

Mathematical modeling of radical-chain reaction of isopropylbenzene oxidation

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Abstracts. Kinetic model of radical-chain reaction of isopropylbenzene oxidation by air oxygen was studied. A comparison of various mathematical models describing this reaction are represented, as well as their results.

1. Introduction

Isopropylbenzene oxidation by air oxygen is one of the stages in industrial process of acetone and phenol production (cumene method). Nowadays cumene method is the most world spread industrial process for these substances synthesis [1]. Isopropylbenzene reacts with oxygen and hydroperoxide of isopropylbenzene (HP IPB) is formed during oxidation. Gross formula for this reaction represented below:



However gross formula of reaction doesn't represent kinetic mechanism of oxidation. Isopropylbenzene oxidation is radical-chained reaction, which means that there great number of different particles (radicals, molecules) which take part in various elementary reactions (decomposition of molecules and large radicals on lesser particles, recombination of radicals, etc) [2,3]. Different authors propose various reactions schemes and kinetic models of isopropylbenzene oxidation but some principles in these models stay the same, such as radical-chained reaction stages (initiation, propagation and termination) and consilience of some elementary stages throw various models [2,3,4,5].

2. Kinetic model of isopropylbenzene oxidation

2.1. Reaction scheme

In this article reaction scheme represented in Table 1 is studied [3]. There are fourteen elementary stages in this model, for each there is corresponding constant of reaction rate.

Elementary stages № 1-5 correspond to initiation step of radical-chained reaction. During this stage initial substances decompose on radical particles which initiate radical-chain. Elementary stages № 6-7 correspond to propagation step in which "main" course of chain reaction is stable and most amount of HP IPB is formed. Number of radicals is increasing rapidly. Elementary stages № 8-14 correspond to termination step. This stages lead to formation of by-products, inhibitors and "side" chain of reaction course take place. [3].

Table 1. Reaction scheme of isopropylbenzene oxidation [3].

№ of elementary stage	Reaction
1	$RH \rightarrow R\cdot + H\cdot$
2	$RH + O_2 \rightarrow R\cdot + HO_2\cdot$
3	$ROOH \rightarrow RO\cdot + \cdot OH$
4	$RO\cdot + RH \rightarrow R\cdot + ROH$
5	$\cdot OH + RH \rightarrow R\cdot + H_2O$
6	$R\cdot + O_2 \rightarrow RO_2\cdot$
7	$RO_2\cdot + RH \rightarrow R\cdot + ROOH$
8	$2 R\cdot \rightarrow R-R$
9	$R\cdot + RO_2\cdot \rightarrow ROOR$
10	$2RO_2\cdot \rightarrow ROOR + O_2$
11	$RO\cdot \rightarrow (C_6H_5)CH_2CO + CH_3\cdot$
12	$CH_3\cdot + O_2 \rightarrow CH_3O_2\cdot$
13	$CH_3O_2\cdot + RH \rightarrow HCHO + H_2O + R\cdot$
14	$RO\cdot + RH \rightarrow \alpha\text{-CH} + H_2O + R$

2.2. Mathematical modeling

Based on reaction scheme above (Table 1) and experimental data [3] mathematical model for isopropylbenzene oxidation reaction is created. Equations (2)-(11) represents rates of elementary stages:

$$\begin{aligned}
 W_1 &= k_1 \cdot [RH] & (2) \\
 W_2 &= k_2 \cdot [RH] & (3) \\
 W_3 &= k_3 \cdot [ROOH] & (4) \\
 W_4 &= k_4 \cdot [RO\cdot][RH] & (5) \\
 W_5 &= k_5 \cdot [\cdot OH][RH] & (6) \\
 W_6 &= k_6 \cdot [R\cdot] & (7) \\
 W_7 &= k_7 \cdot [RO_2\cdot][RH] & (8) \\
 W_8 &= k_8 \cdot [R\cdot]^2 & (9) \\
 W_9 &= k_9 \cdot [R\cdot][RO_2\cdot] & (10) \\
 W_{10} &= k_{10} \cdot [RO_2\cdot]^2 & (11) \\
 W_{11} &= k_{11} \cdot [RO\cdot] & (12) \\
 W_{12} &= k_{12} \cdot [CH_3\cdot] & (13) \\
 W_{13} &= k_{13} \cdot [CH_3O_2\cdot][RH] & (14) \\
 W_{14} &= k_{14} \cdot [RO\cdot][RH], & (15)
 \end{aligned}$$

where W_j – rate of j-th elementary reaction, [mole*min], j – number of elementary reaction in kinetic model ($j = \overline{1,14}$), k_j – constant of j-th elementary reaction rate, for $k_1-k_3, k_6, k_{10}, k_{11}$ [min^{-1}], for $k_4, k_5, k_7-k_9, k_{12}-k_{14}$ [$\text{lit} \cdot \text{mole}^{-1} \text{min}^{-1}$], [...] – concentration of substance, [mole/lit].

