

Kinetic Investigation of Consecutive-Parallel Reactions in the Non-Catalytic Process of Ethylene Oxide Hydrolysis

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ABSTRACT. A large class of consecutive-parallel addition reactions with a large number of steps has been considered. The system of differential equations describing the kinetics of consecutive-parallel reactions in the non-catalytic process of ethylene oxide hydrolysis has been investigated. By a series of assumptions it is possible to obtain the analytical solution for the distribution of reaction products at non-zero initial conditions. The analytical solution of differential equations as a function of time has been obtained. The comparison between the solutions of the kinetics model with the reported experimental data has shown its sufficient adequacy.

KEYWORDS: consecutive-parallel reactions, ethylene oxide hydrolysis, chemical kinetics.

1. Introduction

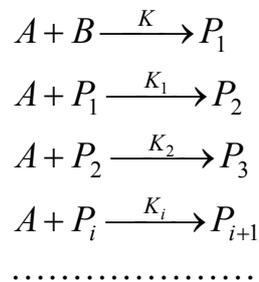
Consecutive-parallel reactions are widely used in the technology of organic synthesis for the production of different products. The main aspect of this class of reactions is the formation of a spectrum of desired products and byproducts. This class of reactions includes: Polyoxoethylation [1], acidic polymerization of olefins [1,2], chlorination [1, 3, 4, 5, 6, 7], fluorination [8, 9], alkylation [1, 10, 11], hydrogenation [3, 12] and sulfonation [13]. The kinetics of most of these processes has been studied [3-14]. From all this class of processes, it is possible to discharge reaction of ethylene glycol synthesis [15]. The non-catalytic process of ethylene oxide (EO) hydrolysis is the most widespread way of ethylene glycol synthesis, because it is the simplest and economically justified [16]. The reactions products include: mono-, di-, tri-, tetra-, and polyethylene

glycols, which are valuable chemicals. Monoethylene glycol (MEG) is used as antifreezing liquid for different kinds of engines, as a plastifier, and as a solvent [15]. Diethylene glycol (DEG) can be used as a solvent, a plastifier and a fogger [17].

In this work, we report the kinetics of consecutive-parallel reactions using the non-catalytic process of ethylene oxide hydrolysis as a model. There are various views on the suggestions concerning the mechanism of the non-catalytic process of ethylene oxide hydrolysis reaction. So the set of differential equations describing the kinetics of this reaction is in many forms. Lebedev et al. had proposed an equation's system to calculate the quantity of the reaction's products [18,19]. Natta and Mantica had proposed another solution [20]. A similar solution was obtained by Gekhtman [3]. A more general form was obtained by Weibull and Nycander [21]. All of these forms are obtained by integrating the system of differential equations at zero initial conditions. In this work an analytical solution for distribution of reaction's products at non-zero initial conditions has been proposed.

2. Kinetic investigation of multi-step consecutive-parallel reactions

The elementary steps of the consecutive- parallel reactions are the following:



The kinetic equations can be described as follows:

$$\begin{aligned}
 \frac{dX}{d\tau} + K \cdot X [Y + m_1 \cdot X_1 + m_2 \cdot X_2 + m_3 \cdot X_3 + \dots] &= 0 \\
 \frac{dY}{d\tau} + K \cdot X \cdot Y &= 0 \\
 \frac{dX_1}{d\tau} + K \cdot X \cdot [m_1 \cdot X_1 - Y] &= 0 \\
 \frac{dX_2}{d\tau} + K \cdot X \cdot [m_2 \cdot X_2 - m_1 \cdot X_1] &= 0 \\
 &\dots\dots\dots
 \end{aligned} \tag{1}$$

$$\sum_{i=1}^{\infty} x_i = C^0 - y \quad (6)$$

$$\text{where: } C^0 = 1 + \sum_{i=1}^{\infty} x_i^0$$

This equation holds true for a finite number of reaction steps n if x_n is small comparing with $\sum_{i=1}^{n-1} x_i + y$. So the system of equations (5) can be written as follows:

$$\begin{aligned} \frac{dx}{dt} + [y \cdot (1 - m) + m \cdot C^0] &= 0 \\ \frac{dy}{dt} + y &= 0 \\ \frac{dx_1}{dt} + [m \cdot x_1 - y] &= 0 \\ \frac{dx_2}{dt} + m \cdot [x_2 - x_1] &= 0 \\ &\dots\dots\dots \\ \frac{d\Theta}{dt} - \frac{1}{C_p \cdot \rho} \cdot \left[(-\Delta H) \cdot y + m \cdot (C^0 - y) \cdot \sum_{i=1}^{\infty} (-\Delta H_i) \right] &= 0 \end{aligned} \quad (7)$$

