Mathematical modeling of isopropylbenzene oxidation reaction and oxidation reactor

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Abstract. In this paper, several kinetic models of isopropylbenzene oxidation are considered. Kinetic model parameters were presented in order to simulate the reaction course in time. The data obtained are may be used to simulate the isopropylbenzene oxidation reactor. This paper represents the results of this computer simulation.

1. Introduction

The major amount of phenol is produced today by cumene method today. Isopropylbenzene (IPB) is the main reagent to this process. It is used to synthesize another intermediate product, which is hydroperoxide of isopropylbenzene (HP IPB). Isopropylbenzene decomposes on phenol and acetone on the next stage of the industrial process. The gross equation of this stage of reactions can be represented as:

\[ \text{IPB} + \text{O}_2 \rightarrow \text{HPIPB} + \text{ACP} + \text{DMPC}, \]

where IPB – isopropylbenzene (cumene), \( \text{C}_9\text{H}_{12}\text{CH(CH}_3)_2 \); HP IPB – hydroperoxide of isopropylbenzene, \( \text{C}_9\text{H}_{12}\text{CH(CH}_3)_2\text{COOH} \); ACP – acetophenone, \( \text{C}_6\text{H}_5\text{CHO} \); DMPC – dymethylphenilcarbinol, \( \text{C}_9\text{H}_{12}\text{CH(CH}_3)_2\text{COH} \) [1,2].

In order to predict outcome of the technological process and reaction mathematical simulation may be used [3,4]. In order to simulate reaction behavior we need to solve direct kinetic and inverse kinetic tasks [5,6,7].

2. Isopropylbenzene oxidation process simulation

The oxidation of isopropylbenzene is a radical chain reaction. As in many radical chain reactions, many different step reactions may occur with the formation of a multitude of different particles. Different authors distinguish different directions of the course of reactions [8,9,10,11]. There are different parameters that influence on reaction (temperature, water on the feed, initial composition) [12,13,14,15,16]. In simulation below main used parameter is temperature of reaction.

2.1. Kinetic models of isopropylbenzene liquid-phase oxidation and their parameters

In [8,9,11] different kinetic models of isopropylbenzene oxidation are presented, as well as experimental data for some cases. Kinetic model from [9] represented below on figure 1:
Figure 1. “Simple” kinetic model of isopropylbenzene oxidation.

Mathematic model based on kinetic scheme above.

From analysis of the data from [8] and [9], and solving the direct and inverse kinetic tasks, we obtain the values of activation energies and pre-exponential factors of the Arrhenius equation (Ea – activation energy and k0 – pre-exponential coefficient) for a model represented in [9]. Annealing simulation method was used. Obtained values are represented in Table 1 (based on data from [8]) and Table 2 (based on data from [9]).

### Table 1. Kinetic parameters (1).

| Reaction stage number | Ea, kDj/mole | k0          |
|-----------------------|--------------|-------------|
| 1                     | 114.5        | 2.18×10³    |
| 2                     | 132.6        | 6.38×10⁶    |
| 3                     | 115.0        | 9.53×10⁴    |
| 4                     | 159.7        | 1.03×10⁹    |
| 5                     | 160.0        | 2.83×10⁹    |

### Table 2. Kinetic parameters (2).

| Reaction stage number | Ea, kDj/mole | k0          |
|-----------------------|--------------|-------------|
| 1                     | 118.7        | 7.56×10⁴    |
| 2                     | 196.6        | 6.47×10⁴    |
| 3                     | 119.0        | 6.71×10⁴    |
| 4                     | 133.7        | 7.81×10⁹    |
| 5                     | 181.4        | 5.63×10⁹    |

2.2. Reactor simulation

In industry, bubbling reactors are used, in which liquid isopropylbenzene feed is oxidized by air oxygen. Isopropylbenzene and air flow countercurrently in column. Liquid isopropylbenzene is fed to the top of the reactor, so the product with an increased content of hydroperoxide is taken from bottom of apparatus; air is fed to lower part of the column, and on top of the apparatus abgases (with a reduced amount of oxygen and with some amount of carried liquid hydrocarbons) go out from reactor. We take the value reactor parameters based on [10,12,13,7] data. We also assume such simplifications:

