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Predictive Modeling of the Kinetics of Deactivation of Liquid-Phase Alkylation of Hydrocarbons Processes

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Abstract

Theoretical and experimental studies of dynamic phenomena in liquid-phase catalytic processes of sulfuric acid alkylation of isobutane by isobutylenes with the formation of high-octane alkylates and HF- alkylation of benzene by higher olefins with the formation of linear alkylbenzenes (LAB) are performed. The dynamic mode of operation of liquid-phase catalysts is justified, which leads to the need for maximum selectivity and stability of the chemical-technological system by development and application of predictive mathematical models.

Keywords*: Sulfuric acid and HF- alkylation; Linear alkylbenzenes; Alkylgasoline; Mathematical model.*

1. Introduction

Modern alkylation technologies are represented by a wide class of various industrial processes, which, despite all the differences, have a principal common mechanism. Among the problems common to all alkylation processes (obtaining components of gasoline, ethylbenzene, cumene, linear alkylbenzenes), we can note the presence of concomitant side reactions that lead to a decrease in the selectivity of the process and deterioration of product quality. Reconstruction of existing plants to modern solid catalysts is often economically impractical due to the high costs of reconstruction of production [1-3]. Therefore, at present, petrochemical and oil refineries are faced with the problem of increasing the efficiency of production of alkylates. This complex multi-objective problem can be solved using the method of mathematical modeling.

2. Materials and methods

2.1. Theoretical background of the performed research

In recent years, alkylation processes have been widely studied around the world and, according to published data, one of the key problems of these processes is the deactivation of catalysts.

Mathematical modeling as a science is based on the optimal ratio of experimental and computational data. Many phenomena are not available for study and modeling expands the possibilities for research, allowing, for example, to describe the reactivity of conversion of hydrocarbons on various industrial catalysts (testing of catalysts), to solve the inverse kinetic problem and determine the numerical values of the rate constants of the reactions, predict the duration of the ipso cycle and the total life of the catalyst. Conditions are created for the functioning of intellectual technological plants. The development of any industrial production is based on the close interaction of two fundamental components: material and intellectual. This contributes both to the introduction of high-tech technologies and to the increase of the intellectual potential of engineering and technical personnel. The introduction of intellectual catalyst control modules, developed on the basis of predictive models, allows plant operators

to make technical decisions taking into account the recommendations promptly issued by this module. The methodology of mathematical modeling of multicomponent catalytic processes, which are all the processes of production of petrochemistry, was developed at Tomsk Polytechnic University with the active support of Russian refineries. For more than 30 years, the scientific school has been carrying out systematic work on the development of catalytic processes for various purposes. Using this methodology, the operational modes of catalysts for reforming, isomerization, dehydrogenation and alkylation, catalytic cracking and hydrocracking were studied, and methods and techniques for their modification were proposed and implemented, which ultimately increase the resource of the catalyst by optimizing their operation modes. Conducted research using the method of mathematical modeling and intellectual systems allow us to develop the scientific basis for the preparation of mixed fuels based on the physical and chemical laws of transformation of the components of the mixture. Technical support for the production of gasoline and the use of intellectual systems has increased the efficiency of use of raw materials in the preparation of commercial gasoline at OJSC "Gazpromneft – Omsk refinery by taking into account changes in the hydrocarbon composition of the feedstock, the catalyst activity and the intermolecular interactions of the components of the mixture.

The most developed from the point of view of modeling are the processes of alkylation of isobutane with butylenes, as well as the processes of alkylation of benzene with lower olefins [4-6].

At the same time, the literature practically does not address issues related to the deactivation of liquid acid catalysts. However, in homogeneous liquid-phase alkylation processes, the activity of the catalyst (acid) decreases as a result of the formation of by-products [7]. Deactivation of the catalyst may be associated with the formation of unsaturated hydrocarbons C5-C8, and also with the resulting high-molecular compounds with C9+ [8-9]. Such by-products are high-molecular alkylaromatic compounds that have a double bond in the side chain. While the full use of the potential of the catalyst largely determines the efficiency of the entire production as a whole. At the same time, almost all catalysts are subject to deactivation, a lot of work has been devoted to the study and modeling of this process [10]. Deactivation is a result of deposition of coked compounds on surface for heterogeneous catalysts of reforming, isomerization, dehydrogenation. In these processes' deactivation is accompanied by self-regeneration of coke under the influence of the components of the mixture (hydrogen, water, etc.). The level of stationary (optimal) activity is established when the rates of deactivation and self-regeneration are compared [10].

