Mathematical modeling of a fractionation unit in the production of phenol and acetone by cumene method

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Abstract. In this paper we review the modelling of a unit for separation of phenol and acetone and we use the computer simulation for the quantitative analysis of the model under consideration.

1. Introduction
It is impossible to imagine the modern world without phenol. Phenol is closely connected with all industries of the modern world: production of paint and varnish materials and pharmaceutics, production of polycarbonates and epoxy resins, antioxidants, surface-active agents and a lot more. 95% of phenol is produced by cumene method, since it is the cheapest and most practical one [1-3]. The production of phenol has two stages. At the first stage, benzene is alkylated with propylene to produce isopropylbenzene. The process involves various catalysts and different temperature conditions.

The catalysts are aluminum chloride (AlCl3), hydrogen fluoride (HF), zeolite-based catalysts and alkylation in the presence of dimethylchlorosilane. Further, the isopropylbenzene undergoes a purification stage by passing through a block of fractionating columns. At the second stage, isopropylbenzene is oxidized to isopropylbenzenehydroperoxide and is further decomposed into phenol and acetone.

At the oxidation stage, isopropylbenzene is fed to the upper part of reactors installed in parallel, and air is fed from the bottom of the column in counter-flow. The resulting mixture goes from the middle of the reactors to the strengthening stage, where the mixture passes through a block of fractionating columns, where the content of isopropylbenzenehydroperoxide increases to 90%. After that, the final mixture enters the decomposition stage, where it decomposes into phenol and acetone under the effect of temperature. Further, the mixture proceeds to the separation of phenol and acetone from their homologues, isopropylbenzene and other impurities to obtain pure components.

This phase is the most interesting for us. Purification of phenol and acetone involves passing through a block of fractionating columns. And the aim of this dissertation is to model the fractionation unit in the process of phenol production by the cumene method [4, 5].

2. Process mechanism and chemical properties
The production of phenol and acetone is highly hazardous, as liquid products (phenol, acetone, isopropylbenzene) form explosive mixtures with air and are highly toxic.

The cumene method of phenol production occupies a leading position nowadays. The process can be described by the following scheme:
At the first stage, cumene (isopropylbenzene) is produced by the alkylation of benzene with propylene, at a temperature of 130 °C, the catalyst is aluminum chloride \([6-8]\).

Although ethyl, butyl, isopropyl and isobutyl derivatives can be used to synthesize phenol, so far only isopropyl derivatives are of industrial importance.

At the second stage, the cumene obtained is oxidized with oxygen or air to form a fairly stable cumylhydroperoxide:

Further, the cumylhydroperoxide is concentrated, since its oxidation involves decomposition processes, which do not allow to increase the concentration in the oxidant to a considerable extent. Finally, catalytic acid decomposition of cumylhydroperoxide into phenol and acetone is carried out:

After that, the reaction mass is decomposed to produce individual acetone and phenol and to disengage the by-products.

The reaction mass after the hydroperoxide decomposition is a complex mixture of phenol, acetone, hydroperoxide conversion byproducts, and resinous substances. The fractionation of the products of the cumylhydroperoxide acid decomposition is carried out in a system of fractionating columns. In addition to acetone and phenol, \(\alpha\)-methylstyrene is disengaged, and phenolic resin is sent to combustion or processing \([9, 10]\). Such a purification system allows to obtain phenol of high purity with the efficiency of 97% of resources in raw materials.

3. Brief description of the modeled process

After the decomposition unit the mixture proceeds to the separation unit. After the stage of feed preparation, namely, its saturation with water and salt sedimentation, DRM (decomposition reaction mass) is fed to the columns 70, where the process of azeotropic fractionation takes place \([11]\). To separate phenol and acetone, water is added to the mixture, which creates a mixture with acetone and its homologues that leaves through the top of the column, while phenol and other high-boiling residues leave through the bottom of the column.

Further, the flows will be considered separately from each other. Acetone and light residues enter the column 80, where the raw acetone is separated from the \(\alpha\)-methylstyrene fraction \([12, 13]\). Raw acetone leaves through the top of the column, while alfamethylstyrene leaves through the bottom of the column and proceeds to the post-cleaning and further isolation of pure \(\alpha\)-methylstyrene.

