Mathematical modeling of the synthesis process of vinyl acetate

D Arapov¹, S Tikhomirov², S Podvalny³, V Denisenko¹ and I Avcinov²

¹Chair of Higher Mathematics and Information Technology, Voronezh State University of Engineering Technologies, 19 Revolution Avenue, Voronezh 394036, Russian Federation
²Chair of Information and Control Systems, Voronezh State University of Engineering Technologies, 19 Revolution Avenue, Voronezh 394036, Russian Federation
³Head of the Department of Automated and Computing Systems, Voronezh State Technical University, 14 Moskovsky Avenue, Voronezh 394026, Russian Federation

E-mail: arapovdv@gmail.com

Abstract. A complete mathematical modeling of the technological process of manufacturing vinyl acetate monomer by vapor-phase method has been implemented. The model is partial differential equations of the material and energy balance and catalyst aging. An algorithm for an integrated equation based on the second-order Gregg-Bulirsh-Shter rectangle symbol has been developed. The error in modeling the process is equal (CH₂COOCH=CH₂) ± 5.4% rel. for the target matter, and (CO₂) ± 6.4% rel. for the secondary substance. The kinetic coefficients of differential equations, namely the pre-exponential factors and the activation energy have been refined. The obtained data of the modeling of the vapor-phase manufacturing process of vinyl acetate are shown in the form of tables and graphic three-dimensional dependencies of quality indicators on technological parameters.

1. Introduction

Vinyl acetate (VA) is an important raw material for petrochemical synthesis. On its basis they receive a large number of valuable chemical products. Each year, the global chemical industry produces approximately 6·10⁹ tons of this product [1]. The most progressive method of VA manufacturing is its vapor-phase synthesis from the initial components (C₂H₄, O₂, CH₃COOH) using a catalytic complex based on palladium, applied to a porous carrier, resistant to acetic acid (AA) and mechanical and thermal influences. These can be aluminosilicates, silica gels, zeolites, coals and other similar substances.

The catalyst for the synthesis of VA is a compound complex of noble metals (palladium and gold) and salt AA, deposited in a finely dispersed state on a porous substrate, a catalyst carrier, which, in addition to performing the function of the substrate, changes certain characteristics of the active centers. Due to the donor-acceptor interaction of the carrier with the catalyst, the surface proton-acid characteristics of the metal, its coordination ability, and the characteristics of the crystal lattice change. The nature of the carrier significantly affects the ability of the catalytic metal to be deposited on the surface of the catalyst. The carrier is able to change the activity of the catalyst within small limits, showing a certain promoting effect.
The main catalytically active component of the catalytic complex is palladium, without which the reaction of the formation of VA is not realized. The content of palladium in catalysts is from 0.1 to 10% [2]. In addition to palladium or its salts, the catalyst contains from 1 to 30% of alkali metal acetates, which are a cocatalyst for the synthesis of VA. Potassium acetate is the most commonly used [3]. It contributes to a significant, an order of magnitude and more acceleration of the reaction of formation of VA and increases the selectivity of the catalyst.

It has been established [4] that the efficiency of a promoter is extremely dependent on its quantity in the composition of a complex catalyst. In most cases, there is a maximum activity of the catalyst with a certain content of the promoter. In the production of VA a promoter, fine gold, is added in small quantities to the catalyst, and this significantly increases [5] the stability of the catalyst and its activity.

In the manufacturing of VA by using vapor-phase method, a significant amount of liquid toxic substances are formed, which are then destroyed. But the total mass of these substances is small, approximately 1% of the mass of the manufactured VA. Carbon dioxide (CD) is formed in sufficient quantities. Therefore, in mathematical modeling of the process, it was assumed that only two substances are formed, namely VA and CD [6, 7]:

\[
\begin{align*}
C_2H_4 + \frac{1}{2}O_2 + CH_3COOH & \rightarrow CH_3-COO-CH=CH_2 + H_2O + 146 \text{ kJ}; \\
C_2H_4 + 3O_2 & \rightarrow 2CO_2 + 2H_2O + 1327.2 \text{ kJ}.
\end{align*}
\]

Over time, the mixed catalyst undergoes structural changes, its reactivity and the yield of VA decreases. To maintain the reacting power of the mixed catalyst at the level of profitability of the entire production, the VA manufacturing process is to be realized with a low rise in temperature – from 140 to 200 °C per 1 year.

