

DEVELOPMENT OF COMPUTER MODELING SYSTEM AS A TOOL FOR IMPROVEMENT OF LINEAR ALKYL BENZENE PRODUCTION

Irena O. Dolganova*, Igor M. Dolganov, Emilia D. Ivanchina, Elena N. Ivashkina

*Chemical Engineering Department, Tomsk Polytechnic University, 30, Lenin Avenue, Tomsk, 634050, Russia; *corresponding author e-mail: dolganovaio@sibmail.ru*

Received April 21, 2011, Accepted October 15, 2011

Abstract

The estimation of reactions occurrence probability in liquid-phase catalytic benzene via olefins alkylation process with use of quantum chemical methods for thermodynamic functions was carried out. Built on calculation results formalized reaction network became the base for mathematical model of alkylation reactor development. Method for inverse kinetic problem solving was proposed and implemented. The developed computer modeling system is sensitive to raw materials composition of process conditions. This makes it effective in problems of industrial plant for the production of linear alkyl benzene optimization solving.

Keywords: *mathematical modeling; alkylation; efficiency of production.*

1. Introduction

Alkylation of benzene higher olefins is the final stage of LAB manufacturing. From literary data [1] it is known that conditions of alkylation process determine yield and composition of obtained alkylbenzenes.

The prerequisite for this stage simulation was that it is the structure of LAB that affects biological degradability of synthetic detergents, their solubility and washing performance. LAB biodegradability is primarily affected by the structure of the side hydrocarbon chain in the molecule: unlike the previously widely used alkylbenzenes with branched hydrocarbon chain, "linear" alkylbenzenes and obtained synthetic detergents (SD) are almost completely decomposed by bacteria in natural conditions [2]. Another factor determining LAB biodegradability is the share of 2-phenylalkanes among other isomers obtained. The high content of 2-phenylalkanes in LAB increases solubility of detergents that is good for their cleaning characteristics.

The length of the hydrocarbon radical in LAB also affects the cleaning ability of SD and, according to [3], fraction C₁₁-C₁₂ has the best characteristics.

The complexity of this process modeling is its multicomponence: raw material is olefins C₉-C₁₄ fraction delivered from dehydration stage. Variants of reactions with different isomers, as well as combinations of substances in formation of, for example, dialkylbenzenes are very diverse.

Thermodynamic analysis of reaction occurrence probability under these conditions also requires a consolidation of individual substances in groups of substances and reactions - in the types of reactions. However, when substances aggregating, formalized model should keep sensitivity to changes in raw materials composition and target and by-products output.

The aim of present work is mathematical model development and its application to alkylation and HF-catalyst regeneration processes optimization application.

2. Experimental

2.1. Reduction of mathematical description of the alkylation process dimension

For most complete description of the target product quality consideration of side chain carbon skeleton isomerism and location of double bond in reacting olefin is necessary, as it affects biological degradability SD obtained.

Given the fact that the content of 2-phenylalkanes in LAB is an important industrial and regulated parameter, separation of reactions of their formation in reaction network is useful.

An important characteristic of the target and by-products of alkylation process is a

bromine number (BN) which is directly related to the mass of the unsaturated compounds in the product flow:

$$BN = \frac{X_{uns} \cdot 160}{M_{uns}}$$

The concentration of unsaturated alkyl aromatic compounds influences bromine number of product, respectively, the reaction network should include reaction of unsaturated alkylbenzenes and dialkylbenzenes formation. Values of thermodynamic properties of reactions of benzene alkylation with decene are listed in tab. 1.

Table 1 Thermodynamic characteristics of benzene alkylation with decene reactions (T=328 K)

Reaction	ΔG , kJ/mole	ΔH , kJ/mole	Equilibrium constant
1. Benzene+Olefin-1,2=LAB-2	-42.98	-96.11	1.016
2. Benzene+Olefin-3,4..=LAB-3,4..	-22.86	-74.62	1.008
3. Benzene+i-Olefin=BAB	-6.47	-80.40	1.002
4. Olefin-3,4..=i-Olefin	2.02	0.28	0.999
5. Olefin-1,2=Olefin-3,4..	9.85	3.64	0.996
6. pseudoLAB+pseudoOlefin=DAB	-26.56	-85.63	1.010
7. Benzene+DiOlefin=LABuns	-8.50	-68.75	1.003
8. LABuns+pseudoOlefin=DABuns	-0.53	-43.53	1.0002
9. Benzene+LABuns=DPA	4.14	-36.62	0.998

Thermodynamic characteristics were calculated using HyperChem 8 – software for quantum chemical calculations (ab initio method, 3-21G basis), enthalpies of substances formation calculated with use of PM3 semi empirical method. Taking all above arguments into account the resulting reaction network will look like following (fig. 1).

