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DEVELOPMENT OF BENZENE WITH ETHYLENE ALKYLATION MODEL IN THE PRESENCE OF ALUMINUM CHLORIDE

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Abstract

The paper considers the benzene alkylation with ethylene model development with the use of acid catalyst. A list of reactions occurring in the alkylation reactor was made and the thermodynamic possibility of determination of these reactions by the change of Gibbs energy was defined. The developed model allows to obtain recommendations for optimization of technological operation modes of alkylation reactor.

Keywords: mathematical modeling; alkylation; ethylbenzene; aluminium chloride; thermodynamics.

1. Introdiction

The alkylation of aromatic hydrocarbons with olefins is applied on a large scale in the chemical industry. The worldwide capacity for ethylbenzene (EB) is currently estimated to be 23 million metric tons per year with an annual growth rate projected to be approximately 4%. Over 90% of the world's production of EB is used in the manufacture of styrene, but it is also used in the production of paint solvents and pharmaceuticals [1-2].

Nowadays modern solid zeolite catalysts are mostly used in the processs of alkylation [3-5]. However, in the Russian industry of ethylbenzene production the use of acid catalyst is still widespread: replacement of acid catalyst with zeolites is economically impractical due to high costs of reconstruction. Therefore, Russian refineries are confronted by maximising of effectiveness of existing units for alkylate production and benzene with ethylene alkylation using aluminum chloride catalyst as well.

The purpose of this work is to identify and study thermodynamic and kinetic patterns of benzene with ethylene alkylation using aluminum chloride catalyst, and to develop mathematical model of the process for one of the Russian refineries.

Recently kinetic and thermodynamic modelling provide information about process energy and reaction products structure, allows to evaluate qualitatively and quantitatively the possibility of reactions, determines the optimal parameters of the process, ensuring the maximum yield of target product at the lowest production cost. Also such analysis allows to reduce mathematical description of the process in the model preparation [6-12].

2. Experimental

2.1. Thermodynamic analysis of the process

In industry in the presence of acid catalyst the process of benzene with ethylene alkylation occurs at temperature 110 – 135°C and at pressure 0.5 - 3.0 atm. It is known that alkylation proceeds through activation of the olefin catalyst, and then the activated complex reacts with benzene and alkylbenzene [13-14].

Numerical studies have been conducted using the Semi-empirical method based on Neglecting of Diatomic Overlap approximation at PM3 level in the computational chemistry software *Gaussian* [15].

The considered reactions proceed in the liquid phase, so it was necessary to take into account the solvation effect. Benzene was chosen as a solvent because the ratio of benzene to ethylene in the industry is maintained at (8–14) : 1 ratio. The following conditions were set: temperature – 393 K, pressure – 1 atm., catalyst – $AlCl_3$.

Activation energy and pre-exponential multiplier in Arrhenius' equation are determined with the theory of transition state [15]:

1. To define the pre-exponential multiplier in the Arrhenius' equation the following expression is used:

$$k_0 = \chi \frac{k \cdot T}{h} e^{\frac{\Delta S_0^{\neq}}{R}} \quad (1)$$

Expression for bimolecular reaction:

$$k_0 = \chi \frac{k_b \cdot T}{h} e^{\frac{RT}{RT}} = \chi \frac{k_b \cdot T}{h} e \quad (2)$$

2. Activation energy:

$$E_a = \Delta H^{\neq} + nRT \quad (3)$$

As a result of numerical studies thermodynamic and kinetic parameters of benzene with ethylene alkylation in the presence of aluminum chloride were defined (Table 1).