Our previous studies of catalyst deactivation refer to its reversible types. Thus, when maintaining the equilibrium conditions of the reaction of coke formation and hydrogenation of the intermediate products of compaction, the level of optimal activity of the catalyst is reached, at which its self-regeneration occurs [11]. Working under conditions of equal rates of reactions of coking and hydrogenation, which in industrial conditions are regulated by temperature, consumption of raw materials and recirculating hydrogen-containing gas, allows to significantly extend the period of inter-generation run of reforming catalysts [12]. Based on the conditions of thermodynamic equilibrium of the oxidation reaction of coxogenic compounds formed on the surface of platinum-containing dehydrogenation catalysts, the optimal modes of water supply to the industrial reactor were determined, which provided an increase in the service life of the catalyst by 20 % [13]. As a continuation of work in this direction should be considered research carried out for the HF catalytic alkylation of benzene higher olefins in the technology of linear alkylbenzene and sulphuric acid alkylation of isobutane by isobutylene in the technology of production of high-octane alkylate. The main task in this case is the theoretical justification of the existence of optimal conditions for the operation of the catalyst and the development of recommendations for maintaining the optimal consumption of acid for regeneration, to ensure stable operation of the chemical-technological system.

The study of the laws of transformation of hydrocarbons is a sequence of stages of thermodynamic, kinetic and hydrodynamic studies.

The activity of the liquid catalyst is determined by the ratio of the concentration of pure (catalytically active acid, not deactivated by side compounds) to its total volume in the reactor,

it can be regulated by the consumption of fresh acid. Therefore, we will operate with the concept of optimal consumption of fresh acid. In this regard, it is necessary to compensate for the decrease in the activity of the catalyst as a result of the accumulation of side compounds by increasing the consumption of fresh acid. However, an excessive increase in the flow of acid to the alkylation reactor can lead to an increase in the rate of adverse reactions. When the activity value deviates from the optimal value, there is a decrease in productivity for the target product-alkylate and an increase in the consumption of by-products from the alkylation reactor. Under conditions of excess acid, side reactions are accelerated, which leads to a decrease in yield.

2.2. Mathematical modeling of the process of HF-alkylation of benzene with olefins taking into account the dynamics of formation of high-molecular aromatic hydrocarbons and their fluorine derivatives

The production complex LLC "KINEF" (Kirishi, Leningrad region) includes a number of technologically related units (Fig.1): dehydrogenation of higher paraffins to olefins using a platinum-containing catalyst, hydrogenation of diolefins to monoolefins, alkylation of benzene with monoolefins using an HF catalyst(Fig.1). The technological parameters of the alkylation process are shown in Table 1.