In its turn, the raw acetone, that left the column through its top, enters the columns 80a/1 and 80a/2. The columns are arranged according to the principle of interconnected vessels. NaOH is fed to the plate located above the feeding to neutralize the acid medium and to sediment the aldehydes. Merchantable acetone leaves through the top of the columns.

The second flow that left the columns 70 through the bottom (phenol flow) will be considered in more detail, since it is the target of our modeling. Bottom liquid of the columns 70 enters the column 90/1, and then the column 90/2. The columns are designed to separate phenol from the so-called phenolic resin. The distillation is carried out in vacuum created by steam-jet plant systems.
The whole system of columns and devices for phenol decontamination is in deep vacuum. The process goes under the influence of high temperatures. The temperature mode in the column is maintained by the steam boilers 91/1-3 with the steam pressure of 16 atm. The columns also have the supply of reflux fed to the top of the columns. The light fraction that left trough the top and condensed in dephlegmators 92/1-3 in the chamber 96 is used for the reflux. The bottom liquid, namely the phenolic resin, goes for further processing to produce residual phenol which proceeds to circulate in the columns 70.

Distillate of the columns 90 is fed from the chamber 96 to the feeding of the column 150a. The column is designed for separation of phenol from impurities with a relatively average molecular weight. This is achieved through azeotropic rectification [14]. The azeotrope is diethylglycol. Diethylglycol dissolves phenol and some insignificant amount of impurities, thus increasing their boiling point in a mixture with diethylglycol. The fraction of lighter hydrocarbons leaves through the top of the column, condenses at the reflux coolers and enters the chamber 128a, from which the hydrocarbons are taken for refluxing of the column, and the remainder proceeds to circulation in the columns 70. The temperature mode is maintained by the steam boiler 151a with the steam pressure of 21 atm.

The bottom liquid from column 150a is fed to column 110, which is designed to separate phenol from diethylglycol. Under the influence of high temperatures and vacuum, the raw phenol leaves
through the top of the column, condenses at the reflux coolers at the chamber 116/1, from which the phenolic fraction is taken for refluxing of the column 110, and diethyleneglycol leaves through the bottom to the column 150a, and part of diethyleneglycol goes to post-treatment in column 100. The temperature mode of the column is maintained by a steam boiler with the steam pressure of 21 atm.

![Figure 3. Piping scheme for the column 150a.](image1)

Raw phenol from the tank 116/1 is fed to the reactors 119/1-2. The reactors are designed to separate phenol from residual heavy impurities by passing it through a layer of ion-exchange resin (cationite), which sorbs heavy impurities.

![Figure 4. Piping scheme for the column 110.](image2)

After purification in the reactors, phenol enters the column 110/1, which is designed to separate phenol from light hydrocarbons. The column is equipped with a 50th dead tray, from which the merchantable phenol goes. The distillate of the column is condensed by reflux coolers into the chamber 116/2, from which the hydrocarbon fraction is taken for refluxing of the column 110. The bottom liquid proceeds to circulation in the column 70. The temperature mode is maintained by the steam boilers 111/1-3 with the steam pressure of 21 atm.

4. Methods of mathematical modeling of the fractionation process
Mathematical modeling is a method of analysis of processes or phenomena by applying mathematical models and using computers [15].
The modern level of IT development expands the possibilities of using the method of mathematical modeling for the study of chemical reactions that underlie the industrial processes; as well as for the design of technological schemes for new and modernized chemical production. The processes associated with chemical technology are very complicated. Usually, mathematical models for particular devices are created based on the models of processes in these devices, and then the technological schemes connecting these devices into a single technological process are modeled.

![Diagram](image.png)

**Figure 5.** Piping scheme for the column 110/1.

The processes of chemical technology are complex space- and time-variable physicochemical systems with a dual deterministic-stochastic nature.

The key to solving this problem is the application of the method of mathematical modeling based on the strategy of system analysis, the essence of which is the representation of the process as a complex multilayer interrelated system with the subsequent qualitative analysis of its structure, the development of a mathematical description and the evaluation of unknown parameters.