The rate of change of substances over time involved in reactions will be determined by the differential equations of the following form:

$$\frac{dc_i}{dt} = \sum_{j=1}^I v_{ij} w_j(k_j, k_{0j}, E_j, T, c_i), \quad i = 1, \dots, I \tag{16}$$

where c_i – concentration of i-th substance, [mole/lit], i – number of substance, I – overall number of elementary stages reactions ($I=14$), j – number of elementary reaction in kinetic model ($j = \overline{1,14}$), k_j – constant of j-th elementary reaction rate, for $k_1-k_3, k_6, k_{10}, k_{11}$ [min^{-1}], for $k_4, k_5, k_7-k_9, k_{12}-k_{14}$ [$\text{lit} \cdot \text{mole}^{-1} \text{min}^{-1}$], t – time, [min], k_{j0} – preexponential coefficient for j-th constant of elementary reaction rate, it has same dimension as corresponding constant, T – temperature, w_j – rate of j-th elementary reaction, [mole*min], E_j – activation energy of j-th reaction [KJ/mole] [6,7,8].

Using mathematical model represented above (model (1)) we solve inverse kinetic task at first. In order to do this we use genetic algorithm which is implemented in MATLAB software environment [9].

Then we solve direct kinetic task using model (1) and applying Runge-Kutta method of 4th order in MATLAB software environment with different set of concentrations of initial components.

Also in order to compare model (1) with another kinetic and mathematical model we perform same calculations with model, represented in [9] (model (2)). Model (2) was obtained by simplification of reaction scheme represented in Table 2 [3] and it consists of four differential equations [9].

As a result of model (1) and model (2) solution Fig.1-Fig.6 represented below on which change of IPB and HP IPB concentrations are shown.

On Fig.1 and fig.2 are shown results obtained from these initial conditions [10-12]:

$$\omega_{IPB0}=98\%, \omega_{HPIPB0}=2\%, T = 391\text{ K}, \tag{17}$$

where ω_{IPB0} – initial mass fraction of IPB (%mass.), ω_{HPIPB0} - initial mass fraction of HP IPB (%mass.), T - temperature (K).

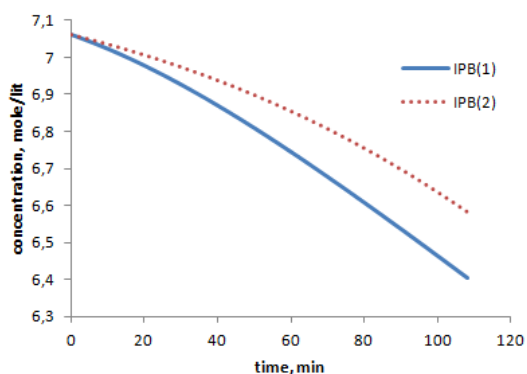


Figure 1. IPB concentration change, model (1) and model (2), $\omega_{HPIPB0}=2$ (% mass.).

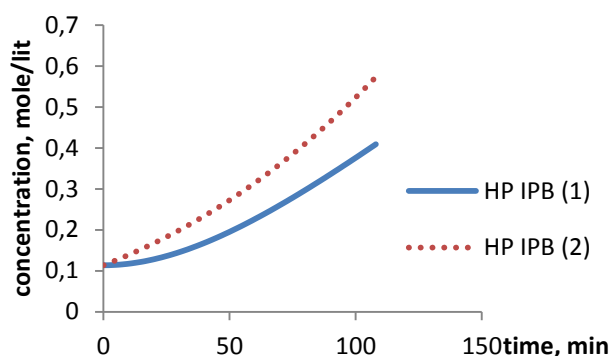


Figure 2. HP IPB concentration change, model (1) and model (2), $\omega_{HPIPB0}=2$ (% mass.).

Fig.1 shows that the finite concentration of IPB, obtained from model (1) is less than the concentration of IPB, calculated from model (2), although, the finite concentration of HP IPB obtained from model (1) is also lower than that calculated by model (2). It is assumed that the contribution of side reactions, which lead to the formation of by-products, as well as to the decomposition of the HP IPB, in model (1) (№ 8-14 in Table 1) is more significant than in model (2).

On Fig.3 and Fig.4 are shown results obtained from these initial conditions:

$$\omega_{IPB0}=97\%, \omega_{HPIPB0}=7\%, T = 391\text{ K}, \tag{18}$$

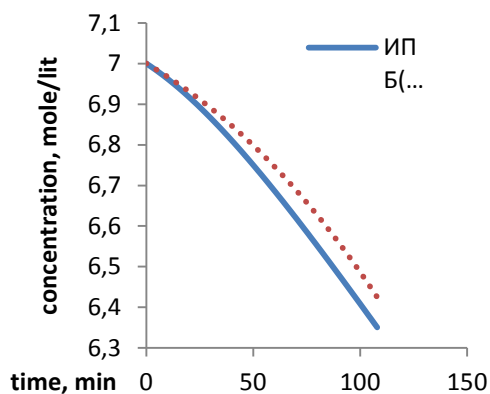


Figure 3. IPB concentration change, model (1) and model (2), $\omega_{HPIPB0}=3$ (% mass.).