- mixing effect in the cross section is neglected;
- hydraulic resistance of air bubbles coming countercurrent to liquid hydrocarbon feed is neglected;
- reactor regime is well established, there are no critical changes in parameters (temperature, flow velocity, composition of streams) at any point of the reactor in time;
- reactor is adiabatic;
- the fact that there is some amount of water going into reactor with liquid feed and air is neglected;
- liquid feed of reactor consists from IPI and GP IPI;
- product flow consists from IPI, GP IPB, ACF, DMPC;
- loss of product with going from reactor gas phase is not taken into account;
- hydraulic resistance of the internal elements of the reactor is neglected.

So such simplifications were made in order to simulate kinetic part of the process, neglecting mass transfer, in order to see how our results will meet with results of other researches and industry data. Reactor parameters represented in Table 3.

### Table 3. Reactor parameters.

| Parameter                      | Value            |
|-------------------------------|------------------|
| Reactor diameter              | 2.2 m            |
| Amount of section             | 9                |
| Section length                | 1.4 m            |
| Liquid feed flow              | 23500 kg/h       |
| IPB fraction in liquid feed   | 98 % mass.       |
| HP IPB fraction in liquid feed| 2 % mass.        |

The reactor is divided into sections, and in industry it is possible to maintain a certain temperature in the sections in accordance with the requirement for a process regime. We assume that the temperature in each section is the same throughout the volume of this section and is maintained constant for simplification. Temperatures of sections are shown in Table 3.

If we know number of such sections – n (in our case – 9, and sections numbers go from top to bottom, so highest section has number 1) [10], and length of each section \( l_1, l_2, l_3, \ldots, l_n \) (in our case they are equal to each other), we can determine constants of chemical reaction rate:

\[
k_{ij} = k_{0j} e^{-E_j/RT_i}
\]

where \( k_{ij} \) – constant of j-th chemical reaction rate, which happens on i-th section, \( k_{0j} \) – constant pre exponential parameter for j-th chemical reaction rate, \( E_j \) – activation energy of j-th chemical reaction, \( R \) – ideal gas constant, \( T_i \) – temperature in i-th reactor section.

So if we know constants of chemical reactions we can determine concentration on output flow from i-the reactor section. These values will be input data for calculation of (i+1) section.

Assumed temperatures of reaction temperatures are represented in Table 4.

### Table 4. Temperatures of reactor sections.

| Number of section | Temperature (°C) | Temperature (K) |
|-------------------|------------------|-----------------|
| 1                 | 121              | 394             |
| 2                 | 121              | 394             |
| 3                 | 120              | 393             |
| 4                 | 121              | 394             |
| 5                 | 121              | 394             |
| 6                 | 119              | 392             |
| 7                 | 118              | 391             |
| 8                 | 117              | 390             |
| 9                 | 115              | 388             |

System of differential equations below is used for mathematical simulation of kinetic scheme represented on figure 1.

\[
\omega_1 = k_1 \cdot [RH]
\] (3)
\[ w_2 = k_2 \cdot [RH] \] (4)

\[ w_3 = k_3 \cdot [RH] \] (5)

\[ w_4 = k_4 \cdot [ROOH] \] (6)

\[ w_5 = k_5 \cdot [ROOH] \] (7)

\[ \frac{d[RH]}{dt} = -w(1) - w(2) - w(3) \] (8)

\[ \frac{d[ROOH]}{dt} = w(1) - w(4) - w(5) \] (9)

\[ \frac{d[ROH]}{dt} = w(2) + w(4) \] (10)

\[ \frac{d[RHO]}{dt} = w(3) - w(5) \] (11)

where \( k \) – constant of chemical reaction rate, \( t \) – time of reaction, \( w_i \) \((i=1, \ldots, 5)\) – rate of \( i \)-th reaction, 

\([RH]\) – concentration of IPB, \([ROOH]\) – concentration of HP IPB, \([ROH]\) – concentration of DMPC, 

\([RHO]\) – concentration of ACP.