4.1 Methodology for making mathematical models of chemical technology processes

Depending on the approach to the mathematical description and the nature of processes occurring in the modelled objects, there are two classes of models: stochastic and deterministic[16].

Stochastic (empirical, static) models represent probabilistic nature of phenomena, when the purpose of calculation is not the true value of process parameters, but the probability of their calculation in a certain range of values. Such models do not provide the information on the physical and chemical nature of the problem, but their simplicity provides for their effective use in modeling of chemical technology processes (CTP).

The stochastic model describes a process in which the output value is not in a one-to-one correspondence with the input value.

Example: Voinov's formula for calculating the molecular weight of narrow oil fractions based on their average boiling temperature.

Deterministic (causal, structural, symbolic) models represent the deterministic (causal) nature of the relationship between the phenomena studied that can theoretically justify the change in the behavior of the system, explain the nature of the relationship of phenomena occurring in the modeled system, and described by the equations of statics and dynamics of chemical, physicochemical, thermal, hydrodynamic processes of chemical technology.

\[ M = 52.63 + 0.246T + 0.01T^2 \]
A deterministic model describes a process in which the output value is uniquely determined by the input value. An example of a deterministic model is the Arrhenius equation describing the effect of temperature $T$ on the value of kinetic constant of chemical reaction $k$, which is valid for any reactions:

$$k = k_0 \cdot e^{-\frac{E}{RT}},$$

where $E$ is the activation energy; $R$ is the universal gas constant; $k_0$ is the preexponential factor.

### 4.2 Physical description of the nature of the modeling object

The development of any model begins with the physical description of the modeling object. Therein the “elementary” processes in the modeling object that shall be reflected in the model are defined. Usually, when modeling the chemical technology objects, the following “elementary” processes are taken into account:

- Movement of phase flows.
- Mass transfer between phases.
- Heat transfer.
- Change of state (evaporation, condensation, dissolution, etc.).
- Chemical transformations.

The application of the method of mathematical modeling is associated with a large amount of calculations performed on computers, which is caused by a large number of equations involved into the mathematical description of the problem.

### 4.3 The algorithm of CTP modelling includes several interrelated stages:

- Development of the initial modeling data. On the basis of the literature values, the necessary information on the simulated process is collected and processed: a list of mathematical description equations and a data bank required to calculate the mathematical description equations are created, the possible hardware for the process is analyzed. At this stage, deterministic mathematical models are formed.

- Development of the mathematical model of CTP. The model is developed with a gradual transition from the lowest level of the hierarchy of the modeled object to the highest one - from a single elementary act to the implementation of the process in a particular hardware design. At this stage, the initial and boundary conditions of the process implementation are also formed.

- Correct simplification of the mathematical model. The ways of simplification of the mathematical model are being searched in order to reduce the calculation time without significant distortion of the results of subsequent modeling.

- Choice of algorithm for solving the mathematical model. The solution of the model requires the use of numerical methods of calculation, the same problem can be solved by various methods, which differ from each other in the complexity of algorithm programming and speed.

- The development of the calculation program, debugging, obtaining of trial solutions. One of the most time-consuming stages of computer modeling.

- Assessment of the adequacy of the developed mathematical model. The calculation results are compared with the practical data obtained during experiments on a real object.

- Interpretation of the results of the simulation experiment and development of practical recommendations.

### 5. Calculation of liquid and vapor loads along column height

We can determine the reflux $R_n$ and vapor $V_n$ numbers for the evaporation part and the stripping part of the fractionating column correspondingly as a ratio of the segments of the thermal diagram:

$$R_n = g_n / D = G_{n+1}D / g_nG_{n+1} \quad \text{and} \quad V_n = G_n / W = W_{g_n+1} / g_{n+1}G_n,$$

i.e. for the tray 1:

$$R_1 = g_1 / D = 32/12.5 = 2.56.$$
for the tray 8:

\[ V_8 = \frac{G_8}{W} = 29.9 / 13.4 = 2.23. \]

