Chemistry for Sustainable Development **25** (2017) 213–220

UDC 66.011

Development of a Transalkylation Reactor Model to Increase the Energy and Resource Efficiency of Ethylbenzene Production

S. A. KOSHKIN[1,2], I. O. DOLGANOVA[2], and E. N. IVASHKINA[2]

[1]*Research organization Sibur-Tomskneftekhim Ltd.,*
Tomsk, Russia

[2]*Tomsk Polytechnic University,*
Tomsk, Russia

E-mail: dolganovaio@tpu.ru

(Received June 21, 2016; revised December 14, 2016)

Abstract

An approach was disclosed to the development of mathematical models of industrial processes using quantum chemical calculation methods of thermodynamic parameters of target and side reactions in combination with experimental data analysis of the operation of an industrial transalkylation process that is one of the preparation stages of ethylbenzene. A scheme of transformations in the transalkylation process was elaborated, thermodynamic parameters of target and side reactions were determined, a kinetic model was compiled and its parameters defined. Adequacy of a model implemented in the HYSYS medium was tested resulting from comparison with industrial data. Application prospects of the developed mathematical model for the transalkylation process to increase energy and resource efficiency of ethylbenzene production were noted from the viewpoint of an increase in process selectivity and minimization of costs on developing a given quantity of the products.

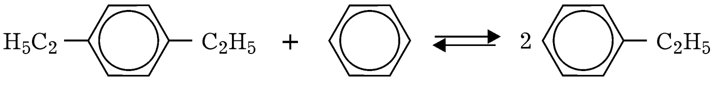
Key words: ethylbenzene, alkylation, transalkylation, mathematical model

INTRODUCTION

Alkylation of benzene with ethylene is the major direction of consumption of benzene (50 % of the total volume). Ethylbenzene (EB) resulting from this is an intermediate in the chain of preparation of acrylonitrile butadiene styrene (ABS) and styrene-acrylonitrile copolymer (SAN) plastic, styrene-butadiene rubber, polystyrene. The world production of EB was assessed in 2014 as 37 million t per year [1].

The first technologies of EB preparation applied a homogeneous catalyst based on aluminium chloride, however, the process of alkylation of benzene with ethylene over a chloroaluminium catalyst has become morally obsolete since the development of heterogeneous catalysts and currently, new installations are not being built. Technologies using a heterogeneous catalyst include two consecutive stages: alkylation of benzene with ethylene and transalkylation (TA) of polyethylbenzenes (PEBs) to EB. The both processes proceed over zeolite-containing catalysts in adiabatic reactors [2–4].

High competition in the final market of EB, economic and environmental aspects dictate tasks of increasing the resource efficiency of products. Reaching such results is possible due to combining experimental data with mathematical modeling by the introduction of applied mathematical models into industrial production to search for optimum technical regimes. Simi-



Scheme 1.

lar models have already been developed for some refining and petrochemical processes [5–7] that are successfully used in production to monitor and predict the operation of installations for processing of hydrocarbon raw materials, as simulators for technical staff, and differ from the existing analogues by considering the physicochemical essence of the processes proceeding in reactors. Some authors studied kinetic regularities and determined parameters of equations for the proposed kinetic schemes of alkylation and TA processes, proposed the mechanisms of the occurring reactions [8–15], as well as developed approaches to process modeling using data for industrial installations [16, 17]. However, currently, one has not managed to find the description of the model constructed for a liquid-phase process of EB preparation over heterogeneous catalysts excluding both the alkylation stage and TA.

The construction of mathematical models for such a multistage process is complicated by the fact that, in comparison with homogeneous technologies, the efficiency of heterogeneous processes is determined by a greater number of parameters, such as the distribution (quenching) of ethylene in an alkylation reactor, the ratio of benzene and PEB in a TA reactor. These and other technological parameters depend on the composition of the processed raw materials and the activity of the catalysts used, therefore, they require adjustment during operation of industrial installations. The developed mathematical model will be useful to carry out similar optimisation studies, which can be used as a simulator when training technicians-and-engineers of petroleum enterprises.

The work goal was the development of a mathematical model for a liquid-phase reactor of TA of PEB over a zeolite-containing catalyst to predict the composition of the products (Scheme 1).