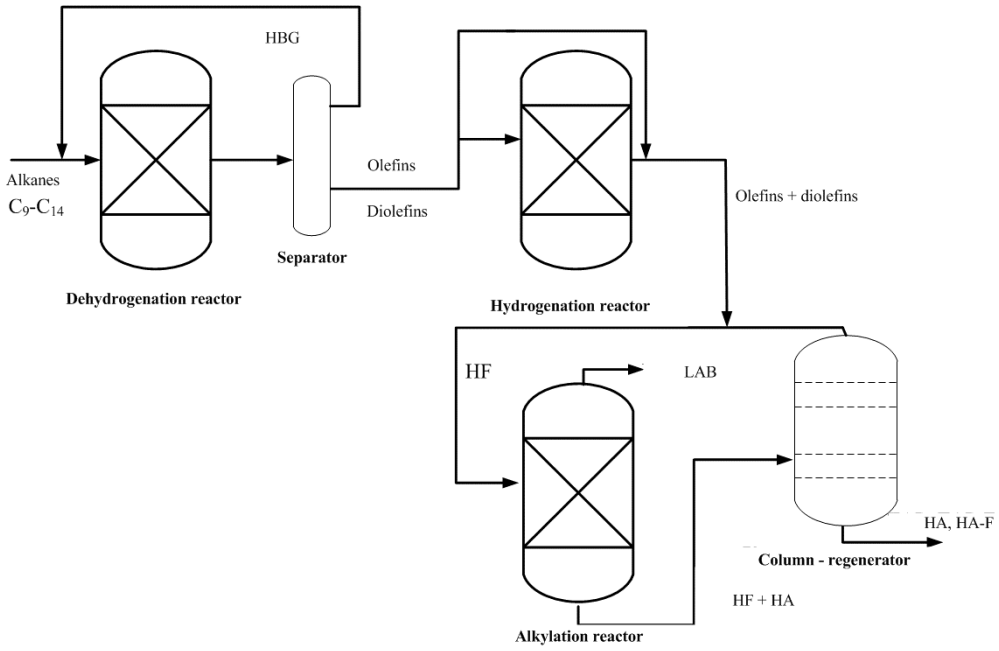


Figure 1.Technological scheme of production of LAB

Table 1. Technological parameters of the alkylation process

№	Parameter	Unit	Value
1	Volume flow of hydrocarbon raw materials to the reactor	m^3/h	70 – 128
3	Volume flow rate of the catalyst to the reactor	m^3/h	105 – 192
4	Temperature in the reactor	°C	50 – 60
5	Pressure in the reactor (IZB.)	MPa	0.4 – 0.6

Experimental and industrial research (passive experiment) at the plant LLC "KINEF" showed an extreme dependence of the change in the activity of HF-catalyst on the consumption of the selected acid for regeneration. In Table. 2 the values of obtaining LAB, HAB and heavy alkylate (TA) at different activity of HF-catalyst of the alkylation process are given.

Table 2. LAB, HAB values and heavy alkylate production at different activity of HF-catalyst of alkylation process

Input stream composition(reagent flow rate, kg/hour)							HF activity, Rel. units	HF consumption to re-generator,м³/ hour	LAB consumption, kg /hour	HAB consumption, kg/hour	HA consumption, kg /hour
paraffins C_{10}-C_{14}	α- olefins C_{10}-C_{14}	β,γ..η- olefins C_{10}-C_{14}	isoolefins C_{10}-C_{14}	diolefins C_{10}-C_{14}	benzene	hydrogen fluoride					
47791.1	865.2	4350.1	105.7	53.0	17845.4	1120.8	0.5	3	6772.8	20.0	269.8
Output stream from the reactor											
HAB consump-tion, kg/hour		bromine index LAB, mg/100g		bromine number HA, g/100g		mass fraction 2-phenylalkanes in LAB, %	0.7 (opt.)	4.5 (opt.)	6812.7	23.0	202.9
330.6		4.5		2.2		16.1	0.9	7	6717.1	27.0	290.5

The model of an industrial reactor allows to predict the behavior of the investigated system with high accuracy when changing the technological regime and the composition of raw materials, as well as to conduct the necessary amount of research without interfering with the operation of the plant.

Earlier, the Department of chemical fuel technology and chemical Cybernetics of Tomsk Polytechnic University developed mathematical models of the processes of dehydrogenation of n-paraffins C9 – C14, hydrogenation of diolefins and alkylation of benzene with olefins. The mathematical model of benzene alkylation with olefins took into account the reactions of formation 2, 3, 7-phenylkanes, nonlinear alkylbenzenes, dialkylbenzenes and olefin dimers, which provided the calculation of the product stream composition without taking into account the dynamic phenomena of coke formation and, as a consequence, without taking into account changes in the activity of the HF catalyst [14].

The thermodynamic analysis confirmed the probability of reversible reactions of coke formation (δ ΔG ≤ 100 kJ/mol), Table 3.