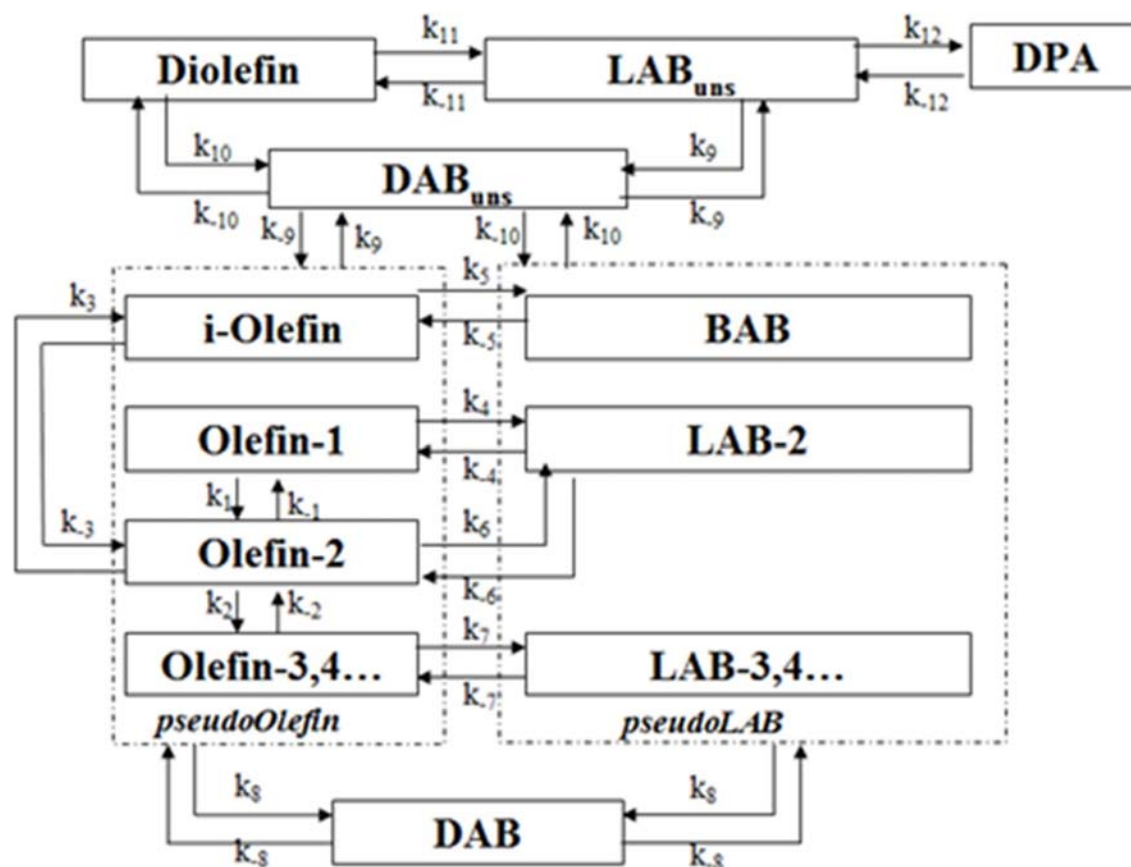


Fig. 1. Formalized reaction network of alkylation process

Here the following Olefin-1,2 – olefins C10-C14 of linear structure with double bond after first and second carbon atoms; Olefin-3,4 – olefins C10-C14 of linear structure with double bond after third and fourth carbon atoms; i-Olefin – branched olefins C10-C14 (independently on double bond position); BAB – branched alkylbenzenes (alkylbenzenes

with side chain of branched structure); DAB – dialkylbenzenes; LAB-2 – 2-phenylalkanes; LAB-3,4 – 3,4-phenylalkanes; LABuns– alkylbenzenes with unsaturated side chain; DABuns– dialkylbenzenes with unsaturated side chain; diolefin – diolefins of linear and branched structure; DPA – diphenylalkanes.