The TA reaction is accompanied by the displacement an alkyl group from one molecule to another. The target transformation of the system under consideration is an equilibrium reaction of diethylbenzenes (DEB) and benzene in EB (see Scheme 1). Herewith, equilibrium concentrations of the obtainable products are little temperature dependent (thermal effect of reaction $\Delta H_{600} = 5.8$ kJ/mol [1]) but highly dependent on the initial B/DEB ratio). The mechanism of the TA reaction over Brønsted sites is presented in Fig. 1.

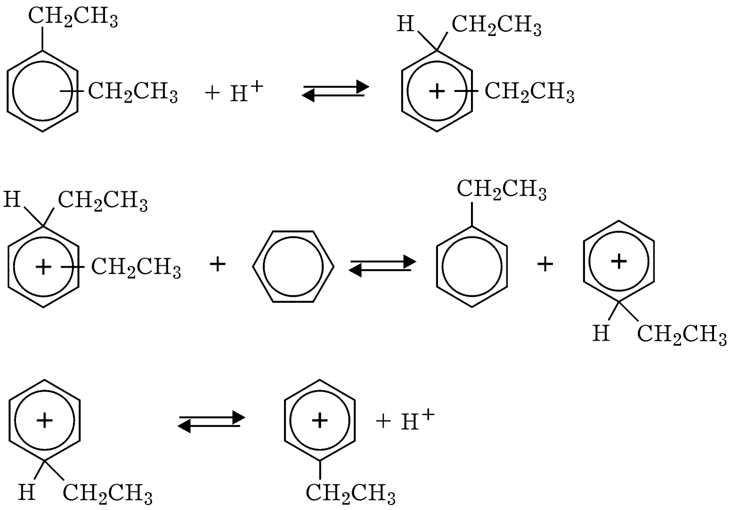


Fig. 1. Transalkylation mechanism.

INDUSTRIAL DATA ANALYSIS OF TRANSALKYLATION REACTOR OPERATION

Industrial installation operation indicators are the basis of the model developed of the TA process. Operational data analysis of an industrial reactor for TA for a period from October 1, 2013 to August 31, 2015 was performed: sensor readings of temperature control, consumption and pressure of the process, as well as data from laboratory tests of raw materials and products of the installation.

Figure 2 presents data on the average monthly consumptions of basic flows into a TA reactor on raw materials and the ratio of benzene to PEB. The ratio of uses of benzene to PEB in the period considered and the load on the reactor continuously changed to decrease. Experimental data from the industrial installation were used as initial when developing the equations of mathematical model and solving the inverse kinetic problem.

To determine the key components to construct equations of their consumption and formation (kinetic equations) in a model of the process the value of the concentrations for the substances determined in the laboratory was compared. Table 1 presents the composition of the raw and product flows: the average and minimum observed concentrations for the period considered. To decrease the number of components and, accordingly, the dimension of the mathematical model only those substances, the concentration of which is no less than 0.1 mass %, were considered when its constructing. This assumption is justified by the fact that the error of the method of gas chromatography is no less than 0.1–5 mass %. On the assumption of the data in Table 1, light hydrocarbons (LHC), C_6 naphthenes (CH), C_7 naphthenes (MCH), benzene (B), ethylbenzene (EB), diethylbenzenes (DEB), butylbenzene (BB), triethylbenzene (TEB), heavy fractions (HF), diphenylethanes (DPE) represent such substances. Herewith, with experimental determination of the composition of raw materials and the products individual compounds are united into groups: LHC (a mixture of hydrocarbons (alkanes and alkenes) to C_5); C_6 naphthenes that mainly consist of cyclohexane with an admixture of methylcyclopentane; C_7 naphthenes that mainly consist of DEB; TEB; DPE (all possible isomers are included); heavy components (HC) of the products of further alkylation.