The general solution can be presented as:

$$\begin{aligned}
y &= \exp(-t) \\
x(t) &= (m-1) \cdot [1 - \exp(-t)] - m \cdot C^0 \cdot t + x^0 \\
x_1(t) &= \frac{1}{m-1} \cdot [\exp(-t) - \exp(-m \cdot t)] + x_1^0 \cdot \exp(-m \cdot t) \\
x_{i+1}(t) &= \frac{m}{m-1} \cdot \left[x_i^*(t) - \frac{1}{m} \cdot \exp(-m \cdot t) \cdot \frac{1}{i!} \cdot (m \cdot t)^i \right] + \\
&+ \exp(-m \cdot t) \cdot \left[\sum_{k=1}^{i+1} x_k^0 \cdot \frac{1}{(i-k+1)!} \cdot (m \cdot t)^{i-k+1} \right] \\
i &= 1, 2, 3, \dots
\end{aligned} \tag{8}$$

where: $x_i^*(t) = x_i(t) - x_i^0 \cdot \exp(-m \cdot t)$, $i = 1, 2, 3, \dots$ - the solution at zero initial conditions.

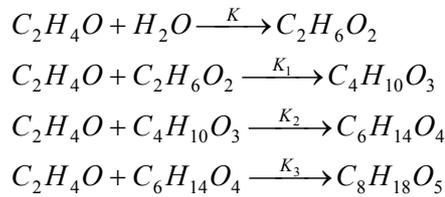
A similar solution at zero initial conditions on x_i had been reported [18], which is a particular case of our work. Moreover, such solution does not include calculations for reactors with recycles.

The final distribution of products can be obtained, if the left side of the second equation of the system (8) equals zero, i.e. $x(t) = 0$, then:

$$0 = (m-1) \cdot [1 - \exp(-t_f)] - m \cdot C^0 \cdot t_f + x^0 \tag{9}$$

By solving equation (9) for t_f and substituting it in remaining equations of the system (8) it is possible to obtain values for y^∞ , x_1^∞ , x_2^∞ , \dots etc.

Let's consider the goodness of the proposed solution on the non-catalytic process of EO hydrolysis as a model of consecutive-parallel reactions. The elementary steps of the non-catalytic process of EO hydrolysis were presented as follows [24]:



The rate constant of the first step (K) as a function of temperature was determined by Miki et al. as $K = 2.88 \cdot 10^5 \cdot [H_2O]_0^2 \cdot \exp(-21000/RT)$ [23], where $[H_2O]_0^2$ is the initial concentration of water. An equation of the form $K = 7.123 \cdot 10^8 \cdot \exp(-21193/RT)$ was suggested [24]. The ratio of rate constants $\frac{K_1}{K}$, $\frac{K_2}{K}$ and $\frac{K_3}{K}$ were determined as 2.0, 2.0, 2.0 respectively [23] and 2.946, 3.229, 3.114 respectively [24]. In this work the ratio of rate constants are assumed to be equal to the average value, i.e. $m = \frac{K_i}{K} = 3.096$.

The adequacy of the solution we have obtained to the previously obtained experimental data [17] has been checked. Fig.1, Fig.2, and Fig.3 illustrate the comparison of experimental data with the solution of the kinetic model for MEG,