Table 3. Thermodynamic characteristics of reactions of benzene alkylation process with olefins (at T = 328 K, P=0.5 MPa)

Reaction	Δ*G*, kJ/mol	Δ*H*, kJ/mol	Direct reaction rate constant, $m^3 * mol^{-1} \bullet h^{-1}$	Reverse reaction rate constant , $m^3 * mol^{-1} \bullet h^{-1}$
1. Conversion of 2-phenylalkanes from α-olefins and benzene	–33.7	–94.4	$6.33 \cdot 10^{-2}$	$6.23 \cdot 10^{-2}$
2. Conversion 3..7-phenylalkanes from α, β..γ-olefins and benzene	–26.3	–71.8	$2.54 \cdot 10^{-2}$	$2.51 \cdot 10^{-2}$
3. Formation of nonlinear alkylbenzenes from branched olefins and benzene	–10.0	–52.6	$5.19 \cdot 10^{-2}$	$5.17 \cdot 10^{-2}$
4. Formation of dialkylbenzenes	–10.5	–76.4	$3.24 \cdot 10^{-3}$	$3.19 \cdot 10^{-3}$
5. Formation of dimers from olefins	–13.2	–66.6	$1.80 \cdot 10^{-3}$	$1.79 \cdot 10^{-3}$
6. HAR-1 formation from LAB and di-olefins	-51.7	–69.3	$2.40 \cdot 10^{-3}$	$2.35 \cdot 10^{-3}$
7. Formation of TAR-2 from TAR-1 and diolefins	-48.2	–81.5	$1.75 \cdot 10^{-3}$	$1.72 \cdot 10^{-3}$

Thus, the scheme of hydrocarbon transformations contains reversible reactions of TAR formation of different structures, the possibility of which is confirmed by thermodynamic analysis. During the development of the mathematical model, the components were aggregated into groups: the LAB group includes the components α, β, γ-olefins and isoolefins; the LAB group includes the components LAB-2, LAB-3,7, NAB; the HA group includes components HA-1 and HA-2. TA in the mathematical model refers to dialkylbenzenes. In this case, linear alkylbenzenes are intermediates in the formation of high-molecular aromatic and alkylaromatic compounds. In this case, both target and side reactions are catalyzed by HF

The mathematical model of the alkylation reactor (1) contains a parameter for changing the activity of the RA-catalyst AO, which is determined by the content of TAR and depends on the consumption of acid for regeneration.

$$\begin{cases} G \cdot \frac{\partial C_i}{\partial z} + G \cdot \frac{\partial C_i}{\partial V} = \sum_{j=1}^{m} a_j \cdot r_{ij} \\ G \cdot \frac{\partial T}{\partial z} + G \cdot \frac{\partial T}{\partial V} = \frac{1}{\rho \cdot C_p^m} \cdot \sum_{j=1}^{m} Q_j \cdot a_j \cdot r_{ij} \end{cases} \quad (1)$$

entry conditions: when z = 0, Ci = Ci0, T = Ten; when V = 0, T = Tan, Ci = Ci0;
where G is the load on raw materials, m^3/h; C_i-the concentration of the i-th component, mol/m^3; Z volume of processed raw materials, m^3; i=1, ..., N; j=1, ... M; N - number of substances involved in the reaction; M is the number of reactions r_j - flow velocity j-th reaction, $mol/м^3с$; V - volume of the alkylation reactor, m^3; T-temperature in reactor, °C; ρ the density, mol/m^3; Q_j heating effect of the j-th reaction, J/mol; C^p_m specific heat of reaction mixture, J/(mol·deg), a- relative catalyst activity.

$$a_j = \frac{k_{j,current}}{k_{i,initial}} \quad (2)$$

$k_{j,initial}$ - the rate constant of the j-th reaction on a fresh catalyst; $k_{j,current}$ – the rate constant of the j-th reaction at the current moment; a_j – change in the rate of the j-th reaction as a result of accumulation of by-products; C^k – concentration of by-products, mol/L (HA).

The adequacy of the mathematical model to the real process is confirmed by the convergence of the calculated indicators with their experimental values, Table. 4.