To assess the direction of reaction behaviour by components (consumption or formation) the average conversion degree for each of them for the studied period was calculated by the equation

$$X_i = \frac{F_{\text{in}}x_i - F_{\text{out}}x_i}{F_{\text{in}}x_i} \cdot 100\,\% \tag{1}$$

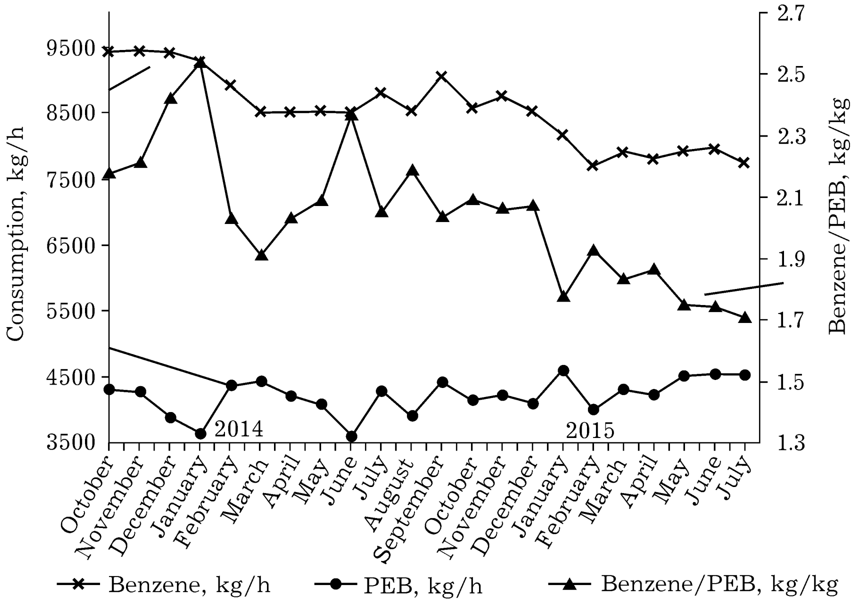


Fig. 2. Operational experimental data for transalkylation (TA) of polyethylbenzenes (PEBs) installation over a period of from October 1, 2013 to August 31, 2015.

TABLE 1

Composition of feed and product streams during transalkylation

Substances	Yield, mass %			Input, mass %					
	Reacting mass			PEB			Benzene		
	max	average	min	max	average	min.	max	average	min.
Light hydrocarbons	7.00	3.59	0.76	0.03	0.01	0.00	5.65	3.14	0.30
Naphthenes C_6	1.18	0.46	0.16	0.02	0.00	0.00	4.17	2.14	0.50
Naphthenes C_7	0.08	0.02	0.00	0.00	0.00	0.00	0.47	0.21	0.02
Benzene	71.67	52.95	45.02	0.02	0.00	0.00	98.48	94.32	90.73
Toluene	0.05	0.01	0.00	0.01	0.00	0.00	0.05	0.01	0.00
Ethylbenzene	39.44	29.90	11.11	9.84	0.06	0.00	0.91	0.19	0.01
Isopropylbenzene	0.02	0.00	0.00	0.07	0.01	0.00	0.00	0.00	0.00
n-Propylbenzene	0.05	0.01	0.00	0.14	0.02	0.00	0.00	0.00	0.00
m- and *p*-Xylenes	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
o-Xylene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Styrene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ethyltoluene	0.06	0.01	0.00	0.36	0.05	0.00	0.00	0.00	0.00
Methyltoluene	0.01	0.00	0.00	0.03	0.00	0.00	–	–	–
Diethylbenzene	16.80	10.73	2.00	95.18	89.33	82.30	0.00	0.00	0.00
Butylbenzene	0.98	0.53	0.00	3.22	1.93	0.53	0.00	0.00	0.00
Trimethylbenzene	0.02	0.01	0.00	0.08	0.02	0.00	0.00	0.00	0.00
Triethylbenzene	2.88	1.25	0.04	10.17	7.38	2.41	–	–	–
Heavy fractions	0.28	0.13	0.01	0.30	0.08	0.00	–	–	–
Diphenylethane	0.21	0.06	0.00	0.24	0.00	0.00	–	–	–
X-impurities	1.16	0.33	0.06	6.47	1.11	0.17	0.00	0.00	0.00

Note. Dash – not detected.

where X_i is the conversion of the i-th component; F_{in} and F_{out} are the mass flow of the input and output flows; x_{i} is the mass fraction of the i-th component.

The average conversion degree for each component was the following (mass %): LHC −73.36, CH 66.75, MCH 84.87, B 17.50, EB −34574.69, DEB 62.18, BB 13.04, TEB 47.07, HF −695.23, and DPE −2655.16. The components, conversion of which is negative, are formed during TA, those with positive are generated during the alkylation process.