2.2. Development of mathematical description

Based on presented reaction network, kinetic model of alkylation process was developed. Expressions for chemical reaction rates for each component were built according to the law of mass action are presented in tab. 2.

Table 2 Expressions for rates of reactions in alkylation process

Component	Reaction rate expression
Olefin-1,2	$\frac{dC_{olefin-1,2}}{dt} = -k_1 C_{olefin-1,2} C_{benzene} + k_{-1} C_{LAB-2} - k_5 C_{olefin-1,2} + k_{-5} C_{olefin-3,4} -$ $-k_6 C_{olefin-1,2} C_{pseudoLAB} + k_{-6} C_{DAB} - k_8 C_{olefin-1,2} C_{LABuns} + k_{-8} C_{DABuns}$
Olefin-3,4..	$\frac{dC_{olefin-3,4}}{dt} = -k_2 C_{olefin-3,4} C_{benzene} + k_{-2} C_{LAB-3,4} - k_4 C_{olefin-3,4} + k_{-4} C_{i-olefin} -$ $-k_6 C_{olefin-3,4} C_{pseudoLAB} + k_{-6} C_{DAB} - k_8 C_{olefin-3,4} C_{LABuns} + k_{-8} C_{DABuns}$
i-Olefin	$\frac{dC_{i-olefin}}{dt} = -k_3 C_{i-olefin} C_{benzene} + k_{-3} C_{BAB} + k_4 C_{olefin-3,4} - k_{-4} C_{i-olefin} -$ $-k_6 C_{i-olefin} C_{pseudoLAB} + k_{-6} C_{DAB} - k_8 C_{i-olefin} C_{LABuns} + k_{-8} C_{DABuns}$
Diolefin	$\frac{dC_{diolefin}}{dt} = -k_7 C_{diolefin} C_{benzene} + k_{-7} C_{LABuns}$
Benzene	$\frac{dC_{benzene}}{dt} = -k_1 C_{olefin-1,2} C_{benzene} + k_{-1} C_{LAB-2} - k_2 C_{olefin-3,4} C_{benzene} +$ $+ k_{-2} C_{LAB-3,4} - k_3 C_{i-olefin} C_{benzene} + k_{-3} C_{BAB} -$ $-k_7 C_{diolefin} C_{benzene} + k_{-7} C_{LABuns} - k_9 C_{LABuns} C_{benzene} + k_{-9} C_{DPA}$
LAB-2	$\frac{dC_{LAB-2}}{dt} = k_1 C_{olefin-1,2} C_{benzene} - k_{-1} C_{LAB-2} - k_6 C_{pseudoolefin} C_{LAB-2} + k_{-6} C_{DAB}$
LAB-3,4..	$\frac{dC_{LAB-3,4}}{dt} = k_2 C_{olefin-3,4} C_{benzene} - k_{-2} C_{LAB-3,4} - k_6 C_{pseudoolefin} C_{LAB-3,4} + k_{-6} C_{DAB}$
BAB	$\frac{dC_{BAB}}{dt} = k_3 C_{i-olefin} C_{benzene} - k_{-3} C_{BAB} - k_6 C_{pseudoolefin} C_{BAB} + k_{-6} C_{DAB}$
LABuns	$\frac{dC_{LABuns}}{dt} = k_7 C_{diolefin} C_{benzene} - k_{-7} C_{LABuns} - k_9 C_{LABuns} C_{benzene} + k_{-9} C_{DPA} -$ $-k_8 C_{LABuns} C_{pseudoolefin} + k_{-8} C_{DABuns}$
DAB	$\frac{dC_{DAB}}{dt} = k_6 C_{pseudoolefin} C_{LAB-2} - k_{-6} C_{DAB}$
DABuns	$\frac{dC_{DABuns}}{dt} = k_8 C_{LABuns} C_{pseudoolefin} - k_{-8} C_{DABuns}$
DPA	$\frac{dC_{DPA}}{dt} = k_9 C_{LABuns} C_{benzene} - k_{-9} C_{DPA}$

Initial conditions: $t=0$, $C_i=C_{0i}$. The constants k_1-k_9 and $k_{-1}-k_{-9}$ are effective as combination of constants of all the intermediate stages.