A significant number of papers, for example [8–14], are devoted to the study of the mechanism of VA synthesis based on ethylene. However, they do not give a mathematical description of this process.

A relatively small number of publications [1, 6, 7, 15-18] have been devoted to the modeling and control of the synthesis of VA based on AA, ethylene and oxygen. In [15], a mathematical model of VA synthesis based on ethylene in the form of ordinary differential equations of matter and heat balance is presented without deriving kinetic equations. The model is used to monitor and control the process in existing production unit. The regressive fractional linear model of this process on the basis of the domestic catalyst is given in [1, 7], and essentially nonlinear models with an estimated error are described in [15-17]. In connection with the development of catalytic complexes with new properties [1, 7, 16-18], parameters and structure and kinetic model [15] are subject to refinement.

In industrial production of VA, the most important indicator [15] of catalyst efficiency and profitability of the entire production is the removal of VA expressed in terms of its amount in grams, obtained from 1 liter of catalyst charged into the reactor per hour. Further study of the synthesis of VA based on ethylene, automatic control and optimization of its quality indicators is difficult without creating a complete mathematical description of the process based on differential equations of the kinetics of the partial derivative process, algorithms for solving model equations and their software implementations. In this regard, this work, devoted to solving this problem, is relevant.

2. Theoretical analysis

2.1. Kinetic equations of the model

It is assumed in [15] that reactions of formation of VA and CD have first and second orders, respectively. The rates of these reactions are described by equations:

\[
W_1 = k_1 P_{O_2} Q; \quad W_2 = k_2 P_{O_2}^2; \quad P_{O_2} = n_{O_2} P;
\]

where \( k_1 \) and \( k_2 \) are Arrhenius constants for the reaction rates of the formation of VA and CD; \( P_{O_2} \) is partial pressure of oxygen; \( n_{O_2} \) its mole fraction, \( P \) is pressure in the reactor; \( Q \) is catalytic complex activity index.
Let us express the value \( n_{O_2} \) through oxygen conversions for the formation of VA and CD and the molar ratios of ethylene and oxygen to the oxygen at the reactor inlet. Conversions of oxygen into the formation of VA and CD are respectively equal:

\[
X_1 = \frac{N_{VA}}{N_{O_2}} \quad X_2 = \frac{N_{CD}}{N_{O_2}},
\]

where \( X_1, X_2 \) are the conversions of oxygen; \( N_{O_2}^0 \) is the number of moles of oxygen at the reactor inlet; \( N_{VA}^0, N_{CD}^0 \) are the number of oxygen moles, which had gone to the formation of VA and CD, respectively. Mole ratios of ethylene (\( \alpha_1 \)) and AA (\( \alpha_2 \)) to oxygen at the reactor inlet are calculated by formulas:

\[
\alpha_1 = \frac{N_{E_h}^0}{N_{O_2}^0} \quad \alpha_2 = \frac{N_{AA}^0}{N_{O_2}^0},
\]

where \( N_{E_h}^0, N_{AA}^0 \) are the number of moles of ethylene and AA at the reactor inlet.