2.3. Results

In order to solve system of differential equations (3-11) MATLAB software was used. Different kinetic data from table 1 and table 2 was used. Ode23s MATLAB algorithm was used.

On figure 2 results of using kinetic parameters from table 1 are shown. In Table 5 represented composition of output flow from reactor.

![Figure 2. Substances concentrations change throw time of reaction (1).](image)

| Substance | Concentration, mol/lit |
|-----------|------------------------|
| IPB       | 4.8709                 |
| HP IPB    | 1.6385                 |
| ACP       | 0.6614                 |
| DMPC      | 0.0046                 |

Table 5. Composition of output flow (1).

On figure 3 results of using kinetic parameters from table 2 are shown. In Table 6 represented composition of output flow from reactor.

Second set of temperature is used in order to compare results above with results received with higher temperature. Second set of temperatures represented below in Table 6.
Table 6. Composition of output flow (2).

| Substance | Concentration, mol/lit |
|-----------|------------------------|
| IPB       | 6.1066                 |
| HP IPB    | 0.6224                 |
| ACP       | 0.4461                 |
| DMPC      | 0.0034                 |

Figure 3. Substances concentrations change through time of reaction (2).

Table 7. Temperatures of reactor sections.

| Number of section | Temperature (°C) | Temperature (K) |
|-------------------|------------------|-----------------|
| 1                 | 126              | 399             |
| 2                 | 126              | 399             |
| 3                 | 125              | 398             |
| 4                 | 126              | 399             |
| 5                 | 126              | 399             |
| 6                 | 124              | 397             |
| 7                 | 123              | 396             |
| 8                 | 123              | 395             |
| 9                 | 120              | 393             |

Figure 4. Substances concentrations change through time of reaction (1).
Table 8. Composition of output flow (1).

| Substance | Concentration, mol/lit |
|-----------|------------------------|
| IPB       | 4.4770                 |
| HP IPB    | 1.9119                 |
| ACP       | 0.7808                 |
| DMPC      | 0.0056                 |

Figure 5. Substances concentrations change throw time of reaction (2).

Table 9. Composition of output flow (2).

| Substance | Concentration, mol/lit |
|-----------|------------------------|
| IPB       | 5.9292                 |
| HP IPB    | 0.7166                 |
| ACP       | 0.5291                 |
| DMPC      | 0.0038                 |

Comparison of models results for different temperature sets shows us that:
- Increasing temperature on 5 °C while using kinetic parameters set from table 1 gives us IPB concentration decrease on 8.1 %, HP IPB concentration increase on 16.7 %, ACP concentration increase on 18.1 %, DMPC concentration increase on 21.7 %;
- Increasing temperature on 5 °C while using kinetic parameters set from table 2 gives us IPB concentration decrease on 2.9 %, HP IPB concentration increase on 15.1 %, ACP concentration increase on 18.6 %, DMPC concentration increase on 11.8 %.

HP IPB output concentration from Table 5 is higher than HP IPB output concentration from Table 6 on nearly 38% IPB concentration is lower on 25.3% . So model represented in (3-11) shows us higher reactions rates at same temperature with kinetic parameters from Table 1, than with parameters represented in Table 2. But output HP IPB concentration value received in second case are more near to real process data [11-14]. At the same time by-products (ACP and DMPC) calculated concentrations values are significantly higher than real process data values [11-14].

3. Conclusion
Simulation of isopropylbenzene oxidation using kinetic model shown on figure 1 and equations (3-11) with different set kinetic parameters (Table 2 and Table 3) has given us output flow concentration results. Output concentrations of IPB and HP IPB (especially in second case) are quite similar to industrial data from different sources, but calculated concentrations of ACP and DMPC are too high . Such inaccuracy may be fixed by using more complicated model and using mass transfer part of process in calculations.
4. References

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