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Solving inverse problems of chemical kinetics by metaheuristic methods

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Abstract

The paper continues the cycle of works devoted to the development of a bank of meta-heuristic methods for solving conditional global optimization problems that arise when solving inverse problems of chemical kinetics. This work discusses the process of sulfuric acid alkylation of isobutane with olefins. Sulfuric acid alkylation of isobutane with olefins allows the processing of butane-butylene fraction to obtain a high-octane component of motor gasoline with a minimum content of aromatic hydrocarbons that does not contain benzene. The main schemes of transformations of sulfuric acid alkylation of isobutane by olefins, probable from the point of view of thermodynamics, are considered. Based on the literary analysis of possible transformation schemes, the mechanism of the process and on the basis of literary data, a mathematical model of the reactor unit of the process was developed and kinetic parameters were determined. Calculations were carried out to find the optimal ratio of isobutane:olefin in raw materials to increase the yield of the target and reduce the yield of by-products of the sulfuric acid alkylation of isobutane by olefins.

Keywords Kinetic model · Inverse problems of chemical kinetics · Mathematical modeling · Sulfuric acid alkylation

Introduction

Currently, there is a tendency to improve the environmental characteristics of automobile fuel while maintaining a high octane number. Sulfuric acid alkylation of isobutane with olefins makes it possible to obtain a high-octane component of

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gasoline with a minimum content of aromatic hydrocarbons. Therefore, it is a significant process of the modern refinery. The main advantage of alkylate is the high octane number: according to the research method, it is 96, according to the motor method, it is 92. The alkylation product is non-toxic, does not contain benzene, and has a low saturated vapor pressure, hence it does not evaporate much during storage and transportation [1]. In the middle of the twentieth century, at the design and construction stages of most industrial installations, including reactors, insufficient attention was paid to in-depth study of the mechanism of most processes. Now the intensive development of information technologies, such as the theory of analysis and storage of large amounts of data, parallel computing technology, artificial neural networks, etc., has led to the creation of universal software systems that allow you to develop detailed kinetic models of production processes [2, 3]. The most complete account of thermodynamic and kinetic regularities of target and side reactions during modeling will allow predicting the yield of the target product with the highest degree of confidence. What can be used in the future to find optimal technological conditions and intensify the process [4]. When modeling this process, it is necessary to take into account the properties of acid catalysts with high corrosion activity and low selectivity, which leads to the fact that along with the target alkylation reactions, a large number of side reactions occur. They lead to a loss of activity and an increase in the consumption of the catalyst, as well as to the formation of lighter and heavier hydrocarbons than the target product, which lowers the octane number of the alkylate [1, 5].

Experimental section

A mathematical model of sulfuric acid alkylation of isobutane with olefins, presented in the work of the East China University of Science and Technology, was chosen as a prototype [4]. The model used includes targeted reactions to obtain the alkylate product, as well as side reactions leading to the formation of heavy fractions. The formation of the latter can be regulated by changing the temperature and composition of the raw materials. The experiments were carried out at the batch process at the temperature range of 3–12 °C and 0.5 MPa.

The object of the study is the reactor unit of the sulfuric acid alkylation of isobutane with olefins. Butane-butylene fraction was used as a raw material. The pressure in the reaction zone was 0.5 MPa. The inlet temperature was selected in the range of 3–12 °C. Sulfuric acid with a concentration of 95–98% was used as a catalyst for the process. The feedstock compositions and reaction conditions of alkylation experiments are listed in Table 1.

The initial stage of the mathematical description of the object is to draw up a scheme of reactions of conversion of hydrocarbons during the process. It should be noted that the accuracy of calculations and the adequacy of the mathematical model to the real process directly depends on the degree of detail of chemical transformations. Therefore, the transformation scheme should sufficiently reflect the physicochemical essence of the process, in our case, a combined graph compiled using graph theory was constructed (Fig. 1).