Using the stoichiometric equations of the formation of the target and by-products [6, 7, 15], we calculate the mole expenditures of the participants in the reactions at the time \( t \):

\[
\begin{align*}
N_{O_2}(t) &= N_{O_2}^0 - N_{O_2}^{E_h} - N_{O_2}^{AA} - N_{O_2}^{VA} - N_{O_2}^{CD}, \\
N_{E_h}(t) &= 2N_{E_h}^{O_2}, \\
N_{AA}(t) &= N_{AA}^0 - 2N_{AA}^{O_2}, \\
N_{VA}(t) &= 2N_{E_h}^0 - \frac{1}{3}N_{O_2}^0 - 2N_{E_h}^{O_2} - 2N_{AA}^{O_2}, \\
N_{CD}(t) &= \frac{2}{3}N_{O_2}^{CD}, \\
N_{H_2O}(t) &= \frac{2}{3}N_{O_2}^{CD} + 2N_{E_h}^{O_2} \\
\end{align*}
\]

We express the right-hand sides of (4) through the conversions \( X_1, X_2 \) and the molar ratios \( \alpha_1 \) and \( \alpha_2 \):

\[
\begin{align*}
N_{O_2}(t) &= N_{O_2}^0 - (X_1 + X_2)N_{O_2}; \\
N_{E_h}(t) &= 2X_1N_{O_2}; \\
N_{AA}(t) &= \alpha_2N_{O_2}^0 - 2X_1N_{O_2}^0; \\
N_{VA}(t) &= \alpha_1N_{O_2}^0 - \frac{1}{3}X_2N_{O_2}^0 - 2X_1N_{O_2}^0; \\
N_{CD}(t) &= \frac{2}{3}X_2N_{O_2}^0; \\
N_{H_2O}(t) &= \left(\frac{2}{3}X_2 + 2X_1\right)N_{O_2}^0. \\
\end{align*}
\]

After adding the left and right sides of (5) we obtain:

\[
\sum N(t) = (1 + \alpha_1 + \alpha_2 - X_1)N_{O_2}^0.
\]

Then the mole fraction of oxygen will be:

\[
n_{O_2} = \frac{N_{O_2}(t)}{\sum N(t)} = \frac{1 - X_1 - X_2}{1 + \alpha_1 + \alpha_2 - X_1}.
\]

Assume that the molar flow and pressure along the length of the reactor \( l \) are constant:

\[
V(l) = V^0 = \text{const}; \quad P(l) = P = \text{const}.
\]

Then there are the equations of material balance for the elementary volume of a reactor with an internal section of a tube $S$ equal to $dv = Sdl$:

\[
\begin{align*}
\frac{dN_{O_2}^{\text{VA}}}{dl} &= \frac{1}{2} W_{\text{VA}} dv \\
\frac{dN_{O_2}^{\text{CD}}}{dl} &= \frac{3}{2} W_{\text{CD}} dv
\end{align*}
\]

(9)

or taking into account (7) and (9):

\[
\begin{align*}
V_0 C_0^O dX_1 &= \frac{1}{2} W_{\text{VA}} Sdl \\
V_0 C_0^O dX_2 &= \frac{3}{2} W_{\text{CD}} Sdl
\end{align*}
\]

(10)

where $C_0^O$ is the initial concentration of oxygen, mol/mol.

Let us express:

\[
A = \frac{S}{V_0 C_0^O} = \frac{\pi d_0^2}{4V_0 C_0^O},
\]

(11)

where $d_0$ is the internal section of the reactor tube, m.

Substituting (11) into (10) we obtain the system of kinetic equations of the mathematical model:

\[
\frac{\partial X_1}{\partial l} = 0.5 \cdot A \cdot n_{O_2} \cdot k_1 \cdot Q, \quad l = [0, L]
\]

(12)

\[
\frac{\partial X_2}{\partial l} = 1.5 \cdot A \cdot n_{O_2} \cdot p^2 \cdot k_2 \cdot Q,
\]

(13)

where $L$ is the length of the reactor tube filled with catalyst.