DEVELOPMENT OF THE FORMALIZED SCHEME OF TRANSFORMATIONS

Statistical analysis of TA reactor operation led to the isolation of the key components to develop the scheme of formalized transformations: LHC, CH, MCH, B, EB, DEB, BB, TEB, HF, and DPE. Literature data analysis demonstrated that the following reactions might proceed in the medium of the isolated components: TA, disproportionation, dealkylation, catalytic cracking, cyclization of alkenes, cracking of cycloparaffins, conjugated hydrogenation, condensation [2–12]. The formalized scheme of transformations (FST) of hydrocarbons in a TA reactor was developed on the basis of the listed types of reactions (Fig. 3).

The FST includes ten reversible and two irreversible bonds. Ethylbenzene is formed on account of through TA of DEB and TEB with benzene (*1*, *3*), disproportionation of two DEB molecules (*2*), alkylation of benzene with ethylene (*4*), and decomposition of DPE with an additional formation of one benzene molecule (*5*), dealkylation of BB with the formation of ethylene (*9*). Diphenylethane is formed along route (*5*) during the interaction of benzene and EB. Butylbenzene is subjected to dealkylation during TA and produces either benzene and butene

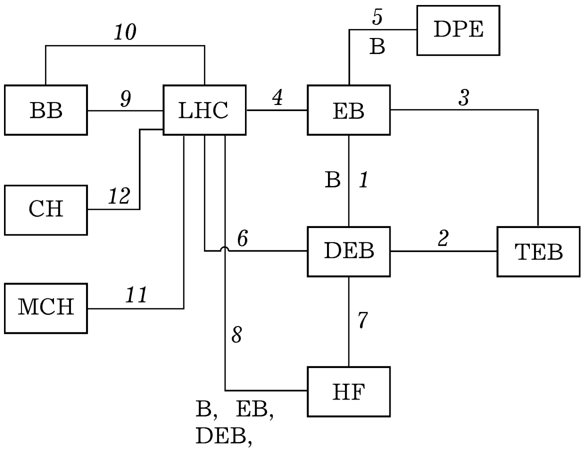


Fig. 3. Formalized scheme of transformations of hydrocarbons during TA.

(*10*) or ethylene and EB (*9*). Cracking of cycloalkanes and conjugated hydrogenation (*11*, *12*), cracking of HF (*8*), dealkylation of aromatic compounds (*4*, *6*, *9*, *10*) lead to the LHC component. Dehydrocyclization and condensation of DEB (*7*), alkylation of DEB, EB, TEB with alkenes (*8*) result in HF. It was necessary to confirm the occurrence of these reactions at the next stage by calculations of the Gibbs energy (ΔG) through quantum chemical calculations (QCC).

RESULTS AND DISCUSSION

Confirmation of the thermodynamic probability of reactions proceeding

To confirm thermodynamic possibility of reactions proceeding during TA QCC were used. The calculations were performed in the Gaussian-98 program using the density functional theory (DFT) method at the B3LYP level with a temperature of 200 °C and 3.4 MPa pressure of the process. This technique was selected due to a relatively high accuracy in comparison with empirical methods. The B3LYP level is highest among DFT levels used by the Gaussian program, and a basic set was selected in such a way to preserve the governability of calculations but herewith, not to decrease the accuracy of the description of the physical situation [13]. Since the reactions occurring between components and substances forming them are numerous, typical reactions by type were undertaken to assess ΔG. For example, decomposition reactions of cyclohexane into two propylene species or a molecule of butane and ethylene were considered for the reaction of cracking of naphthenes. Consequently, the interaction in FST was characterized by the lowest Gibbs energy out of the considered typical reactions of its type. Thus, the lowest calculated QCC is −28.36 kJ/mol for transalkylation of *ortho*-, *metha*- and *para*-isomers of DEB forming DEB FST, for *o*-

TABLE 2

Values of ΔG for FST reactions (temperature 200 °C, pressure 3.4 MPa)

Reaction number in FST	Reactions	ΔG, kJ/mol (for the right component)
1	DEB + B ↔ 2EB	−28.36
2	2DEB ↔ EB + TEB	−36.01
3	TEB + B ↔ EB + DEB	−11.00
4	B + P ↔ EB	−33.69
5	EB + B ↔ DPE	25.99
6	DEB ↔ EB + P	−1.86
7	DEB → HC	242.80
8	P + B/EB/DEB/TEB ↔ HC	−19.36
9	BB ↔ EB + LHC	150.80
10	B + LHC ↔ BB	−11.21
11	MCH ↔ LHC	2.89
12	CH ↔ LHC	38.23

DEB, correspondingly. The ΔG for reaction 1 in FST is identical (Table 2).

