Mathematical model of process of production of phenol and acetone from cumene hydroperoxide

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Abstract. In this paper we review the industrial process of phenol and acetone production and apply the mathematical modelling and computer simulation in order to choose the optimal conditions for the process of isopropylbenzene hydroperoxide decomposition by cumene method.

1. Introduction
Currently, one of the most promising directions in organic synthesis is the production of phenol and acetone through isopropylbenzene hydroperoxide [1].

Earlier we have provided the overview of the technological process and its role [2]. We have chosen a DRM (decomposition reaction mass) decomposition unit of an active plant as a target of our research. The decomposition reaction, being one of the stages of the industrial process of coproduction of phenol and acetone by the cumene method (Figure 1), largely determines the selectivity of the process as a whole [3]. The product of the production is used widely in various industries. Phenol is one of the most important products of petrochemical synthesis. The greater part of phenol is processed into diphenylolpropane, phenol-formaldehyde resins, alkylphenols, and is also used in the purification of petroleum oils and the production of oil additives [4], in the synthesis of pharmaceuticals and many other chemical products. In addition, phenol is used as feedstock for the production of plasticizers, crop protection chemicals, chemical fluoro products, aniline ink materials.

It should be noted that no mathematical model of the industrial reaction has been created during the 60 years of existence of the industrial process of cumene hydroperoxide production.

In 2011, an automated process control system (PCS) was implemented into the production process: the pneumatic equipment for measuring, adjustment and recording of technological process parameters was replaced with the modern electronic systems. The on-line meters installed in the area of cumene hydroperoxide production improved the monitoring of the most explosive unit modules. But, nevertheless, the improved PCS does not eliminate the security issue completely, and it is still impossible to predict the process in case of changing of input parameters along the stream directions.

The relevance of our research is justified by the need to improve the phenol production technology due to the fact that phenol is a basic product of the chemical industry. The existing technology is complicated by multiple recycles of streams, which leads to the accumulation of by-products in the system and to the decrease in the technological production indicators (the speed and selectivity of the main processes, the quality of end products), and also to the increase in the energy intensity of production [5]. The production is carried out using old facilities and there is practically no software.
that could predict the technological process. The software based on the mathematical model developed by us will allow to make a simulator. The simulator will allow to train high-skilled operators for work in explosion hazardous blocks.

2. Mathematical model of cumene hydroperoxide decomposition process

The most widely used industrial method of cumene hydroperoxide decomposition has two stages (Figure 2): the process of catalytic cumene hydroperoxide decomposition takes place at atmospheric pressure in the DRM environment – equimolar mixture of phenol and acetone (products of cumene hydroperoxide decomposition) at the ratio of 18-20:1 to that fed to the cumene hydroperoxide decomposition in the presence of a catalyst - sulfuric acid - into the DRM 0.02 – 0.10 % mass.

During cumene hydroperoxide decomposition the following chemical reactions take place at the first stage.

The main reaction is cumene hydroperoxide decomposition into phenol and acetone:

\[
\begin{align*}
\text{CH}_3\text{C}_6\text{H}_5\text{OH} + \text{H}_2\text{SO}_4 \rightarrow \text{CH}_3\text{C}_6\text{H}_5\text{O} + \text{CH}_3\text{C}_6\text{H}_5\text{OH} + 432.1 \text{kJ/mol}
\end{align*}
\]

Figure 1. Basic scheme of phenol and acetone production.

Figure 2. Hardware components of the cumene hydroperoxide decomposition unit.
In addition to the main reaction, the following side reactions take place: condensation of phenol with dimethylphenylcarbinol (DMPC), dehydration of DMPC, cumene hydroperoxide condensation with DMPC to form PIPB (poly-isopropylbenzene), dimerization of two molecules of alpha-methyl styrene, condensation of two molecules of acetone to form mesityl oxide (MO) [6]. The kinetic parameters of these reactions are provided in the Table 1.

In the process of cumene hydroperoxide decomposition with the reactor top temperature (2) of the main reactor being 52-56°C, up to 10% mass of the PIPB is formed in the DRM. At the second stage of the decomposition, the process of thermal decomposition of the PIPB into phenol, acetone, and alpha-methyl styrene takes place in a second-stage reactor at a temperature of up to 100°C. The PIPB decomposition reaction proceeds with the release of heat according to the following formula:

$$\text{CH}_3\text{CH}_3 \rightleftharpoons \text{O}$$

$$| \text{C}_6\text{H}_5 - \text{C} \rightarrow \text{O} \rightarrow \text{O} \rightarrow \text{C} \rightarrow \text{C}_6\text{H}_3 \Rightarrow \text{C}_6\text{H}_5 - \text{OH} + \text{CH}_3 - \text{C} \rightarrow \text{CH}_3 + \text{phenol}$$