We supplement (12) and (13) with the equations of heat transfer and dynamics of catalyst aging:

\[
\frac{\partial T}{\partial l} = \frac{S}{V_0 C_p} \left( (\Delta H_1 W_1 + \Delta H_2 W_2) - \frac{M \pi d \cdot k_f}{S \cdot 3600} (T - T_{cool}) \right);
\]

\[
\frac{\partial Q}{\partial \tau} = -Q^{1.755} \cdot k_1 (T) ; \tau \in \left[ \tau_0, \tau_f \right],
\]

(14)

(15)

$\Delta H_1, \Delta H_2$ are the thermal effects of reactions of formation of VA and CD; $C_p$ is the heat capacity of the vapor-gas mixture at the reactor inlet; $M$ is the number of tubes in the reactor; $d$ is the average diameter of the reaction tube; $d_0$ is the outer diameter of the tube; $k_f$ is the heat transfer coefficient; $T_{cool}$ is the absolute temperature of the refrigerant is found from the solution of the equation:

\[
P_{cool} = 22.064 \exp \left( \frac{-7.85823 \xi + 1.8399 \xi^{1.5} - 11.7811 \xi^3 + 22.6405 \xi^{3.5} - 15.9393 \xi^4 + 1.77516 \xi^{7.5}}{\tau_{cool}} \right),
\]

(16)

where $P_{cool}$ is the absolute pressure of saturated water vapor, MPa; $\xi = 1 - \tau_{cool}$; $\tau_{cool}$ is the reduced temperature $\tau_{cool} = T_{cool} / 647.14$. Equation (16) is valid for the saturated water vapor temperature range of 100-300 °C and the degree of its dryness 0.7-1.0. In the simplest case, it can be determined from the Antoine equation for water vapor:

\[
T_{cool} = \frac{3737.4}{11.595 - \ln P_{cool}} - 50.
\]

(17)

In the equations (12)-(15), the rate constants of the reactions are equal to:

\[
k_j(T) = \exp \left( A_j - \frac{E_j}{T} \right) , j = 1,3,
\]

(18)
where $A_j$ is the pre-exponential $j$ reaction factor; $E_j$ is the activation energy.

Initial and Boundary Conditions:

$$X_1(0,r) = X_2(0,r) = 0; T(0,r) = T_0(\tau); Q(l,\tau_0) = Q_0(l). \quad (19)$$

Equation (15) is analytically integrated:

$$Q(l,\tau) = \left( Q_0^{0.755} + 0.755 \int_{\tau_0}^{\tau} k_3(T) d\tau \right)^{-1.3245} \quad (20)$$

In the general form, taking into account (20), the reactor equation is written as follows:

$$\frac{dY}{dl} = f\left\{ Y, Q\left[ \int_{\tau_0}^{\tau_3} k_3(T) d\tau \right] \right\}, \quad \text{where} \quad Y = \begin{pmatrix} y_1 \\ y_2 \\ y_3 \\ T \end{pmatrix}. \quad (21)$$

2.2. Algorithm for integrating the equations of kinetics

To integrate (20) and (21), the Gregg-Bulirsch-Shter method [19] of the second-order approximation was chosen, which has strong stability and provides accuracy to 3-4 significant digits for a sufficiently large integration step. As applied to the integral (20), the method of rectangles has the form:

$$Q(l,\tau_m) \approx Q^{m+1} = Q\left[ S^m(l) + h, K_3 \left( \frac{T^m + T^{m+1}}{2} \right) \right], \quad \int_{\tau_0}^{\tau} K_3(T) dt \approx S^m(l) = S^{m-1}(l) + h, K_3 \left( \frac{T^m + T^{m-1}}{2} \right);$$

$S^0 = 0.$

For (21), the difference scheme will be written as follows:

$$Y_{m+1}^{n+1} - Y_n^m = hf\left\{ \frac{Y_{m+1}^n + Y_{m+1}^{n+1}}{2}, Q[ S^m(l_n + \frac{1}{2}) + h, K_3 \left( T^m(l_n + \frac{1}{2}) + \frac{1}{2} (T_{m+1}^n + T_{m+1}^{n+1}) + \right. \right. \right.$$

$$\left. \left. \left. \frac{1}{2} (T_{m+1}^n + T_{m+1}^{n+1}) \right) \right) \right), \quad (22)$$

here $Y_m^n = Y(l_n, \tau_m).$

The implementation of the implicit difference scheme (22) with respect to equations (12-14) and (20) is realized by reducing the system of 3 nonlinear equations (22) to one equation with respect to $T_{m+1}^n.$ To this end, we write (14) in the form:

$$\frac{dT}{dl} = \frac{1}{V_0 C_p} \left[ \frac{2S}{A} \left( A^l dX_1 / dl + H_2^l dX_2 / dl \right) - b[T - T_0], \quad (23)$$

where $b = M \pi \cdot d_1 \cdot K_T / 3600.$

The difference scheme (22) for equations (12), (13), (23) has the form (we omit the time indices $m$ for $Y$ and $Q$ for brevity):

$$Y_{1,n+1} - Y_{1,n} = \frac{1}{5} \cdot h \cdot A \cdot P \cdot K_1 \left( \frac{Y_{3,n+1} + Y_{3,n}}{2} \right) \left( 2 - Y_{1,n+1} - Y_{2,n+1} - Y_{1,n} - Y_{2,n} \right) \cdot Q \quad (24)$$

$$Y_{2,n+1} - Y_{2,n} = \frac{1}{5} \cdot h \cdot A \cdot P^2 \cdot K_2 \left( \frac{Y_{3,n+1} + Y_{3,n}}{2} \right) \left( 2 - Y_{1,n+1} - Y_{2,n+1} - Y_{1,n} - Y_{2,n} \right)^2 \cdot Q \quad (25)$$
\[ Y_{3,n+1} - Y_{3,n} = \frac{h}{V_0 C_p} \left[ 2S \left( \Delta H_1 \left( Y_{1,n+1} - Y_{1,n} \right) + \frac{\Delta H_2}{3} \left( Y_{2,n+1} - Y_{2,n} \right) \right) - b \left( \frac{Y_{3,n+1} + Y_{3,n}}{2} - T_s \right) \right] \]  

(26)

Having squared (24) and having divided (25) by the equality obtained, we have:

\[ \frac{Y_{2,n+1} - Y_{2,n}}{(Y_{1,n+1} - Y_{1,n})^2} = \frac{6K_2}{hAK_1^3 Q} \tag{27} \]

Having expressed the difference \((Y_{1,n+1} - Y_{1,n}) = Z\) out of (27) we obtain:

\[ Y_{2,n+1} - Y_{2,n} = \frac{6K_2}{hAK_1^3 Q} Z^2 \tag{28} \]

Substituting (28) into (24) we obtain the quadratic equation with respect to \(Z\):

\[ 2Z \left[ 2 + 2(\alpha_1 + \alpha_2) - Z - 2Y_{1,n}\right] = hAPK_iQ \left[ 2 - Z - \frac{6K_2}{hAK_1^3 Q} Z^2 - 2(Y_{1,n} + Y_{2,n}) \right] \]

or \(AQ \cdot Z^2 + BQ \cdot Z - CQ = 0\),

(30)

where \(A = 6P \cdot K_2 \cdot K_i - 2; \ B = 4 \cdot Y_d + h \cdot A \cdot P \cdot K_i \cdot Q; \ C = 2 \cdot h \cdot A \cdot P \cdot K_i \cdot Q \cdot Y_i; \ Y_d = 1 + \alpha_1 + +\alpha_2 - Y_{1,n}; \ Y = 1 - Y_{1,n} - Y_{2,n}.\) Solving (30), omitting the smallest (negative root) and freeing from irrationality in the numerator, we obtain:

\[ Z = 2CQ / (BQ + \sqrt{BQ^2 + 4AQ \cdot CQ}) \; \tag{31} \]