Table 1 Initial data. Composition of raw materials

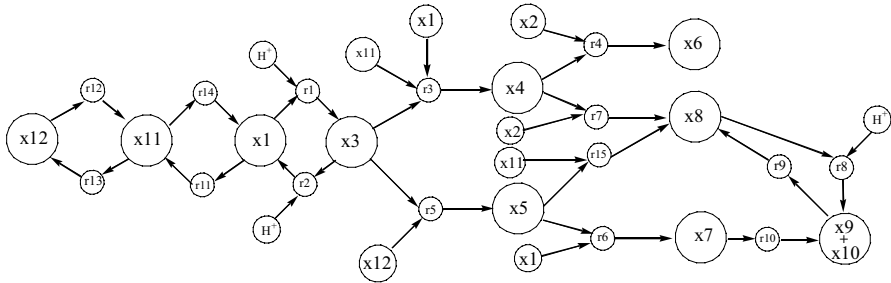|	Concentration of components (mass fractions)			
	1- butene	2- butene	Isobutene	Isobutane
Feedstock-#1	2.39	9.09	1.42	87.1
Feedstock-#2	3.4	93	0	87.3
Feedstock-#3	0	8.8	4.6	86.6

Fig. 1 Combined graph of reactions for the process of sulfuric acid alkylation of isobutane with olefins, where x_1 is iC_4H_8; x_2 is iC_4; x_3 is iC_4+; x_4 is TMPs+; x_5 are DMHs+; x_6 are TMPs; x_7 are DMHs; x_8 are HEs; x_9 are $iCx+$; x_{10} are $iCy=$; x_{11} is $2-C_4H_8$; x_{12} is $1-C_4H_8$ and TMP are trimethylpentanes; DMH are dimethylhexanes; HEs are heavy ends

It is known that reactions in the process of alkylation of olefin isobutane in the presence of sulfuric acid proceed according to the classical carbonium-ion mechanism. In this case, the thermodynamics of the process is the basis. The result of thermodynamic analysis is a list of reactions that are likely to occur under given conditions. The probability of reactions occurring under the technological conditions of the process is estimated by the value of the Gibbs energy ΔG. The resulting combined graph includes 12 individual components and 15 reaction stages.

The mathematical model of the process is a system of nonlinear differential equations:

$$\frac{dx_1}{dt} = -k_1x_1 + k_2x_3 - k_3x_1x_3 - k_7x_1x_2x_4 - k_{11}x_1 + k_{14}x_{11}$$

$$\frac{dx_2}{dt} = -k_4x_2x_4 - k_6x_2x_5 - k_7x_1x_2x_4 - k_{15}x_{11}x_2x_4$$

$$\frac{dx_3}{dt} = k_1x_1 + k_4x_2x_4 + k_6x_2x_5 - k_3(x_1 + x_{11})x_3 - k_5x_{12}x_3 - k_2x_3 + k_7x_1x_2x_4 + k_{15}x_{11}x_2x_4$$

$$\frac{dx_4}{dt} = k_3(x_1 + x_{11})x_3 - k_4x_2x_4 - k_7x_1x_2x_4 - k_{15}x_{11}x_2x_4$$

$$\frac{dx_5}{dt} = k_5 x_{12} x_3 - k_6 x_2 x_5$$

$$\frac{dx_6}{dt} = k_4 x_2 x_4$$

$$\frac{dx_7}{dt} = k_6 x_2 x_5 - k_{10} x_7$$

$$\frac{dx_8}{dt} = k_7 x_1 x_2 x_4 + k_{15} x_{11} x_2 x_4 + k_9 x_9 x_{10} - k_8 x_8$$

$$\frac{dx_9}{dt} = k_8 x_8 - k_9 x_9 x_{10}$$

$$\frac{dx_{10}}{dt} = k_8 x_8 - k_9 x_9 x_{10}$$

$$\frac{dx_{11}}{dt} = -k_3 x_{11} x_3 - k_{15} x_{11} x_2 x_4 + k_{11} x_1 + k_{12} x_{12} - k_{13} x_{11} - k_{14} x_{11}$$