The direction of the equilibrium shift is primarily indicated by a value of ΔG. It was assumed that the reaction was reversible under the condition $\Delta G = \pm 50$ kJ/mol. For reactions 7 and 9, ΔG has a positive value, which even in case of considering the product of concentrations, excess in DEB and BB indicates a low probability of the occurrence of such transformations in the system under study, therefore, these reactions were excluded from the formalized scheme. Thus, the final formalized schema contains ten reversible transformations, 7 and 9 ones are not considered.

Development of mathematical description of a transalkylation process

Based on the FST, kinetic equations for the considered reactions with assumption about pseudohomogeneity were written [14–17].

It is known that TA reactions proceed in the kinetic region with the minimum diffusion limitations due to using a catalyst with a larger diameter of pores and cavities [18]. The plug flow reactor (PFR) model was selected as a model:

$$dX_i = r_i S dl / C_{i_0} V \quad (2)$$

$$dC_i = r_i S dl / V \quad (3)$$

where X_i is conversion of the i-th component; r_i is the rate of consumption and the rate of formation of the i-th component; S is the cross is the sectional area of the reactor; C_{i_0} is the initial concentration of the i-th component, mol/L; C_i is the current concentration of the i-th component, mol/L; V is the volumetric flow of the reaction mixture, m^3/s.

This assumption was accepted on the base of the data of the apparatus design and its geometrical sizes: the ratio of the length and diameter of an industrial apparatus (the ratio is 4.6) and the presence of a bulk catalyst that largely contributes to the flow regime of the PFR model [19, 20].

It is preferable to use expression form (3) for the substances formed as a result of the process, and form (2) for the substances consumed.

To simplify the model an assumption about the isothermal operation mode of the apparatus was also taken, since a TA process was characterized was characterized by an insignificant temperature drop in −1...1 °C in the time peri-

TABLE 3

Determination results of parameters of kinetic equations

Reaction number in FSP	Form of reaction equation	Direct		Reverse	
		A	*E*, J/mol	*A*	*E*, J/mol
1	$k_1 C_{\text{DEB}} C_{\text{B}} - k_{-1} C_{\text{EB}}^2$	$3 \cdot 10^8$	78 373	115 596	50 757
2	$k_2 C_{\text{DEB}}^2 - k_{-2} C_{\text{EB}} C_{\text{TEB}}$	$3 \cdot 10^8$	65 333	91 977	28 997
3	$k_3 C_{\text{TEB}} C_{\text{Б}} - k_{-3} C_{\text{EB}} C_{\text{DEB}}$	$3 \cdot 10^8$	82 008	2532	40 002
4	$k_4 C_{\text{EB}} - k_{-4} C_{\text{B}} C_{\text{LHC}}$	$1.54 \cdot 10^6$	96 966	143	94 937
5	$k_5 C_{\text{EB}} C_{\text{B}} - k_{-5} C_{\text{DPE}} C_{\text{LHC}}$	3573	63 475	16 912	26 818
6	$k_6 C_{\text{DEB}} - k_{-6} C_{\text{EB}} C_{\text{LHC}}$	2937	96 793	436	96 070
8a	$k_{8\text{a}} C_{\text{LHC}} C_{\text{B}} - k_{-8\text{a}} C_{\text{HF}}$	1248	57 606	67 249	47 655
8b	$k_{8\text{б}} C_{\text{LHC}} C_{\text{EB}} - k_{-8\text{b}} C_{\text{HF}}$	1787	88 954	98 091	49 075
8c	$k_{8\text{в}} C_{\text{LHC}} C_{\text{DEB}} - k_{-8\text{c}} C_{\text{HF}}$	1787	88 954	98 091	49 075
8d	$k_{8\text{г}} C_{\text{LHC}} C_{\text{TEB}} - k_{-8\text{d}} C_{\text{HF}}$	1787	88 954	98 091	49 075
10	$k_{10} C_{\text{BB}} - k_{-10} C_{\text{B}} C_{\text{LHC}}$	92 050	96 084	0.006	122 189
11	$k_{11} C_{\text{MCH}} - k_{-11} C_{\text{LHC}}$	238 246	12 761	30 097	69 366
12	$k_{12} C_{\text{CH}} - k_{-12} C_{\text{LHC}}$	39 477	13 586	64 303	25 498