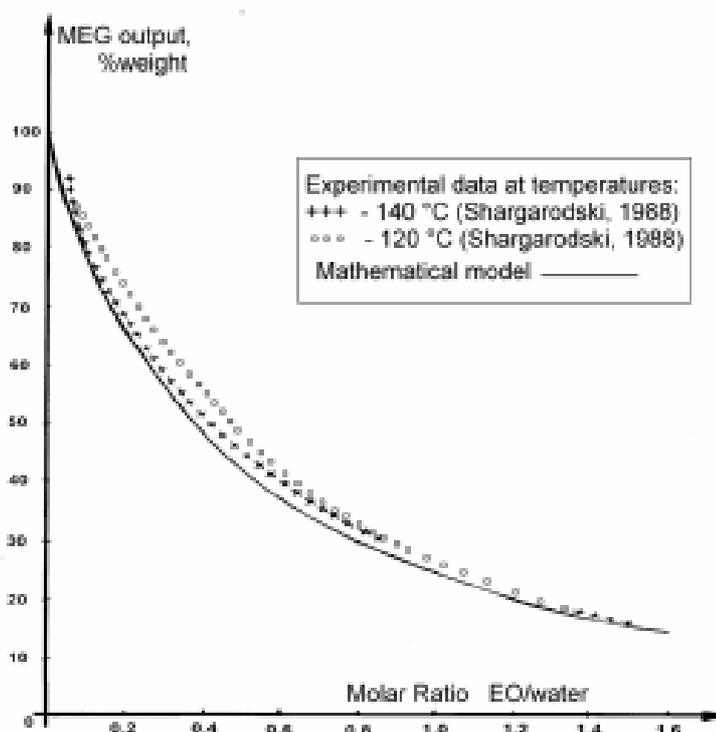


Fig.1 Distribution of monoethylene glycol output.

The enthalpies of all reaction steps are assumed to be equal [17], i.e. $(-\Delta H_1) \cong (-\Delta H_2) \cong \dots$

Then the equation of heat balance can be written as:

$$\frac{d\Theta}{dt} - \alpha \cdot [(1-m) \cdot y + m \cdot C^0] = 0 \quad (10)$$

Where: $\alpha = \frac{(-\Delta H)}{C_P \cdot \rho}$

By comparing equation (10) with the first equation of system (7), the

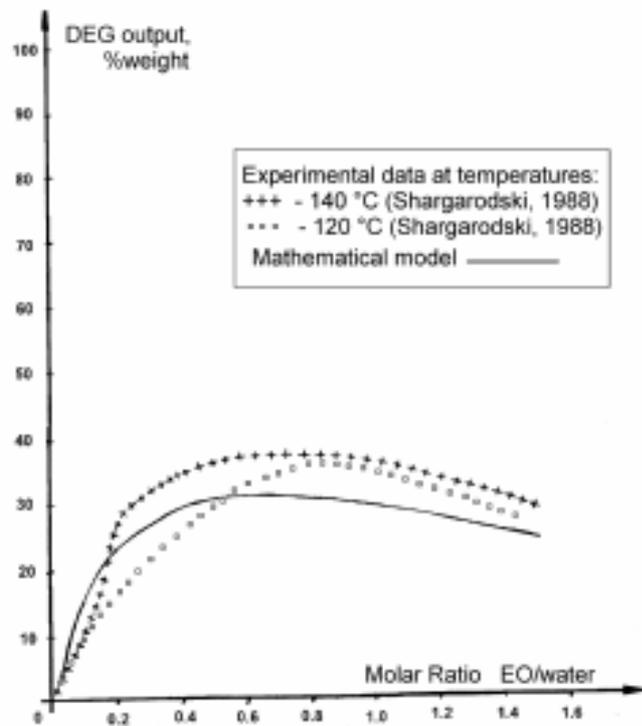


Fig. 2 Distribution of diethylene glycol output.

temperature can be determined as:

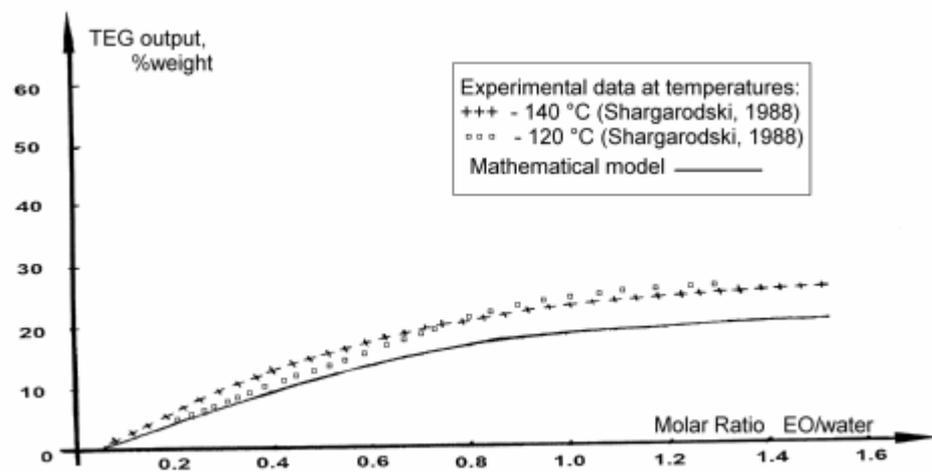


Fig. 3 Distribution of triethylene glycol output.

$$\frac{d\Theta}{dt} = -\alpha \cdot \frac{dx}{dt}, \text{ or } \Theta = \Theta^0 + \alpha \cdot (x^0 - x) \quad (11)$$

Consider now some particular cases.