$$\frac{dx_{12}}{dt} = -k_5 x_{12} x_3 + k_{13} x_{11} - k_{12} x_{12}$$

here x_i are concentrations of substances involved in the reaction in mole fractions; k_j are reaction rate constants. The initial conditions are t = 0, $x_1 = x_1^0$; $x_2 = x_2^0$; $x_3 = 0$; $x_4 = 0$; $x_5 = 0$; $x_6 = 0$; $x_7 = 0$; $x_8 = 0$; $x_9 = 0$; $x_{10} = 0$; $x_{11} = x_{11}^0$; $x_{12} = x_{12}^0$. The corresponding species are (1) iC_4H_8; (2) iC_4, (3) iC_4+; (4) TMPs+; (5) DMHs+; (6) TMPs; (7) DMHs; (8) HEs; (9) iCx+; (10) iCy=; (11) 2-C_4H_8; (12) 1-C_4H_8. The mathematical model is constructed according to the mass-action law [6, 7].

In the Python programming language, a program code was written to develop a kinetic model of the process of sulfuric acid alkylation of isobutane with olefins, the system of differential equations was solved using the method of the Radau-II A method of the fifth order.

To determine the rate constants k_j of reactions occurring during the process of sulfuric acid alkylation of isobutane with olefins, a genetic algorithm was chosen that is used in solving optimization and modeling problems by sequential selection. This algorithm is chosen based on the following advantages: no derivative information is required, speed, efficiency, parallel calculation capabilities and optimization of continuous multi-purpose tasks. The solution of the inverse kinetic problem is determined by the objective function:

$$F = \sum_{i=1}^{N} \sum_{j=1}^{M} \left| x_{ij}^{\exp} - x_{ij}^{calc} \right| \rightarrow \min \tag{1}$$

here N is the number of observed components of the reaction ($N=2$); M is number of experiments ($M=12$); $x_{ij}^{\exp}$ and x_{ij}^{calc} are the experimental and calculated values of i-th observed component at j-th experiment.

The number of optimization parameters was 15 (n = 15). The estimated parameters of $k_1 - k_{15}$ are listed in Table 2. To solve the optimization problem, a gravitational algorithm was used [8].

Further, using the constants of the calculated reaction rate constants, the direct kinetic problem was solved, thus the change in the concentrations of the reaction components over time was calculated. Figs. 2, 3, 4 and 5 show the calculated concentration profiles of the target components, the markers indicate the literature data. At the beginning of the process, HEs is formed by the reaction of isobutylene or 2-butene with TMP+ or DMH+, followed by the transfer of the hydride by isobutene. Thus, the initial content of TMP and DMH is small, while HEs sharply increases to the maximum value in tens of seconds. HEs cations are then converted to LEs in the reaction of cleavage and hydride transfer, which corresponds to a sharp decrease in the HEs content. This observation corresponds to the rapid consumption of olefins, and also demonstrates the nature of the very rapid alkylation reaction of isobutane.

DMH are mainly formed at the initial stage of the reaction and subsequently decreases slightly. The concentration of TMP gradually increases over time. In