The coefficients (31) depend only on \(Y_{3,n+1} = T_{n+1}\). Substituting (28) and (31) into (26) we obtain one equation with one unknown \(T_{n+1}:

\[ V_0 C_p(T_{n+1} - T_s) = \frac{2S}{A} \left[ \Delta H_1 Z + \frac{2\Delta H_2 K_2}{hAK_1^3} Z^2 \right] - h b \left( \frac{T_{n+1} - T_s}{2} - T_{cool} \right), \]

which for the method of simple iterations is more convenient to be transformed to the form:

\[ T_{n+1} = \left( A_i \cdot \frac{Z^2 + B_i \cdot Z + C_i}{D_i} \right) / D_i, \]

where \(A_i = 4S \Delta H_2 / hA^2; \ B_i = 2S \Delta H_1 / A; \ C_i = V_0 C_p Y_{3,n} + h b \left( T_{cool} - \frac{T_s}{2} \right); \ D_i = V_0 C_p + \frac{h b}{2}.\) As a result, we obtain a formula for calculating the iterations:

\[ T_{n+1}^i = \left( A_i \cdot \frac{K_2(T')^2}{K_i^2(T')} Z^2(T') + B_i \cdot Z(T') + C_i \right) / D_i, \; i = 1, 2 \tag{32} \]

As a zeroth approximation, values are taken at the previous step of integration or the results of quadratic extrapolation:

\[ T_{n+1}^0 = \begin{cases} T_s, & n = 0, 1; \\ T_{n-1}^0 + \frac{3(T_n - T_{n-1}) + T_{n-2}}{3}, & \text{with } n > 2. \end{cases} \tag{33} \]

The results of a numerical experiment in the field of variation of the regime parameters of the process showed the sufficiency of two iterations to achieve accuracy up to 4 significant digits when choosing the initial approximation by formulas (33) and an acceptable integration step.

3. Research results and discussion
The software package that implements the mathematical model of VA synthesis is implemented in C# language in MS Visual Studio 2010 environment, in which the system of differential equations (12)-(15) is solved by the method of rectangles. The implicit equation (16) is solved by dividing the segment by 1.13.
Parametric identification of the mathematical description was carried out by the genetic algorithm and by the Hook-Jeeves method [16], the required constants are the pre-exponential factors or (and) activation energies in the Arrhenius equation (18). As a target function, we take a quadratic criterion of the deviation of the calculated values of the VA and DC outputs from the experimental ones:

$$\sum_{n=1}^{N} \sum_{k=1}^{2} \left(1 - \frac{B_{bn}}{B_{kn}}(A,E)\right)^2 \rightarrow \min A,E$$

(34)

where $B_{bn}$, $B_{kn}$, respectively, are the calculated and measured value of the output of the $k$ product of the synthesis of VA in the $n$ experiment; $N$ is the number of experiments; 2 is the number of basic VA synthesis products used for identification. The search is based on the pre-exponential factors $A$ and (or) the activation energies $E$. The initial values of the activation energies and the pre-exponential factors are taken from [15]: $A_1 = 22.75$; $E_1 = 7140$; $A_2 = 27.6$; $E_2 = 10000$; $A_3 = 21.3$; $E_3 = 11900$.

Table 1 gives the refined values of the kinetic parameters of the model for the synthesis of VA. The average relative error of the model is: $\pm 5.4\%$ for vinyl acetate, $\pm 6.4\%$ for carbon dioxide.

Figures 1 and 2 show the results of the software implementation of the VA synthesis model. The program requests the following parameters: the length of the run of the reactor in days, the time step in days and the number of nodes of the difference scheme for solving differential equations. The results of the calculations are the values of conversions $X_1$, $X_2$, the temperature of the reaction mixture along the length of the reactor equal to 5.85 m and catalyst selectivity and VA take off, which are calculated by the formulas:

| $j$ | $E_j$ | $A_j$ |
|-----|-------|-------|
| 1   | 7090  | 16.878|
| 2   | 9600  | 22.1631|
| 3   | 12000 | 21.5687|

Table 1. Values of the kinetic parameters for (18)

Figure 1. Calculation of the synthesis of vinyl acetate by the method of rectangles with Length of run 5 of days.