I) Assume, that the component B is in considerable excess, i.e. $y = y_0 = 1$. The system of differential equations (5) can be written as:

$$\begin{aligned} \frac{dx}{dt} + \left[1 + m \cdot \sum_{i=1}^{\infty} x_i \right] &= 0 \\ \frac{dx_1}{dt} + m_1 \cdot x_1 &= 1 \\ \frac{dx_2}{dt} + m \cdot x_2 &= m \cdot x_1 \\ \frac{dx_3}{dt} + m \cdot x_3 &= m \cdot x_2 \\ \dots\dots\dots \\ \frac{d\Theta}{dt} - \alpha \cdot \left[1 + m \cdot \sum_{i=1}^{\infty} x_i \right] &= 0 \end{aligned} \tag{12}$$

By taking the sum of equations for x_1, x_2, \dots etc, we obtain the following equation:

$$\sum_{i=1}^{\infty} \frac{dx_i}{dt} = 1, \text{ or } \sum_{i=1}^{\infty} x_i = t + \sum_{i=1}^{\infty} x_i^0 \tag{13}$$

The solution can be presented as:

$$\begin{aligned} x_1 &= \frac{1}{m} \cdot [1 - \exp(-m \cdot t)] + x_1^0 \cdot \exp(-m \cdot t) \\ x_{i+1}(t) &= \frac{1}{m} \cdot \left[x_i^*(t) - \frac{1}{i!} \cdot (m \cdot t)^i \right] + \\ &+ \exp(-m \cdot t) \cdot \left[\sum_{k=1}^{i+1} x_k^0 \cdot \frac{1}{(i-k+1)!} \cdot (m \cdot t)^{i-k+1} \right] \end{aligned} \tag{14}$$

In view of the system of equations (14), equation for x can be written as:

$$\frac{dx}{dt} + C_1^0 + m \cdot t, \text{ where: } C_1^0 = 1 + m \cdot \sum_{i=1}^{\infty} x_i^0$$

The solution can be presented as:

$$x = x^0 - C_1^0 \cdot t - \frac{m \cdot t^2}{2} \quad (15)$$

It is possible to find t_f from equation (15), if $x = 0$:

$$t_f = \frac{-C_1^0 + \sqrt{(C_1^0)^2 + 2 \cdot m \cdot x^0}}{m} = \frac{-C_1^0 + \sqrt{\Delta}}{m}$$

In view of equation's system (14), the solution of equation for Θ can be written as:

$$\Theta = \alpha \cdot C^0 \cdot t + \frac{\alpha \cdot m \cdot t^2}{2} + \Theta^0 \quad (16)$$

II) Assume, that the component A is in excess, i.e. $x=x^0=\text{const}$. A system of equations can be presented as:

$$\begin{aligned} \frac{dy}{dt} + y &= 0 \\ \frac{dx_1}{dt} + m \cdot x_1 &= y \\ \frac{dx_2}{dt} + m \cdot x_2 &= m \cdot x_1 \\ &\dots\dots\dots \end{aligned} \quad (17)$$

The solution for y and x_i can be written as the general case (8). Equation for temperature can be presented as:

$$\frac{d\Theta}{dt} - \alpha \cdot [(1-m) \cdot y + m \cdot C^0] = 0$$

Assume, that $y = \exp(-t)$, the solution can be written as:

$$\Theta = -\alpha \cdot [(1-m) \cdot (1 - \exp(-t)) + m \cdot C^0 \cdot t] + \Theta^0 \quad (18)$$

3. Conclusions

The system of differential equations describing the kinetics of consecutive-parallel addition reactions with a large number of steps has been investigated. The analytical solution for distribution of reaction products at non-zero initial conditions has been obtained. The predictions obtained with the solutions of the kinetic model were compared with the experimental data earlier obtained by Shargarodski [17]. It has been shown that, the solutions of the kinetic model are adequately describing the given process. Particular cases of reaction realization in conditions of excess of one of initial reactants have been considered. The solutions for these cases have been obtained.

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Notation

C_p	isobaric heat capacity, J/ kg K
T	temperature of the reaction mixture, K
X	concentration of initial reactant A, mol/l
X_i	concentration of reaction products P_i , mol/l
x_i^*	the solution at zero initial conditions
Y	concentration of initial reactant B, mol/l

Greek letters

ΔH , ΔH_i	enthalpy of the reaction steps, kJ/mol
ρ	density of the reaction mixture, kg/m ³

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