Table 1. Kinetic parameters of benzene with ethylene alkylation at temperature 395 K and pressure 1 atm

№	Reaction	A_0, sec^{-1}	E_a, kJ / mol	k, sec^{-1}
1	$C_6H_6 + C_2H_4 \rightarrow C_6H_5C_2H_5$	$3 \cdot 10^{19}$	152.5	$2.05 \cdot 10^{-1}$
2	$C_6H_5C_2H_5 + C_2H_4 \rightarrow C_6H_4(C_2H_5)_2$	$9 \cdot 10^{15}$	141.6	$1.69 \cdot 10^{-3}$
3	$C_6H_6 + C_6H_4(C_2H_5)_2 \rightarrow 2C_6H_5C_2H_5$	$4.5 \cdot 10^{18}$	171.8	$8.58 \cdot 10^{-5}$
4	$C_6H_3(C_2H_5)_3 + C_6H_6 \rightarrow C_6H_4(C_2H_5)_2 + C_6H_5C_2H_5$	$5 \cdot 10^{21}$	179.9	$8.09 \cdot 10^{-3}$
5	$C_2H_4 + C_2H_4 \rightarrow C_2H_4C_2H_4$	$5 \cdot 10^{12}$	113.9	$4.33 \cdot 10^{-3}$
6	$C_6H_6 + C_2H_4C_2H_4 \rightarrow C_6H_5C_2H_4C_2H_5$	$2 \cdot 10^{10}$	106.4	$1.7 \cdot 10^{-4}$
7	$C_6H_6 + C_3H_6 \rightarrow C_6H_5C_3H_7$	$1 \cdot 10^{17}$	130.4	$5.69 \cdot 10^{-1}$
8	$C_6H_4CH_3 + C_2H_4 \rightarrow C_6H_3CH_3(C_2H_5)$	$4 \cdot 10^{17}$	140.0	$1.22 \cdot 10^{-1}$
9	$2\ C_6H_6 + C_2H_4 \rightarrow 2C_6H_4CH_3$	$5 \cdot 10^{25}$	215.0	$1.85 \cdot 10^{-3}$
10	$C_6H_4CH_3 + 2C_2H_4 \rightarrow C_6H_5C_2H_5 + C_3H_6$	$1 \cdot 10^{17}$	141.0	$2.26 \cdot 10^{-2}$

The list of reactions was compiled on the basis of literature data and according to component composition of input and output streams alkylator. Composition data were obtained from the EB reactor block monitoring in the presence of aluminum chloride from the alkylation plant of one of the Russian petrochemical companies.

Thermodynamic possibility of these reactions has been confirmed by determination of the isobaric-isothermal parameter [16] – the change of Gibbs energy ΔG at T=395 ºK and P=1 MPa. As for the target reaction Gibbs energy is equal to -63.3 kJ / mol and according to all defined

ΔG of the considered reactions, thermodynamic possibility of these reactions is probable. The determination was performed with the use of Gaussian-98 program by PM3 semi-empirical method.

2.2. Development of mathematical description

The obtained kinetic parameters were used as the basis for mathematical model development of the process. This model will allow to predict the quality of alkylate depending on temperature of the process, the feed composition and contact time of reactants in reactor [17].

Equation of mass balance of reactor:

$$\frac{dC_i}{dt} = \frac{1}{\tau}(C_{in} - C_{out}) \pm w_i \qquad (4$$

The expression for reaction rate formation and consumption of ethylbenzene according to the law of mass action is as follows

$$\frac{dC_{ethylbenzene}}{dt} = k_1 \times C_{benzene} \times C_{ethylene} - k_2 \times C_{ethylbenzene} \times C_{ethylene} +$$

$$+2 \times k_3 \times C_{benzene} \times C_{diethylbenzene} + k_4 \times C_{benzene} \times C_{triethylbenzene} + k_{10} \times C_{toluene} \times C^2_{ethylene}$$

2.3. Optimization of alkylation process with the use of simulation software

Program realization was performed using object-oriented programming *Wolfram Mathematica* environment. To check the adequacy of the developed model, calculated and experimental data from existing alkylation unit are compared in Table 2, where Δ - calculation error,%.Calculations were carried out for 2 years operation of one of the Russian the alkylation refineries unit.