Table 4. Comparison of calculated and experimental data on the benzene alkylation reactor with higher olefins

№	LAB consumption, kg/h			TA consumption, kg/h			TAP consumption, kg/h		
	Calculation	Experiment	Error, %	Calculation	Experiment	Error, %	Calculation	Experiment	Error, %
1	6921.7	6857.41	0.94	253.51	263.11	3.65	49.04	47.15	4.01
2	6906.34	7026.63	1.71	257.96	265.8	2.95	49.38	49.33	0.10
3	6914.92	7064.58	2.12	254.02	264.48	3.95	49.35	50.32	1.93
4	6912.14	7064.58	2.16	253.81	264.48	4.03	48.42	50.99	5.04
5	6910.52	7064.58	2.18	253.69	264.48	4.08	48.39	48.98	1.20
6	6845.65	6963.32	1.69	247.63	254.21	2.59	48.61	51.17	5.00

Thus, the model of the alkylation reactor provides a satisfactory convergence of the calculated and experimental values of the main controlled parameters, which means that it can be used to predict the operation of an industrial plant in non-stationary conditions.

3. Results and discussion

3.1. Mathematical modelling of the sulfuric acid isobutene alkylation taking into account the side products formation

Based on the analysis of experimental data, as well as the results of thermodynamic and kinetic calculations, a mathematical model of the process of alkylation of isobutane with olefins was developed. The formalized scheme of transformations of substances in the process is shown in the Fig.2 .

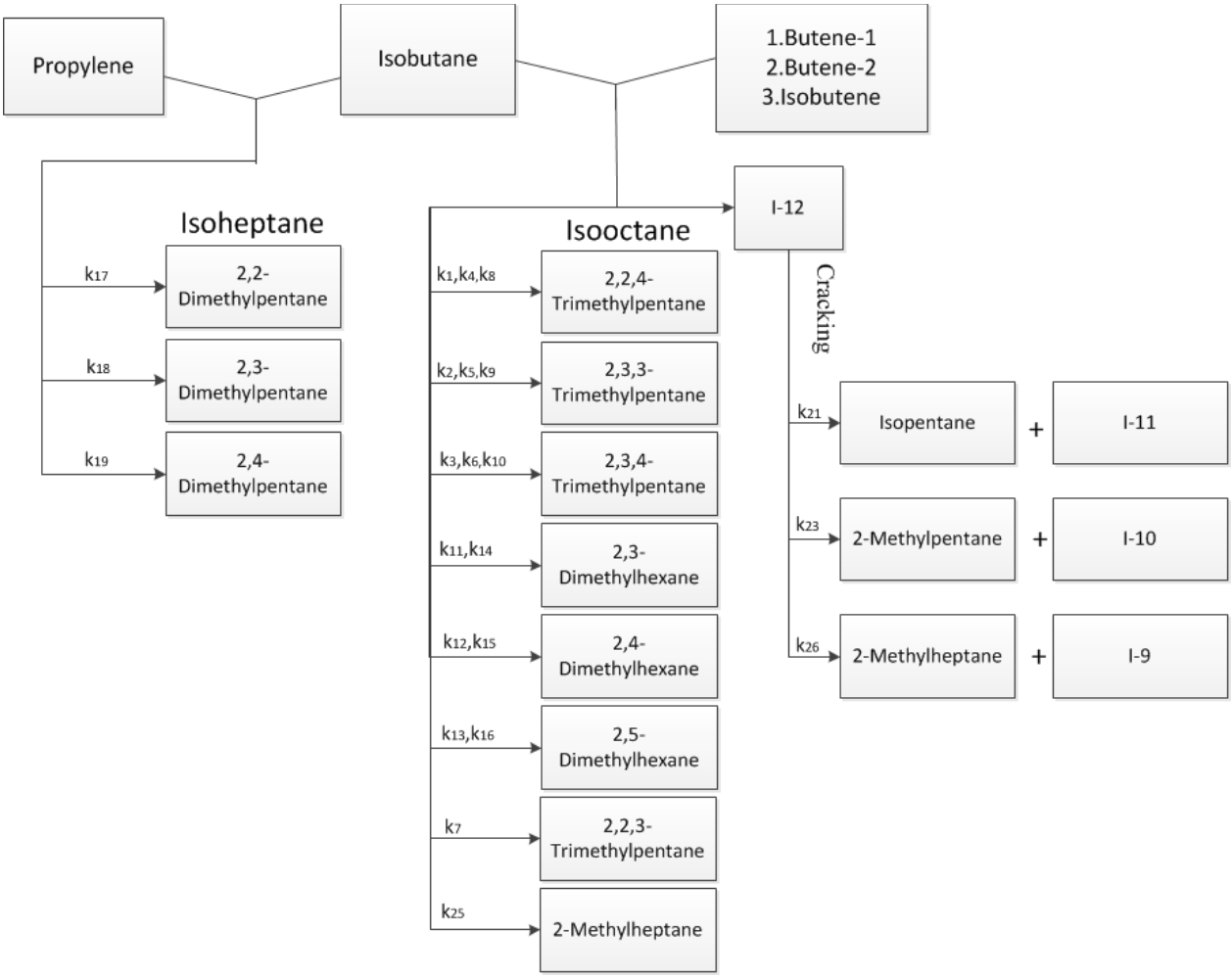
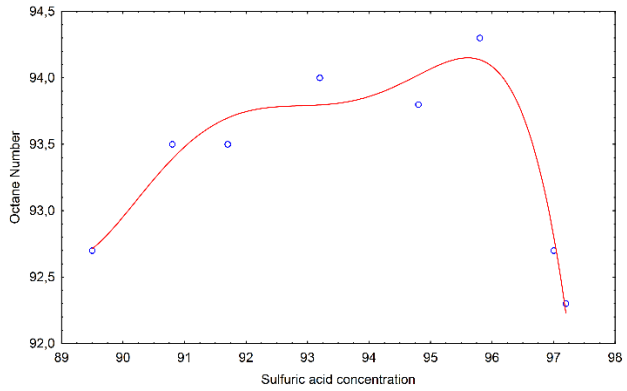