In the stationary regime change in i -th hydrocarbon concentration with reactor volume (contact time) the plug flow reactor model can be written as follows:

$$\frac{dC_i}{d\tau} = W_i$$

Assumption of ideal displacement regime in alkylation reactor was confirmed by

calculation of Peclet criterion ($403.7 > 200$).

According to experimental data, characteristics of benzene alkylation reactor are similar to adiabatic. Then the heat balance equation in steady state can be written as follows:

$$\rho C_p \frac{dT}{d\tau} = \pm \sum_{j=1}^N (-\Delta H_j) W_j$$

Active window of combined computer modeling system simulating synthetic detergents manufacturing is shown in fig.2.

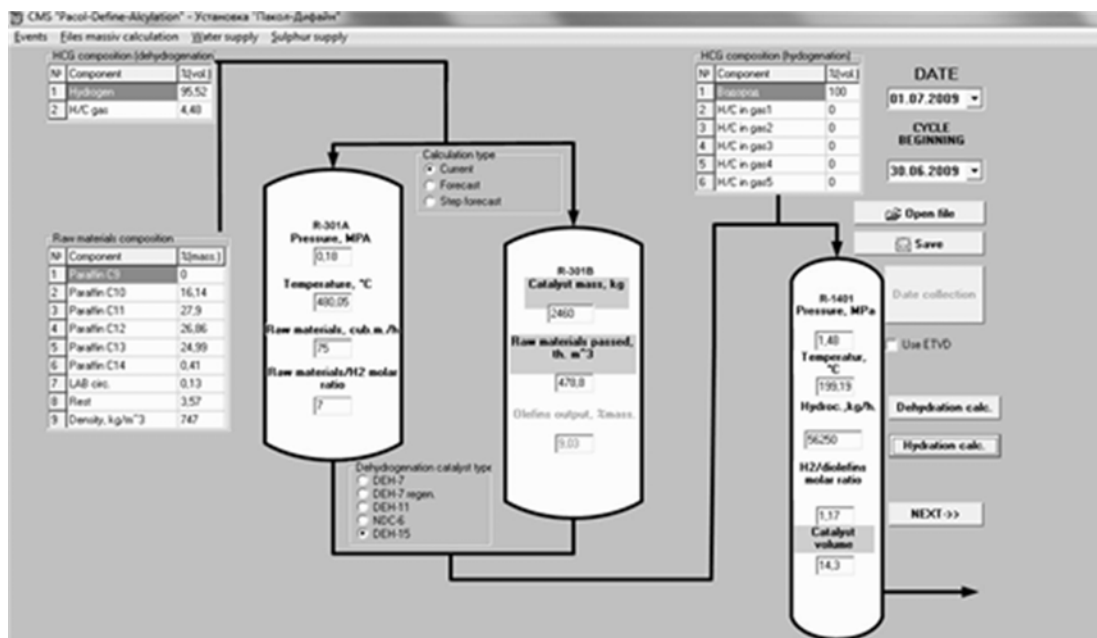


Fig. 2. Active window of combined computer modeling system for LAB production complex

2.3. Algorithm of kinetic parameters identification using the transition state theory

Transition state theory developed in the 30 years of twentieth century by H. Eyring, M. Evans, M. Polanyi is also known as theory of absolute rates of chemical reactions [4]. According to this theory, the rate of elementary chemical reaction can be calculated through the energy characteristics of the transition state:

$$k = \chi \frac{kT}{h} e^{\frac{\Delta S^\ddagger}{R}} e^{\frac{-\Delta H^\ddagger}{RT}} e^{\frac{-E_a}{RT}} = \chi \frac{kT}{h} e^{\frac{-\Delta G^\ddagger}{RT}} e^{\frac{-E_a}{RT}}$$

In case of benzene alkylation the limiting stage of mechanism is sigma-complex formation [5]. Thus, thermodynamic characteristics of transition state formation reaction in the first approximation can be used for calculation of rate constants.

Thermodynamic characteristics of transition states were calculated using HyperChem 8 (ab initio method, 3-21G basis) and are listed in tab. 3.