Figure 2. Calculation of the synthesis of vinyl acetate by the method of rectangles with Length of run 360 days.
\[ S = \frac{6 \cdot 100\% \cdot X_2}{6 + X_2 / X_1}; \quad S_k = \frac{2X_1 \cdot F_o \cdot 86 \cdot 1000}{22.4 \cdot V_c} \],

where \( F_o \) oxygen consumption in the reactor, \( \text{nm}^3/\text{h} \); \( V_c \) catalyst volume equal to 22381 \( \text{m}^3 \); 86 molecular mass VA \( \text{kg/mol} \). With the increase in the run time of the synthesis reactor, the selectivity of the process decreases, and the VA output is significantly reduced.

The 3D graphical dependences of the VA formation rate (catalyst activity) and the catalyst selectivity on the ethylene to acetic acid ratio, temperature and pressure in the reactor, the volumetric supply of the gas vapor mixture and the catalyst operation time calculated by model (12)-(15) are shown in Figures 3-8.

**Figure 3.** Dependence of the specific rate of formation of acetate on the ratio of ethylene/AA and temperature at an oxygen concentration of 6.6%, pressure of 0.91 MPa, volumetric flow steam-gas mixture 7900 h\(^{-1}\), operating time 2800 h.

**Figure 4.** The dependence of the rate of formation of vinyl acetate on the pressure and volumetric flow calibration gas when the oxygen concentration of 6.6%, a temperature of 160 °C, with respect to the ethylene/AA ratio equal to 3.9.

**Figure 5.** The dependence of the rate of formation of vinyl acetate on oxygen concentration and time operation at a pressure of 0.91 MPa, volumetric feed of steam-gas mixture 7900 h\(^{-1}\), a temperature of 160 °C, with respect to the ethylene/AA ratio equal to 3.9.

**Figure 6.** The dependence of selectivity on temperature and the ethylene/AA ratio when the oxygen concentration of 6.6%, a pressure of 0.91 MPa, volumetric feed of steam-gas mixture 7900 h\(^{-1}\), working time of catalyst 2800 h.
Figure 7. The dependence of selectivity on pressure and volumetric feed of steam-gas mixture at an oxygen concentration of 6.6%, a temperature of 160 °C, ethylene/AA ratio equal to 3.9, operating time 2800 h.

Figure 8. Dependence of selectivity on oxygen concentration and operating time, at a pressure of 0.91 MPa, volumetric feed of steam-gas mixture 7900 h⁻¹, temperature 160 °C, ethylene/AA ratio equal to 3.9.

The dependence of the VA formation rate on the ethylene / acetic acid ratio (Figure 3) and on the absolute pressure in the reactor (Figure 4) is of an extreme nature. Similarly, the selectivity of the catalyst depends on these parameters (Figure 6 and Figure 7). With increasing temperature, the rate of VA formation increases exponentially (Figure 3), and the selectivity decreases (Figure 6). With an increase in the volumetric supply of the gas-vapor mixture (Figure 4) and its oxygen content (Figure 5), the VA yield also increases, but the selectivity of the catalyst decreases (Figure 7). Over time (Figure 5 and Figure 8), both the VA yield and the selectivity gradually decrease, due to the aging of the catalyst.

4. Conclusion

Based on the physicochemical laws of ethylene acetoxylation for VA synthesis, a complete mathematical model of this process has been developed and investigated in the form of partial differential equations describing the balance of substances, heat balance and changes in the activity of the catalytic complex. The kinetic parameters of the model, the pre-exponential factors and activation energies in the Arrhenius equations have been refined. The error of the model is: for VA ± 5.4% rel., for CD ± 6.4% rel. The algorithm for integrating differential equations of models based on the Gregg-Bulirsch-Shter method of rectangles has been developed. A software implementation of the synthesis model has been created, it allows calculating changes in the technological parameters and technical and economic parameters of the process along the length of the reactor and the catalyst operation time.