Table 2 Optimal values of rate constants under different temperature conditions

| k_j	Temperature condition			
	3 °C	6 °C	9 °C	12 °C
k_1, min^{-1}	1.686	1.963	2.081	2.814
k_2, min^{-1}	0.316	0.505	0.609	0.677
$k_3/10^2$, kg mol$^{-1}\cdot$ min^{-1}	1.304	2.871	4.020	2.871
k_4, kg mol^{-1} min^{-1}	0.288	0.486	0.777	1.088
$k_5/10^4$, kg mol^{-1} min^{-1}	0.072	0.115	0.149	0.294
k_6, kg mol^{-1} min^{-1}	1.377	2.395	2.837	2.810
$k_7/10$, kg mol^2 min^{-2}	14.911	21.909	24.706	50.314
k_8, min^{-1}	1.463	1.672	1.170	1.775
k_9, kg mol^{-1} min^{-1}	12.060	14.756	20.782	16.498
$k_{10}/10^{-3}$, min^{-1}	9.868	10.746	12.094	12.782
k_{11}, min^{-1}	17.603	23.961	38.338	24.338
$k_{12}/10^2$, min^{-1}	3.103	3.735	2.615	7.478
k_{13}, min^{-1}	10.164	13.822	9.676	13.822
$k_{14}/10$, min^{-1}	2.797	2.886	3.235	4.005
k_{15}, kg mol^{-2} min^{-2}	38.222	88.489	61.942	116.672
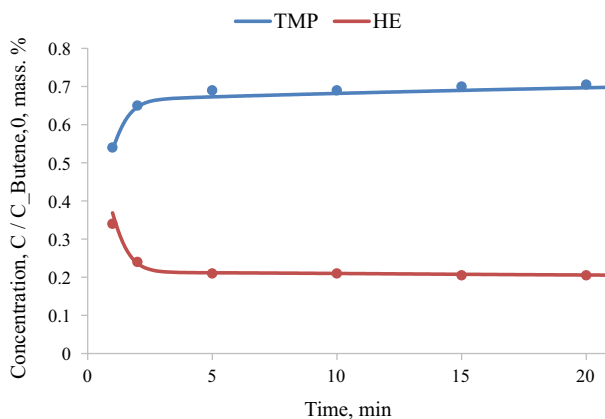
Fig. 2 Concentration profile of the components involved in the alkylation process when using feedstock #1 (3 °C). TMP are trimethylpentanes; DMH are dimethylhexanes
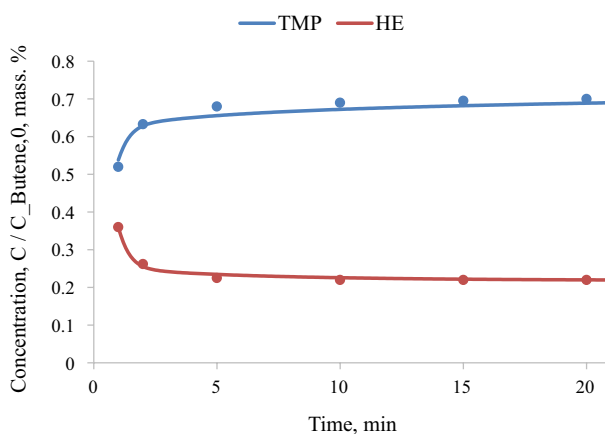

Fig. 3 Concentration profile of the components involved in the alkylation process when using feedstock-#1 (6 °C). TMP are trimethylpentanes; DMH are dimethylhexanes

general, the reaction reaches a stable state after 5 min, which indicates an equilibrium reaction time of sulfuric acid alkylation within 5 min.

Optimization of the process of sulfuric acid alkylation of isobutane with olefins

The improvement of industrial technological processes is one of the most important tasks due to the fact that such improvement allows to increase the output of target products with minimal financial costs. As mentioned earlier, the developed
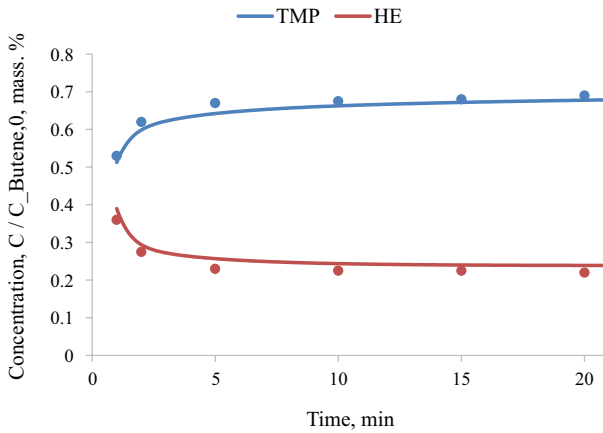
Fig. 4 Concentration profile of the components involved in the alkylation process when using feedstock-#1 (9 °C). TMP are trimethylpentanes; DMH are dimethylhexanes
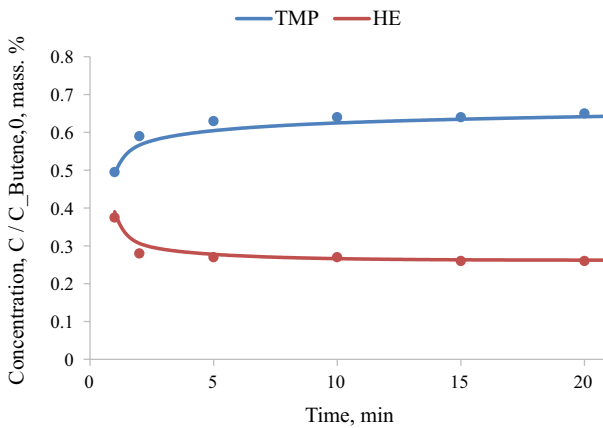