Table 3 Thermodynamic characteristics of transition states formation and estimated values of kinetic parameters of direct reactions in alkylation process ($T = 323 \text{ K}$)

Reaction	ΔH^\ddagger , kJ/mole	ΔS^\ddagger , kJ/mole	E_a , kJ/mole	Reaction rate constant
Benzene+Olefin-1,2=LAB-2	42.9	-137.3	87.9	$6.6 \cdot 10^{-2}$
Benzene+Olefin-3,4..=LAB-3,4..	66.9	-58.0	85.9	$13.9 \cdot 10^{-2}$
Benzene+i-Olefin=BAB	50.9	-107.4	86.1	$13.0 \cdot 10^{-2}$
Olefin-3,4..=i-Olefin	81.1	-10.1	81.1	$8.1 \cdot 10^{-1}$
Olefin-1,2=Olefin-3,4..	77.4	-11.8	83.6	$3.31 \cdot 10^{-1}$
pseudoLAB+pseudoOlefin=DAB	85.2	-33.9	96.3	$3.0 \cdot 10^{-3}$
Benzene+diOlefin=LAB _{uns}	73.7	-31.9	84.1	$2.7 \cdot 10^{-1}$
LAB _{uns} +pseudoOlefin=DAB _{uns}	65.4	-48.4	81.3	$7.5 \cdot 10^{-1}$
Benzene+LAB _{uns} =DPA	71.4	-34.9	82.9	$4.3 \cdot 10^{-1}$

3. Results and discussion

3.1. Model adequacy verification

The results of comparison of calculated and experimental values of main output parameters are shown in fig. 3–5.