Notes. 1. *A* and *E* are the pre-exponential factor and the activation energy of the reaction, respectively. 2. Concentrations are expressed in mol/L. 3. The pre-exponential factor can have the dimensions L/(mol · s) or s^{-1} depending on the equation forms (reaction order).

od under review, therefore, the model does not consider a change in the heat capacity of the system and is not complemented by a heat-balance equation. In addition, an assumption was taken that process conditions were not changed in the time range between laboratory analyses. A production monitoring system allows analysing the composition of the incoming raw materials and the products from the reactor. Herewith, data from analyses are selected twice a day. There is a difference in time between sampling for analysis of the composition of raw materials and the reaction products.

Parameters of equations of consumption and formation of components of raw materials and the products were determined by solution of the reverse kinetic task. Kinetic equations and values of the activation energy and preexponential factors are given in Table 3. To determine parameters of the kinetic model (solution of the inverse kinetic task) experimental data of the composition of raw and product flows for an industrial installation were used (see Table 1), data of a change in the major technological operational parameters of a TA reactor (see Fig. 2), including temperature values, the variation interval of which is 195–210 °C.

The software realization of algorithm for solving the inverse kinetic task was performed in the gPROMS package.

Checking the adequacy of a mathematical model of a transalkylation process

Model verification was carried out by comparing values of concentrations of hydrocarbons in the products with operational data of a TA reactor in a broad time range. A computer model in HYSYS v. 8.8, where calculations of a TA reactor were performed, was developed on the base of equations of a mathematical model. The composition and raw materials consumption, the input and output temperature of the reactor, pressure were set according to the date of selection of raw materials. Figure 4 presents comparison results of calculated and experimental data.

CONCLUSION

1. The formalized scheme of transformations of hydrocarbons during TA was developed with provision for the following components: light hydrocarbons, C_6 naphthenes, C_7 naphthenes, benzene, EB, DEB, BB, TEB, heavy hydrocar-

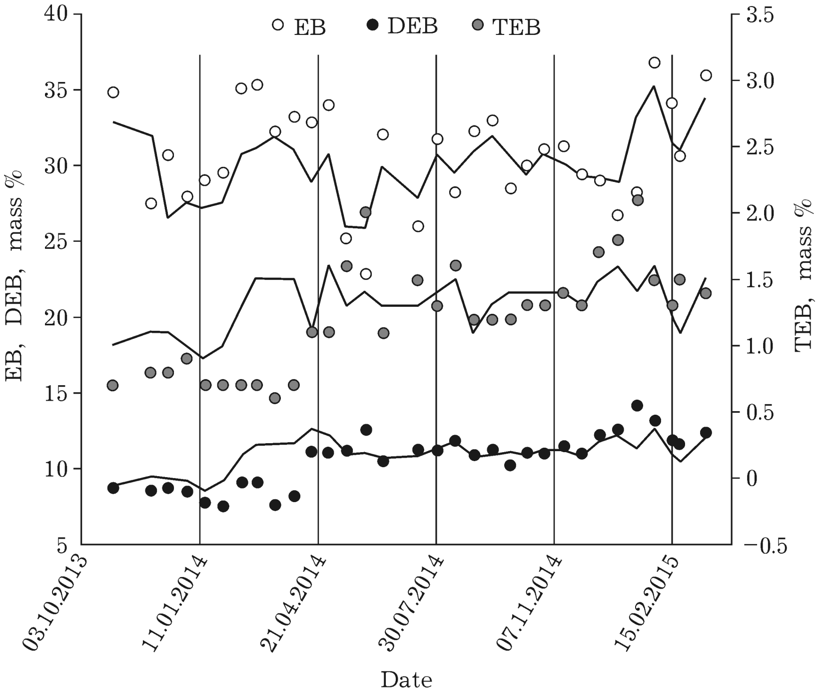


Fig. 4. Comparison of experimental (points) and calculated (lines) concentrations of a transalkylation reactor.

bons, DPE. The model of the reactor, which is based on the developed FCS, describes with sufficient accuracy the change in the concentration of the main products of EB, DEB, and TEB in the temperature change in the range 195–210 °C and ratio of raw materials B/PEB of 1.6–2.6 mass.