Table 2. Results of comparison of design and experimental data by alkylation principle components outlet

		Date			
		1.05.15	5.05.15	16.05.15	19.05.15
		Temperature,°C			
		120	119	120	118
Yield of benzene, kg/h	Design	11746.1	11845.6	13132.0	10154.3
	Exp.	11879.9	11847.8	12485.7	9736.2
Δ, %		**1.1**	**0.02**	**5.2**	**4.3**
Yield of EB, kg/h	Design	5970.2	5750.2	6912.9	5392.0
	Exp.	6144.8	6128.8	7181.5	5903.9
Δ, %		**2.8**	**6.2**	**3.7**	**8.7**
Yield of PAB*, kg/h	Design	1132.3	1071.0	1520.5	1112.9
	Exp.	1092.4	1151.6	1658.9	1225.7
Δ,%		**8.9**	**7.0**	**8.3**	**9.2**
Yield of toluene kg/h	Design	403.4	392.1	439.6	352.4
	Exp.	370.6	370.9	480.2	379.8
Δ, %		**3.6**	**5.7**	**8.5**	**7.2**

**Polyalkybenzene (PAB): summ of isopropylbenzene, ethyltoluene, sec-butylbenzene, diethylbenzene and triethylbenzene.*

It was found that the defined error in the model did not exceed 9 %. This infers that the process is efficient. The developed model was used for numerical research in order to assess the temperature influence of the alkylation process on its selectivity for EB.

To determine the temperature influence in the range from 382 to 400 K for the alkylation process the calculation was conducted with the use of the developed model for two different feed compositions (Table 3). The selected temperature range corresponds to a real change in the modes of an industrial plant.

Table 3. Characteristics of input streams of alkylator

Characteristic, wt.%	No. of feed stock 1	2
Benzene flow	88.115	89.055
Ethylene flow	6.773	7.097
Toluene flow	0.026	0.022
Polyalkylbenzene flow	5.085	3.826

As shown in Fig. 1, the increase of inlet temperature leads to the increase of EB yield, that is, to the increase of the selectivity to the primary product. This may be due to the different values of the activation energies, the primary reaction is accelerated more with increasing temperature, which in combination with the lack of ethylene leads to the suppression of side reactions (Fig. 2).

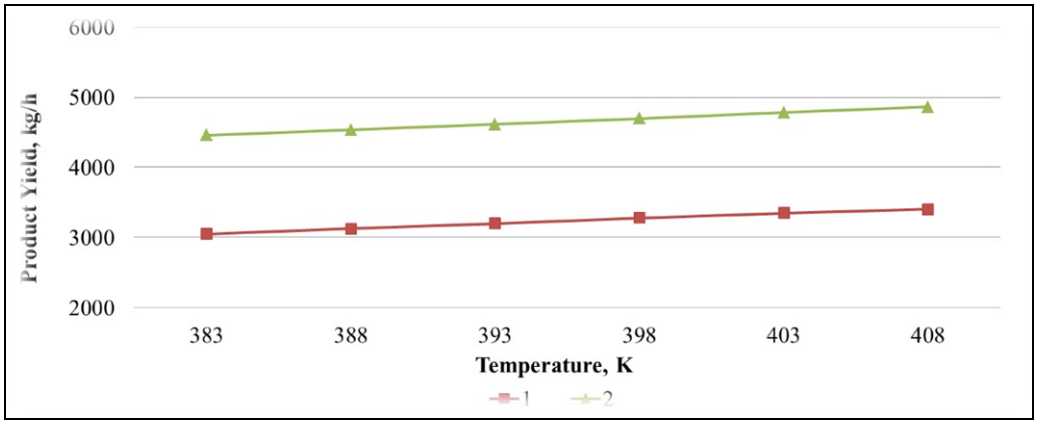

Figure 1. Dependence of ethylbenzene yield on temperature for two various feed compositions