$$\text{acetone}$$

$$\text{PIPB}$$

$$\text{CH}_3$$

$$\text{CH}_3$$

$$\text{CH}_3$$

Currently, the norm of the technological mode of the cumene hydroperoxide decomposition unit is adjusted only by the amount of stream recycle. Analysis of the composition of the reaction mass shows that approximately 3-5% of the components of the phenol resin are formed at the first stage of decomposition (4). In order to increase the efficiency of the cumene hydroperoxide decomposition unit and to optimize the process as a whole, we have developed a mathematical model for the actual production of phenol and acetone, which takes into account all the main reactions that take place at this stage, with the parameters of the Arrhenius equation (Table 1).

| №  | Major reactions of Stage I                          | E, kJ/kmol | A      | ΔH_{\text{arr}} \times 10^{-5}, kJ/kmol |
|----|----------------------------------------------------|------------|--------|---------------------------------------|
| 1  | cumene hydroperoxide decomposition + H⁺ → phenol + acetone | 53500      | 1.75 \times 10^{11} | - 2.353                               |
| 2  | cumene hydroperoxide + DMPC → H⁺, di-cumene peroxide + H₂O | 56400      | 9.51 \times 10^{10} | 0.622                                 |
| 3  | DMPC → H⁺, MS + H₂O                                 | 85100      | 5.23 \times 10^{13} | 1.764                                 |
| 4  | DMPC + phenol → H⁺, CP + H₂O                       | 82500      | 2.58 \times 10^{12} | 0.951                                 |
| 5  | 2 DMPC → H⁺, di-MS + 2 H₂O                         | 72400      | 1.74 \times 10^{12} | 1.360                                 |

E and A are the parameters of the Arrhenius equation; \( \Delta H_{\text{arr}} \)= heats of the reactions calculated under standard conditions; CP – cumylphenol; di-MS – methylstyrene dimer.

The scientific literature mentions the existence of a mathematical model of this process with the location of adiabatic reactors located in parallel and operating simultaneously, respectively. However, in this case, this kinetic model does not correspond to the reactor unit with the devices operating sequentially as the situation is in our case. Also, the existing models do not take into account the parameters of the hardware unit, the real modes of technological processes, their composition, quantity, pressure and temperature, the composition of the initial mixtures, side reactions, etc. [7] The mathematical model developed by us will allow us to determine the effect of recirculation of streams at this stage, the dimension of the unit devices, and the dependence of all parameters of the real mode
of DRM decomposition throughout the entire stream of the cumene hydroperoxide decomposition unit at a real operating plant of “Ufaorgsynthet”.

Later on, based on the mathematical model developed by us, it is planned to create a simulator with real parameters of adjustment and initiation for the workers of similar production plants and divisions, and for young specialists to practice their theoretical knowledge. The production is highly explosive and the slightest error of a decomposition operator can lead to the object explosion [8]. In Russia over the past decades, there have been 4 explosions of decomposition units of cumene hydroperoxide production plant, which resulted in serious accidents. A platform (Figure 3) created on the basis of an adequate mathematical model will also help to avoid significant financial costs for a pilot experimental plant and to obtain an economic effect afterwards [9].

The calculation algorithm and the mathematical model of the process will be calculated in the Mathcad software [10] based on the kinetics of the process. The kinetic model is based on the main reactions shown in the Table 1 [11]. The change in concentrations can be described with the following type of differential equations [12, 13]:

$$\begin{align*}
\frac{d[CHP]}{dt} &= -(k_1[CHP] + k_2[DMPC])[CHP][kat] \\
\frac{d[DMPC]}{dt} &= -(k_3[CHP] + k_4[Ph] + k_5[DMPC])[DMPC][kat] \\
\frac{d[Ph]}{dt} &= (k_6[CHP]^2 - k_4[DMPC][Ph])[kat] \\
\frac{d[Ac]}{dt} &= k_7[CHP][kat] \\
\frac{d[CHP]}{dt} &= k_8[CHP][DMPC][kat] \\
\frac{d[MS]}{dt} &= k_9[DMPC][kat] \\
\frac{d[CP]}{dt} &= k_{10}[DMPC][Ph][kat] \\
\frac{d[dMC]}{dt} &= k_{11}[DMPC]^2[kat] \\
\frac{d[H_2O]}{dt} &= (k_2[CHP] + k_3 + k_4[Ph] + 2k_5[DMPC])[DMPC][kat],
\end{align*}$$

Figure 3. The project of a cumene hydroperoxide decomposition unit simulator platform.
where $k_1$, $k_2$, $k_3$, $k_4$, $k_5$ is the rate constant of the corresponding reactions (Table), $k_{at}$ – catalyst agent, CHP – cumene hydroperoxide, Ph – Phenol, Ac – acetone, CP – cumylphenol, dMS– $\alpha$-methylstyrene dimers.