2. A model of TA reactor describes consumption and formation of other components of the system: light hydrocarbons, C_6 naphthenes, C_7 naphthenes, BB, heavy, DPE. Accounting for these components allows using a model of a TA reactor when modelling preparation processes of EB entirely, including a product separation unit, in such software packages, as Aspen HYSYS. This opportunity allows moving on to optimization of process indicators.

3. Reactions (1), (2), (4–6), (8), (10–12) are transalkylation of DEB with B, disproportionation of two DEB molecules, transalkylation of TEB with B, dialkylation of EB, formation of DPE, alkylation with ethylene homologues of aromatic components of the system, dealkylation of BB and cracking of naphthenes are thermodynamically probable under conditions of the process, condensation reaction of DEB into naphthalenes (seal products) and cracking of a side chain of EB are unlikely, which is confirmed by the results of quantum chemical calculations.

4. Mathematical model of a TA reactor can be used to predict the composition of the studied transalkylation process when changing the structure of processed raw materials and reactor temperature.

REFERENCES

1 Meyers Robert A. (Ed.), Handbook of Petroleum Refining Processes, 3rd ed., McGraw-Hill Professional, New York *etc.*, 2003.

2 Galadima A., Muraza O., *Chem Eng. Proc.: Process Intensification*, 1, 1 (2011) 31.

3 Chua L., Vazhnova T. , Mays T., Lukyanov D., Rigby S., *J. Catal*, 283, 1 (2011) 68.

4 Liu K., Xie S., Liu S., Xu G., Gao N., Xu L., *Fluid Phase Equilibria*, 260, 1 (2007) 146.

5 Al-Kinany M. C., Jibril B. Y., *Chem. Eng. Proc*., 44 (2005) 841.

6 Mokoema K., Alkyl-Transfet (transalkylation) Reactions of Alkylaromatics on Solid Acid Catalyst (Ph. D thesis), 2005.

7 Tseng-Chang T., Shang-Bin L., Ikai W., *Appl. Catal., A*, 181 (1999) 355.

8 Hongjun Y., Wenyu L., Yi P., *Pet. Sci. Technol*., 24 (2009) 1079.

9 Forni L., Cremona G., *Appl. Catal., A*, 121 (1995) 261.

10 Forni L., Amarilli S., *Appl. Catal., A,* 103 (1993) 173.

11 Ebrahimi A. N., Zolfaghari A., *Chem. Eng. Proc*., 50 (2011) 31.

12 Chen X., Huang S., Cao D., Wang W., *Chem. Eng. J.,* 167, 1 (2011) 240.

13 Odedairo T., Al-Khattaf S., *Chem. Eng. Sci*., 65, 8 (2010) 2472.

14 Corma V., Soria M., Schnoeveld E., *J. Catal*., 192, 1 (2000) 163.

15 Ignatov S. K., Kvantovo-Khimicheskoye Modelirovaniye Molekulyarnoy Struktury, Fiziko-Khimicheskikh Svoystv i Reaktsionnoy Sposobnosti (High School Textbook), Univer-Grupp, Samara, 2005.

16 Chudinova A. A. , Nurmakanova A. E., Salishcheva A. A., Ivashkina E. N., Gavrikov A. A., *Chem. Sust. Dev.,* 22, 6 (2014) 569. URL:http://www.sibran.ru/en/journals/KhUR

17 Shcherbakova Yu. A., Dolganova I. O., Ivashkina E. N., Ivanchina E. D., *Izv. Vuzov. Fizika,* 54, 12/2 (2011) 98.

18 Fetisova V. A, Ivashkina E. N., Ivanchina E. D., Kravtsov V. A., *Katal. Prom-sti,* 6, 1 (2009) 27.

19 Nurmakanova A. E., Salishcheva A. A., Chudinova A. A., Syskina A. A., Ivashkina E. N., *Proc. Chem*., 10 (2014) 430.