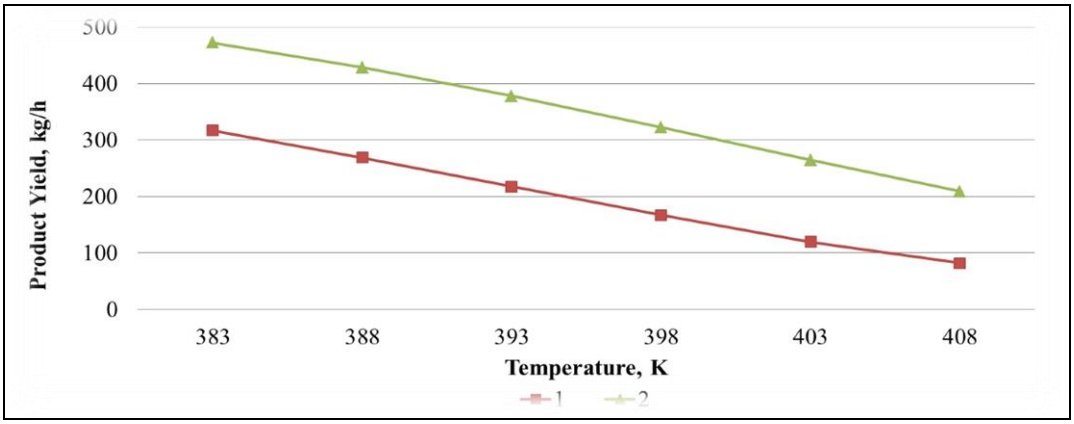

Figure 2. Dependence of diethylbenzene on temperature for two various feed compositions

However, with temperature increases the side reactions of cracking and polymerization lead to the accumulation of heavy hydrocarbons in a catalytic complex that, in turn, involves

decrease in its activity. Besides, the technological operating mode of the alkylation reactor has to provide homogenization of reagents mix with the catalyst, thus it is impossible to allow system heating because of the exothermicity of the proceeding reactions. Therefore, it is necessary to choose an optimal temperature interval for carrying out of the process, but also consider the composition of the refinable raw materials.

Calculations allowed to develop recommendations on technological operating mode optimization of alkylation reactor which is defined by the compositions of the refinable raw materials.

Thus, for raw materials with a high content of benzene and ethylene (feed stock №2) recommended temperature interval for carrying out the alkylation process is 383-393 K, correlation of "Benzene / Ethylene" is 8 - 12 kg / kg, the correlation of "Polyalkybenzene / Feed Stock" is 0.06 – 0.09 kg / kg.

3. Conclusion

1. The obtained enthalpy, entropy and Gibbs energy of activation values according to quantum-chemical modeling allowed to determine the kinetic parameters of each stage of benzene with ethylene alkylation.
2. The obtaned thermodynamic and kinetic patterns of benzene with ethylene alkylation were used to create a mathematical model for predicting of the quality indicators of produced alkylate depending on technological process mode. Accuracy of model calculations for such indicators as the yield of ethylbenzene and secondary components that determine the quality of the product (ethylbenzene, polyalkylbenzene) does not exceed 10%.
3. The model calculations have allowed to develop recommendations for optimization of technological operation modes of alkylation reactor, which is determined by the composition of feedstock.

List of symbols

χ	transmittance (transmission factor);	$\Delta H^{\neq}$	enthalpy of activation;
k	Boltzmann's constant ($1.38 \cdot 10^{-23}$ J/K);	i	reaction number;
T	temperature, K;	C_i	concentration of i - hydrocarbon, mol / m^3;
h	Planck's constant ($6.62 \cdot 10^{-34}$ J/sec);	w_i	rate of chemical reaction, mol / m^3;
$S_0^{\neq}$	enthalpy of activation, kJ/mole;	k_i	constants of reaction rate;
R	gas constant;	τ	contact time, sec.
ΔG	Gibbs energy;		

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