General equations of mathematical description of reactors are as follows:

\[
\begin{align*}
\frac{dx_i}{dh} &= \frac{S}{v} \cdot r_i \\
\frac{dT}{dh} &= \frac{S}{v \cdot \rho \cdot C_p} \sum_i \Delta H_i \cdot x_{0i} \cdot r_i \\
\end{align*}
\]

(2)

where equation (2) is for an adiabatic reactor, (3) – for a heat exchanger reactor, $dx_i/dh$ is the change of the current concentration of a reaction mixture component ($x_i$) along the device height ($h$), $x_{0i}$ is the initial concentration of reagent in a stoichiometric deficiency in the current reaction, $S$ is the total cross-sectional area of the reaction stream, $v$ is the linear feeding speed of the reaction stream, $r_i$ and $\Delta H_i$ are the speed and heat of the corresponding reaction, $T$ and $T_i$ are the temperatures of the reaction mixture and water, $L$ is the total height of the device. The last equation of the system (3) shall have the sign “+” in case of a cocurrent stream and the sign “-” in case of a counter-current stream. The adiabatic temperature changes due to the corresponding reactions ($\Delta T$) are determined from the formulas:

\[
\begin{align*}
\Delta T_i &= \Delta H_i \left[CHP\right]_0 / \rho Cp \\
\Delta T_{2,5} &= \Delta H_{2,5} \left[DMPC\right]_0 / \rho Cp,
\end{align*}
\]

(4)

(5)

where $\rho$ and $C_p$ are the mean average density and heat-absorption capacity of the reaction mixture, taken as constants in the calculations.

To make the description of the process of acid-catalytic cumene hydroperoxide decomposition complete, it is necessary to include a platform for programming into the proposed model, to calculate changes after each recycle with the fixed initial data, to analyze the results obtained, and to find the best operational mode of the entire unit to achieve energy efficiency, selectivity and conversion. We shall note that during recirculation of the decomposition reaction mass the composition of the input stream changes after each recycle, therefore, in case of fixed input values of all power and recycle settings, the system enters the constant mode after a certain number of recycles. Establishing of a relationship between the recycling frequency and other technological parameters of the process has a great practical importance.

The calculation algorithm and the mathematical model of the process are calculated in the Mathcad software based on the kinetics of the process [14]. The kinetic model is based on the main reactions shown in Table 1. The change in concentrations is described in the form of differential equations:
We also review the mathematical model by E M Dakhnavi in terms of its efficacy for the particular reactor unit assembly (Figure 4). The scheme of the reactors arrangement at the first stage of the cumene hydroperoxide decomposition process (Figure 4) is shown below. At this stage, the devices can be referred to both as reactors and heat exchangers.

The suggested calculation algorithm and the mathematical model of the process for the adiabatic mode and the heat exchange mode was compiled by E M Dakhnavi, PhD in Chemistry, using the Mathcad software. The suggested algorithm of E M Dakhnavi and the model developed will allow to determine accurately the technological mode, to predict changes and dependencies of the devices operation under any initial conditions, depending on the composition and consumption of technical cumene hydroperoxide, catalyst concentration, consumption and the power potential of cooling water and streams recycle. The models also take into account the geometric features of the reactor unit. If the cost of the mixture components and the energy resources is available, it is possible to determine the economic efficiency of various schemes, and to optimize the process.

3. Conclusion
At this stage, we have analyzed and developed the mathematical methods and algorithms applied for the reaction of cumene hydroperoxide decomposition. We have studied the algorithms for solving the direct and the inverse problems. Despite the hardware difference and different versions of cumene hydroperoxide production units at PJSC “Ufaorgsintez” and “Kazanorgsintez”, mathematical models are valid for both cases. We have also carried out a production survey and processed the statistical data for various periods of the enterprise operation, and identified weak production units. In the future we plan to integrate the mathematical model of acid catalytic cumene hydroperoxide decomposition for
the purpose of training, forecasting and optimizing the industrial process. The work is underway to calculate the economic and energy efficiency.

**Major industrial ways of CHP decomposition**

![Diagram of reactors arrangement](image)

**Figure 4.** The scheme of the reactors arrangement at the first stage of the cumene hydroperoxide decomposition process.

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**Acknowledgments**

The reported study was funded by RFBR according to the research projects № 18-07-00341.