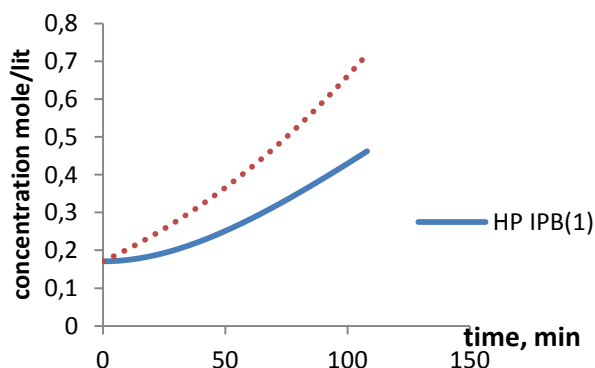


Figure 4. HP IPB concentration change, model (1) and model (2), $\omega_{HPIPB0}=3$ (% mass.).

It is shown that increasing initial amount HP IPB on 1 % (%mass.) leads to significant increasing of finite HP IPB concentrations in both models, although same relation between model (1) and model (2) calculated concentrations remains.

On Fig.5 and fig.6 are shown results obtained from these initial conditions:

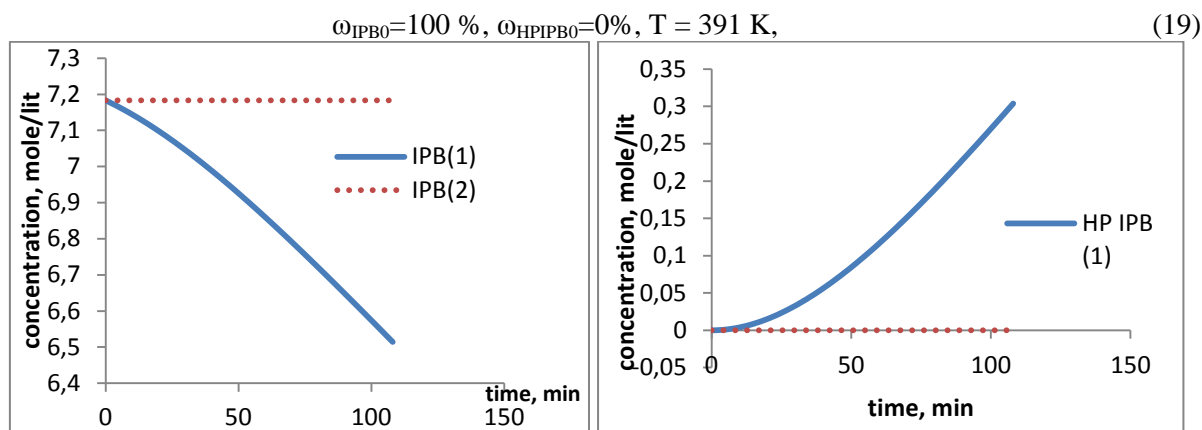


Figure 5. IPB concentration change, model (1) and model (2), $\omega_{HPIPB0}=0$ (% mass.).

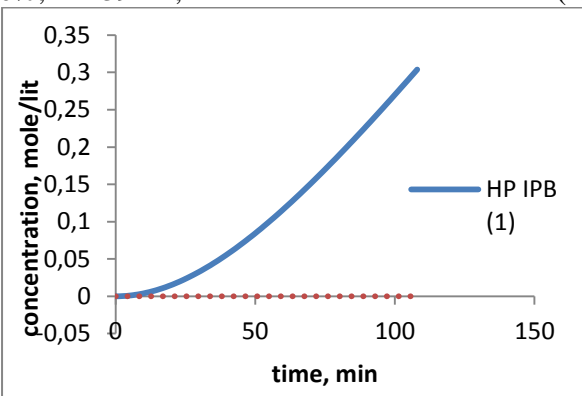


Figure 6. HP IPB concentration change, model (1) and model (2), $\omega_{HPIPB0}=0$ (% mass.).

As can be seen, finite HP IPB concentration calculated from model (1) is lesser than results, obtained from initial conditions (17),(18). As for results obtained using the model (2) it was shown that model (2) is unable to solve direct kinetic task without some initial amount of HP IPB.

Thus, in this study two kinetic and mathematical models were researched and results of these models calculations were compared. Model (1) is more preferable for using in calculations, because it considers influence of side-effect reactions and is able to calculate even if there is relatively small amount of HP IPB in initial compound because it considers initiation reactions without HP IPB.

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