Fig. 5 Concentration profile of the components involved in the alkylation process when using feedstock-#1 (12 °C). TMP are trimethylpentanes; DMH are dimethylhexanes

mathematical model allows us to make predictable calculations and select optimal rate constants.

Based on the purpose of the process of sulfuric acid alkylation of isobutane with olefins, which consists in obtaining a high-octane component of gasoline, the primary criterion for optimizing this process should be such an indicator as the yield of the target product having the highest octane value. In our case, such a product is the sum of trimethylpentanes.

During the process, side polymerization reactions occur, so the next optimization criterion is also the output of by-products—the sum of dimethylhexanes and heavy fractions.

Thus, the optimization criteria are: the total yield of trimethylpentanes and the total yield of by-products. To increase the efficiency of the process, it is necessary that the first criterion tends to the maximum, the second one—to the minimum.

The optimization problem for the process of sulfuric acid alkylation of isobutane with olefins was solved by the "Differential evolution base" method [9]. This is a method of multidimensional mathematical optimization, which belongs to the class of stochastic optimization algorithms (works using random numbers). Earlier, the authors of the article developed kinetic models of other chemical processes using various heuristic algorithms [8, 10–17], which have proven their effectiveness.

According to the literature, it is necessary that the ratio of isobutane:olefin is within (6–10):1. This is due to the fact that an excess of isobutane intensifies the target alkylation reactions and suppresses the occurrence of side effects, but at the same time, a too large excess of isobutane can contribute to the occurrence of side reactions of self-alkylation.

$$
\begin{cases}
x_4 + x_6 \to \max \\
x_5 + x_7 + x_8 \to \min \\
x_1 + x_2 + x_3 + x_4 = 1 \\
6 \le \left(\dfrac{x_2}{x_2 + x_3 + x_4} \right) \le 10
\end{cases}
$$

The results of the calculations carried out to optimize the process of sulfuric acid alkylation are presented in Table 3. The optimal ratio of isobutane is selected for different temperature conditions:olefin. Its effect on the yield of target high-octane trimethylpentanes and the yield of by-products is presented.

Based on Table 3, it can be seen that despite the use of raw materials with an optimal ratio of isobutane:olefin, the highest yield of trimethylpentanes is observed at a temperature of 12 °C and decreases with decreasing temperature. Changes in the concentrations of products of the alkylation process when using raw materials with an optimal isobutane ratio:olefins are shown in Fig. 6.

Fig. 6 shows the calculated concentration profiles of the target components when using the composition of raw materials with an optimal ratio of isobutane:olefin, markers indicate experimental data. At the beginning of the process, HEs is formed

Table 3 Dependence of the yield of the target alkylation products on the isobutane ratio:olefin in feed-stock