References

[1] Voskanyan P S 2010 Effect of the amounts and proportions of active components on the activity and selectivity of a catalyst for vinyl acetate synthesis by gasphase ethylene Acetoxylation Catalysis in Industry 2 167–172
[2] Ioan N and Colling Ph M US Patent No. 5,859,287 (January 12, 1999)
[3] Hagemeyer A, Werner H, Dingerdissen U, Kühlein K, Dambeck G, Geiss G, Rutsch A and Weidlich S DE Patent No. 0058008 (October 05, 2000)
[4] Magaril R Z 1976 Theoretical bases of chemical refining processes [in Russian – Teoreticheskie osnovy himicheskih processov pererabotki nefti] (Moscow: Chemistry)
[5] Hagemeyer A, Werner H and Dingerdissen U DE Patent No. 19721368 (November 26, 1998)

[6] Boyadzhyan V K, Ertyosyan V K, Tatevosyan A V, Alaverdyan G SH and Sergeeva S N 1987 Production of vinyl acetate based on ethylene [in Russian – Proizvodstvo vinilacetata na osnovie etilena] (Moscow: NIITEKHIM)

[7] Vardanyan D V, Litvintsev I Y, Sapunov V N, Voskanyan P S, Ertyosyan V Y and Sergeeva S N 2003 Mathematical model of the process of vinyl acetate production by vapor-phase acetoxylation of ethylene Chem. Ind. nowadays 3 50–54

[8] Al-Megren H and Xiao T 2016 Petrochemical Catalyst Materials, Processes, and Emerging Technologies (IGI Global) p 539

[9] Calaza F, Mahapatra M, Neurock M and Tysoe W T 2014 Disentangling ensemble, electronic and coverage effects on alloy catalysts: Vinyl acetate synthesis on Au/Pd(111) J. of Catalysis 312 37–45

[10] Hanrieder E K, Jentys A and Lercher J A 2016 Impact of alkali acetate promoters on the dynamic ordering of PdAu catalysts during vinyl acetate synthesis J. of Catalysis 333 71–77

[11] Huang Y, Dong X, Yu Y and Zhang M 2017 Kinetic Monte Carlo study of vinyl acetate synthesis from ethylene acetoxylation on Pd(100) and Pd/Au(100) Applied Surface Science 423 793-799

[12] Kuhn, M, Jeschke J, Schulze S, Hietschold M, Lang H and Schwarz T 2014 Dendrimer-stabilized bimetallic Pd/Au nanoparticles: Preparation, characterization and application to vinyl acetate synthesis Catalysis 57 78–82

[13] Mingshu C and Goodman D W 2008 Promotional Effects of Au in Pd-Au Catalysts for Vinyl Acetate Synthesis Chin J Catal 29(11) pp 1178–1186

[14] Pohl M-M, Radnik J, Schneider M, Bentrup U, Linke D, Brückner A and Ferguson E 2009 Bimetallic PdAu–Koac/SiO2 catalysts for vinyl acetate monomer (VAM) synthesis: Insights into deactivation under industrial conditions Journal of Catalysis 262 314–323

[15] Petrov S M, Kuritsyn V A, Khromykh E A and Arapov D V RF Patent No. 2,184,725 (July 10, 2002)

[16] Arapov D V, Karmanova O V, Tikhomirov S G and Denisenko V V 2017 Software-algorithmic complex for the synthesis of catalyst of ethylene acetoxylation process. Int. Multidisciplinary Sci. GeoConf. Surveying Geology and Mining Ecology Management, SGEM 17, Inform., Geoinformatics and Remote Sensing, pp 587–594 https://doi.org/10.5593/sgem2017/21/S07.075

[17] Arapov D V, Skrypnikov A V, Denisenko V V and Chernyshova E V 2018 Mathematical modeling of the process of acetyloxylation of ethylene u asing the domestic catalyst Vestnik of the Voronezh State University of Engineering Technologies 80(1) 124–128 https://doi.org/10.20914/2310-1202-2018-1-124-128

[18] Voskanyan P S 2013 Effect of the nature of a support on the catalytic activity of a palladium catalyst in the synthesis of vinyl acetate by gasphase ethylene acetoxylation Catalysis in Industry 5 90–97

[19] Modern numerical methods for ordinary differencial equations 1976 Edited by G. Hall and J.M. Watt. (Clarendon Press. Oxford)