Based on the data calculated, we can determine mole discharges of fluid \( g_n \) and vapor \( G_n \):

for the evaporation part of the column:

\[ g_n' = R_n \cdot D', \]
\[ G_{n+1} = G_n + g_n' - g_{n-1}', \]

for the stripping part of the column:

\[ g_{n+1}' = G_n' + g_n' - G_{n-1}', \]
\[ G_n = V_n \cdot W', \]

i.e. for the tray 1:

\[ g_1 = 2.56 \cdot 140.5 = 359.68 \text{ kmol/hour}, \]
\[ G_1 = D' = 140.5 \text{ kmol/hour}, \]

for the tray 2:

\[ g_2 = 2.329 \cdot 140.5 = 351.81 \text{ kmol/hour}, \]
\[ G_2 = g_1 + G_1 = 359.68 + 140.5 = 500.18 \text{ kmol/hour}. \]

For the stripping part the calculation is performed from bottom up for the tray 16:

\[ g_{17} = W' = 152.65 \text{ kmol/hour}, \]
\[ G_{17} = 2.213 \cdot 152.65 = 337.81 \text{ kmol/hour}, \]

for the tray 15:

\[ g_{16} = g_{17} + G_{17} = 490.46 \text{ kmol/hour}, \]
\[ G_{16} = 2.23 \cdot 152.65 = 340.41 \text{ kmol/hour}. \]

We will convert the mole discharges determined into mass flow rates using the following equations:

\[ g = g_n \cdot M_{g_n}, \]
\[ G = G_n \cdot M_{g_n}, \]

where \( M_{g_n} \) and \( M_{g_n} \) are the molar-mass averages of the equilibrium flows of liquid and vapor correspondingly leaving the \( n \text{-th} \) tray, in kg/kmol.

\[ M_{g_n} = M_B \cdot x_n' + M_T \cdot (1 - x_n'), \]
\[ M_{g_n} = M_B \cdot y_n' + M_T \cdot (1 - y_n'). \]

for the tray 1:

\[ M_{g_1} = 78 \cdot 0.93 + 92 \cdot (1 - 0.93) = 78.98 \text{ kg/kmol}, \]
\[ M_{G_1} = 78 \cdot 0.97 + 92 \cdot (1 - 0.97) = 78.42 \text{ kg/kmol}, \]
\[ g = 359.68 \cdot 78.98 = 28407.53 \text{ kg/hour}, \]
\[ G = 140.5 \cdot 78.42 = 11018.01 \text{ kg/hour}. \]

| \( n \) | \( R \) | \( G' \) | \( g' \) | \( x' \) | \( y' \) | \( M_{g_n} \) | \( M_{g_n} \) | \( G \) | \( g \) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 2.56 | 140.5 | 359.68 | 0.93 | 0.97 | 78.42 | 78.98 | 11018.01 | 28407.53 |
| 2 | 2.50 | 500.18 | 351.81 | 0.86 | 0.94 | 78.91 | 80.03 | 39469.2 | 28155.51 |
| 3 | 2.45 | 492.31 | 344.65 | 0.77 | 0.89 | 79.54 | 81.22 | 39158.5 | 27992.19 |
| 4 | 2.39 | 485.15 | 336.08 | 0.68 | 0.83 | 80.38 | 82.55 | 38996.08 | 27743.07 |
| 5 | 2.38 | 476.58 | 333.97 | 0.57 | 0.76 | 81.36 | 84.02 | 38774.22 | 28060.03 |
| 6 | 2.33 | 467.47 | 326.8 | 0.49 | 0.69 | 82.34 | 85.21 | 39067.74 | 27846.88 |
| 7 | 2.29 | 467.3 | 321.89 | 0.42 | 0.63 | 83.25 | 86.12 | 38902.97 | 27720.78 |

Table 1. Distribution of loads along the column.
|   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|
| 13 | 2.25 | 344.53 | 492.14 | 0.12 | 0.22 | 88.99 | 90.39 | 30659.82 | 444484.86 |
| 14 | 2.22 | 339.49 | 493.06 | 0.08 | 0.14 | 90.04 | 90.88 | 30568 | 44809.25 |
| 15 | 2.23 | 340.41 | 490.46 | 0.05 | 0.09 | 90.74 | 91.3 | 30888.76 | 44779.4 |
| 16 | 2.21 | 337.81 | 152.65 | 0.03 | 0.06 | 91.23 | 91.59 | 30818.81 | 13981.82 |

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