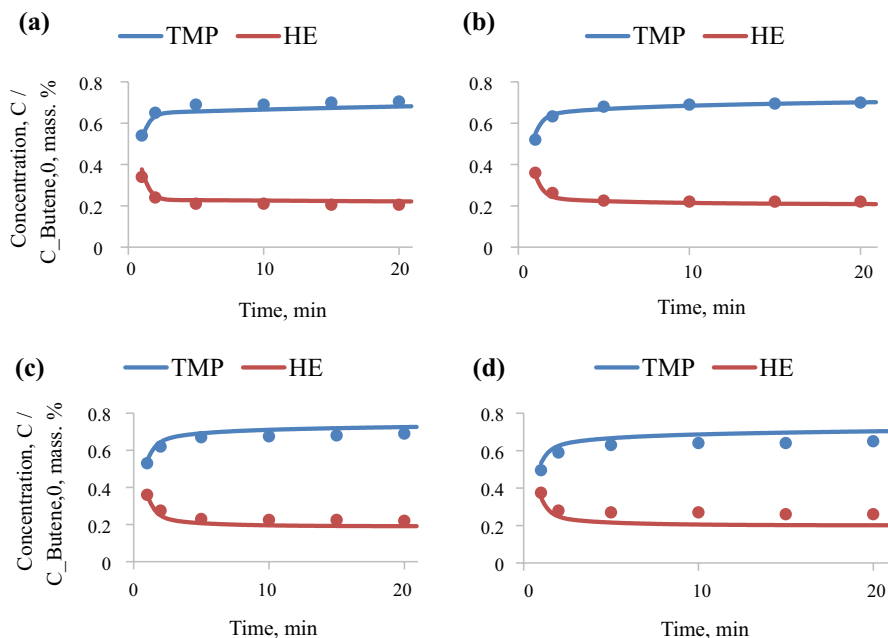| T, °C	Isobutane: olefin	Components (mass.%)						
		Isobutene	Isobutane	Butene-2	Butene-1	Yield of TMP	Yield of HEs	Yield of DMH
3	6.170:1	0.0089	0.8605	0.0603	0.0703	0.6820	0.2214	0.0966
6	7.182:1	0.0729	0.8776	0.0243	0.0250	0.7019	0.2086	0.0895
9	8.886:1	0.0171	0.8988	0.0677	0.0163	0.7262	0.1915	0.0823
12	9.221:1	0.0605	0.9022	0.0078	0.0296	0.7043	0.2015	0.0942

Fig. 6 Concentration profiles of the components involved in the alkylation process under different temperature conditions: **a** 3, **b** 6, **c** 9, **d** 12 °C. TMP are trimethylpentanes; HEs are heavy fractions

by the reaction of isobutylene or 2-butene with TMP+ or DMG+, followed by the transfer of the hydride by isobutene. Thus, the initial content of TMP and DMH is small, while HEs sharply increases to the maximum value in tens of seconds. HEs cations are then converted to LEs in the reaction of cleavage and hydride transfer, which corresponds to a sharp decrease in the HEs content. This observation corresponds to the rapid consumption of olefins, and also demonstrates the nature of the very rapid alkylation reaction of isobutane.

DMH is mainly formed at the initial stage of the reaction and subsequently decreases slightly. The concentration of TMP gradually increases over time. In general, the reaction reaches a stable state after 5 min, which indicates an optimized reaction time of sulfuric acid alkylation within 5 min. Fig. 6 shows that the yield of the TMP reaction product has increased compared to the experimental data (dots), and the yield of the DMH and HEs reaction byproducts has decreased in total as a result of process optimization.

Conclusions

Thus, the article presents a mathematical model of the reaction of sulfuric acid alkylation of isobutane by olefins in the form of a system of ordinary nonlinear differential equations. Software that allows us to determine the numerical values of the reaction rate constants at temperatures of 3, 6, 9 and 12 °C has been developed.

With the help of the developed kinetic model, the process of sulfuric acid alkylation was optimized, where the total yield of trimethylpentanes and the total yield of by-products were used as optimization criteria. To increase the efficiency of the process, it is necessary that the first criterion tends to the maximum, the second to the minimum. The ratio of isobutane to olefin ranged 6–10 to one. As a result of solving the problem of conditional global optimization, the optimal ratio of isobutane:olefin was selected for different temperature conditions.

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