteration number; \( \mathbf{e}_j (1 \leq j \leq N + 1) \) is the \((N + 1)\)-dimensional unit vector, its \( j \)th element being equal to unity and all other elements equal to zero. Parameter \( \sigma^k = \pm 1 \) defines the path direction, and parameter \( \delta s > 0 \) controls the length of admissible step. An approximate solution \( \mathbf{w}^{k+1} \) predicted by the predictor is determined more accurately by Newton’s method. If it is rather close to curve \( F (\mathbf{u}(s), \tau(s)) = 0 \), convergence of Newton’s method to the true solution \( \mathbf{w}^{k+1} \) is ensured and obtained by 5–6 iterations.

5.2. Conditions of existence of a solution

Within the model under consideration, the stationary mode of the reactor operation, which provides existence of a solution of set (30), takes place only when two equilibrium phases occur at the reactor outlet. In this case, the equilibrium value of the fraction of a phase, for example, of the gas phase \( W_G \) must comply with the condition

\[
0 < W_G < 1.
\]

The occurrence of condition \( W_G = 0 \) in the outlet flow is possible when the entire gas fed to the reactor is dissolved in the liquid phase. In the other extreme case, when \( W_G = 1 \), the liquid phase is completely removed from the reactor due to its evaporation to dry gas.

Condition (34) should also be met for the set of equations (30) at \( \tau = 0 \). In the example under consideration, the fulfillment of this condition consists in finding the admissible limit of the coefficient of hydrogen excess \( \chi \) at the reactor inlet, taken to be unity at the stoichiometric ratio \( n_0^1/n_0^1 = 3 \). Investigation of the starting solution showed that as \( \chi \) changes from 1 to 3 \((T = 368 K \text{ and } P = 2.0 \text{ MPa})\), the \( W_G \) value at \( \tau = 0 \) varies from 0.818 to 0.983, i.e., complies with condition (34).

6. Results of numerical analysis

6.1. Isothermal regimes

At the very beginning, it should be noted that dimensionality of the system of equations for the problem stated above for the isothermal case at \( T = T^0 = \text{const} \) decreases by unity \((N = 2N_3)\), and the heat balance equation is excluded from consideration. Parameter \( \tau \) was chosen as the "leading" parameter of continuation, so that \( j = N + 1 \) in Eq. (31).

Fig. 2(a) displays the dependencies of benzene conversion on parameter \( \tau \) at \( \chi = 1.2 \), different values of \( T \) and \( P = 2.0 \text{ MPa} \). Similar dependencies at variation of \( P \) and fixed \( T = 363 K \) are presented in Fig. 2(b).

The figures show that at certain conditions, for example at \( P = 2.0 \text{ MPa} \), \( T = 343–373 K \) or at \( T = 363 K \), \( P = 0.1–0.2 \text{ MPa} \), the \( X–\tau \) curves are S-shaped and there are three stationary solutions in the interval \([\tau^*_1, \tau^*_2]\) at the same value of \( \tau \), where \( \tau^*_1 \) and \( \tau^*_2 \) denote the values of \( \tau \) at the turning points of the curves. The solutions lying on the curve branches between two turns are unstable. Note that these solutions cannot be obtained when other methods are used instead of the homotopy method, for example, the determination method. The width of the interval of existence of unstable solutions \([\tau^*_1, \tau^*_2]\) is dependent on pressure and temperature. The region of multiple solutions may gradually disappear with increasing temperature and pressure.

To explain possible causes of the emergence of multiple stationary solutions, consider the dependencies of the reaction rate (Fig. 3(a)) and equilibrium concentration of hydrogen in the liquid phase (Fig. 3(b)) on benzene conversion at different temperatures and \( P = 2.0 \text{ MPa} \). One may see from Fig. 3(b) that the concentration of hydrogen in the liquid...
Fig. 3. (a) Reaction rate vs. benzene conversion. $P = 2.0 \text{ MPa}$. $T/\text{K}$: 1—343; 2—353; 3—363; 4—373. Dotted line 5—hydrogen solubility in the liquid phase calculated by a simplified model according to Henry’s law, $P = 1.0 \text{ MPa}$, $T = 363 \text{ K}$. (b) Hydrogen solubility in the liquid phase vs. benzene conversion. $P = 2.0 \text{ MPa}$. $T/\text{K}$: 1—343; 2—353; 3—363; 4—373.

Fig. 4. Adiabatic regimes. Benzene conversion (a) and temperature of adiabatic heating (b) vs. residence time $\tau$ at initial temperature $T_0 = 343 \text{ K}$. $P/\text{MPa}$: 1—1.0; 2—2.0; 3—3.0; 4—4.0.

A complicated nature of the reaction rate dependence on benzene conversion may be explained by the nonlinear kinetic equation of the reaction rate (2), on the one hand, and by the extremal dependence of hydrogen solubility in the benzene–cyclohexane mixture. To estimate the contribution of each of these components to the rate variation, the equation of hydrogen equilibrium in system (8) was replaced by the linear equation representing Henry’s law. In this case, the concentration of hydrogen in the liquid phase at constant $T$ and $P$ is independent of the mixture composition. Dotted lines in Figs. 2(b) and 3(a) show the calculation results in comparison with the previously obtained data. Comparison of the $\tau$ dependencies of benzene conversion shows that idealization of hydrogen solubility leads to disappearance of the stationary state’s multiplicity.

6.2. Nonisothermal regimes

First consider the adiabatic regime at a zero value of heat removal parameter $\alpha$ found from Eq. (16). The calculation results are presented in Figs. 4(a) and (b) as benzene conversion (Fig. 4(a)) and temperature of adiabatic heating $T^\text{ad}$ (Fig. 4(b)) vs. parameter $\tau$ at the initial temperature $T_0 = 343 \text{ K}$ and several pressure values. Similar to the case of isothermal regimes, multiplicity of solutions is also observed here. Unstable solutions lie on the branches of curves following the turn, and terminate when the liquid-phase flow disappears due to its complete evaporation into the gas phase. Turning points at low conversions ($\tau = \tau_{\text{sing}}$) are the singular points of the problem, i.e., when the matrix determinant in Eq. (31) vanishes. In calculations by the homotopy method,
heat may appear to be the most practical regime. Figs. 5(a) and (b) show the dependencies of benzene conversion (Fig. 5(a)) and temperature (Fig. 5(b)) on parameter \( \tau \) at various values of heat removal coefficient \( \alpha \). One may see that at insufficient heat removal, when \( \alpha \leq 0.8 \), the reactor temperature even at low conversion attains the values at which the liquid-phase flow disappears, i.e., a complete flow of liquid reactants evaporates into the gas phase. Stationary regimes possibly occur only at \( \alpha > 0.8 \), i.e., while approaching the isothermal regime.

7. Conclusions

The above model, assuming the phase equilibrium condition, is one of the approximations to the model of the system taking into account the interphase heat and mass transfer. Analysis showed that this equilibrium model provides useful information on the process character, amount and composition of gas and liquid flows at the reactor outlet. In the case of strongly nonlinear dependencies of the reaction rate on the reactants concentration, which are typical of some liquid-phase catalytic reactions, the multiplicity of stationary regimes may be expected. The multiplicity of stationary regimes and the presence of unstable solutions region for the chosen reaction of benzene hydrogenation are caused by nonlinear dependence of the reaction rate on the reactants concentration in the liquid phase, on the one hand, and by the behavior of hydrogen solubility in the benzene–cyclohexane mixture, on the other hand.

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