Figure 2. Formalized scheme of substance transformations in the process of sulfuric acid alkylation of isobutane with olefins: k_i - rate constant of the corresponding reaction

The concentration of sulfuric acid in the reactor is one of the main parameters of the process. For alkylation, sulfuric acid is usually used, containing from 88 to 98% of the monohydrate. However, only 95-96 percent sulfuric acid can produce an alkylate with a maximum octane number. The change in the concentration of sulfuric acid is the main cause of process non-stationary. Therefore, it is necessary to maintain the concentration of acid in the reactor at a constant level by regulating the supply of fresh and pumping out spent sulfuric acid. The main reasons for the decrease in the concentration of sulfuric acid are the accumulation of high-molecular organic compounds in it and its dilution with water entering the reactor with raw materials and resulting in some side reactions.

According to the given formalized scheme, the values of the concentration of reacting substances and the octane numbers of alkylate are calculated using the system of equations (1),

taking into account the change in the activity of the catalyst due to the formation of side compounds and water (Fig. 3).



The adequacy of the mathematical model was verified by comparison with the calculated and experimental data on the operation of the industrial plant (Table 5).

Figure 3. Alkylate octane number vs. H_2SO_4 concentration

Table 5. Experimental and calculated data on the operation of the sulfuric acid alkylation plant

Experiment	RON (Experiment)	RON (Calculation)	By-products, % mas	Water concentration, %mas	Error, RON, %
1	95.6	95.9	3.9	4.4	0.89
2	95.5	95.3	4.4	4.6	1.15
3	96.0	95.3	3.3	4.9	1.31
4	95.5	95.3	4.6	5.3	1.00
5	95.6	95.8	3.4	6.7	0.40

4. Conclusion

The occurrence in the alkylation reactor of irreversible reactions of formation of side reactions of various types under thermobaric conditions of the experiment was confirmed by the performed thermodynamic analysis; the kinetic regularities of these reactions were established by solving the inverse kinetic problem from experimental data.

A mathematical model of the alkylation reactor, including the functional dependence of changes in the activity of the catalyst of liquid-phase oxidation from the amount of generated by-products allows to forecast the change in the consumption of fresh acid to ensure maximum selectivity and stability of chemical-engineering production systems LAB and alkylbenzenes.

Based on the developed mathematical models, an intelligent system will be created for managing, optimizing and predicting the operation of industrial oil processing plants into valuable petroleum products.

A frame-production model for presenting knowledge about the operation of industrial plants, a database and a knowledge base for the process of alkylation of isobutane with olefins and benzene with olefins will allow you to practically implement a method for transforming hydrocarbons into "smart" alkylbenzenes with predictable properties, a new principle for managing non-stationary objects in industrial conditions using an intellectual and logistics module.

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