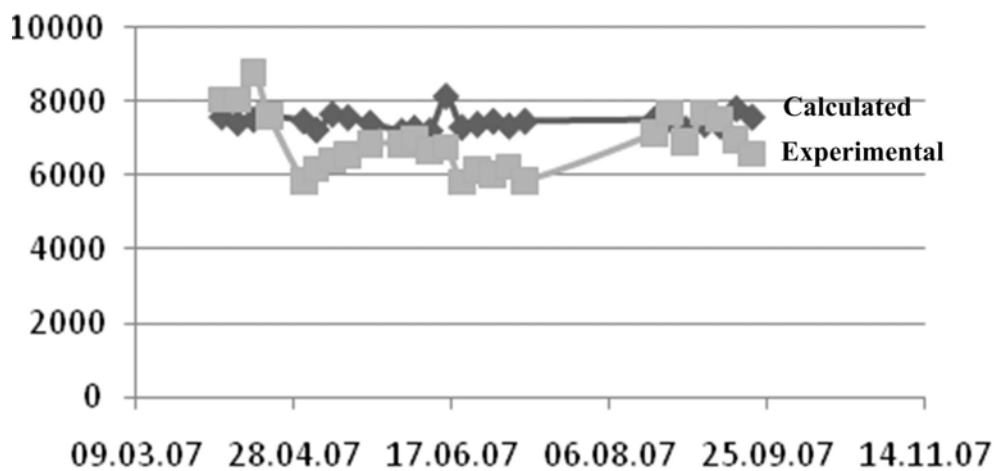


Fig. 3. Calculated and experimental yield of desired product

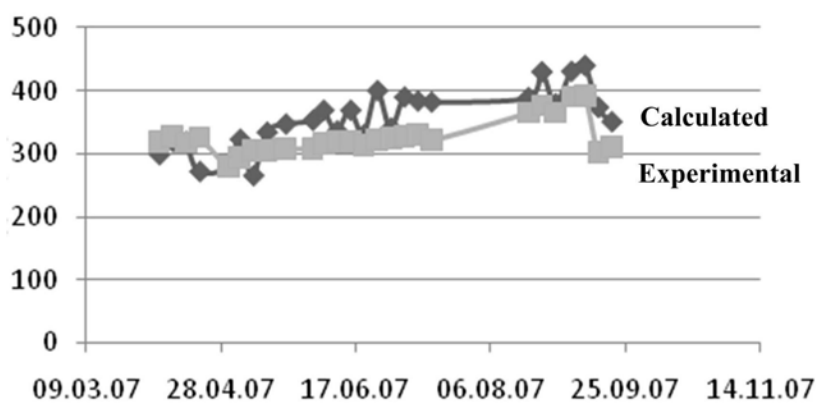


Fig. 4. Calculated and experimental yield of by-product

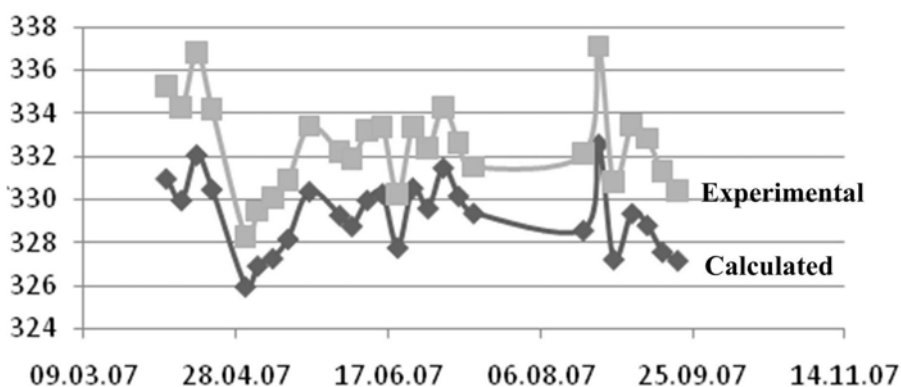


Fig. 5. Calculated and experimental values of temperature at the reactor outlet

The period of verification was from March, 2007 to December, 2010.

As it follows, built with use of evaluated kinetic parameters mathematical model of alkylation reactor describes the increase and decrease in yield of target and by-product as well as the temperature changes in output stream adequately in dependence on changes in process conditions and/or raw materials composition.

Mathematical models of dehydrogenation and hydrogenation processes also give a good convergence of experimental and calculated data. Thus the developed computer programs are suitable for the refinery processes monitoring and optimization.

3.2. Optimization of alkylation and HF-catalyst regeneration processes with use of simulation software

With use of mathematical model of alkylation process variants of different technological regimes maintaining were calculated. From the set of calculation variants the regime meeting following criteria of optimality was chosen:

- Maximal yield of LAB, kg/hour;
- Minimal yield of heavy alkylate (HA), kg/hour;
- Minimal molar content of HA in mixture of HA with HF-acid;
- Maximal molar content of unsaturated hydrocarbons in mixture of HA with HF-acid;
- Minimal bromine index of LAB;
- Minimal bromine number of DAB.

A set of process parameters that provides the efficient operation of alkylation reactor and acid regeneration column is shown in tab. 4.

Table 4 Optimum technological parameters of the alkylation process

T, K	323
Benzene expenditure, kg/hour	22 000
HF, expenditure, kg/hour	18 0000

Calculation results with optimal parameters and comparison of best and current results is shown in fig. 6, 7.

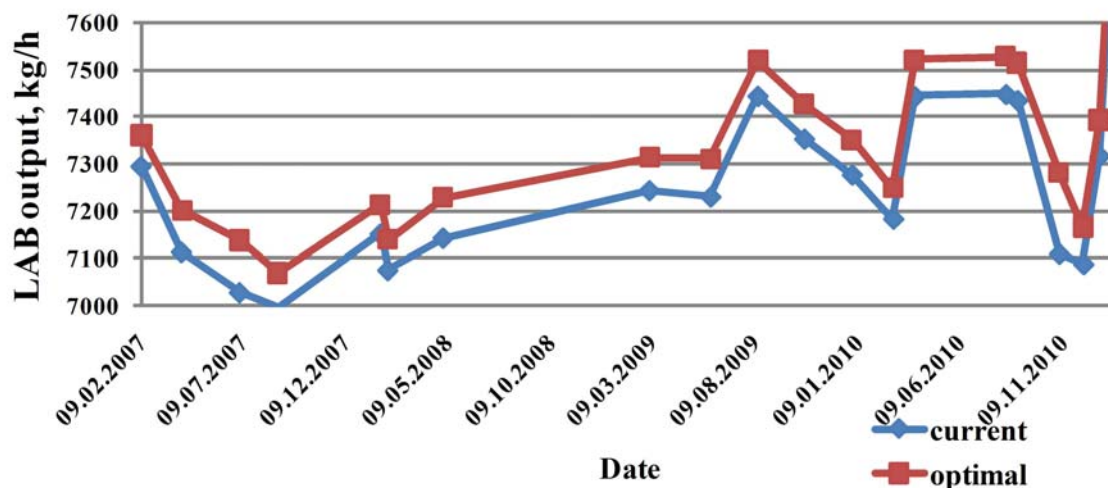


Fig.6. LAB yield under current and optimal technological conditions

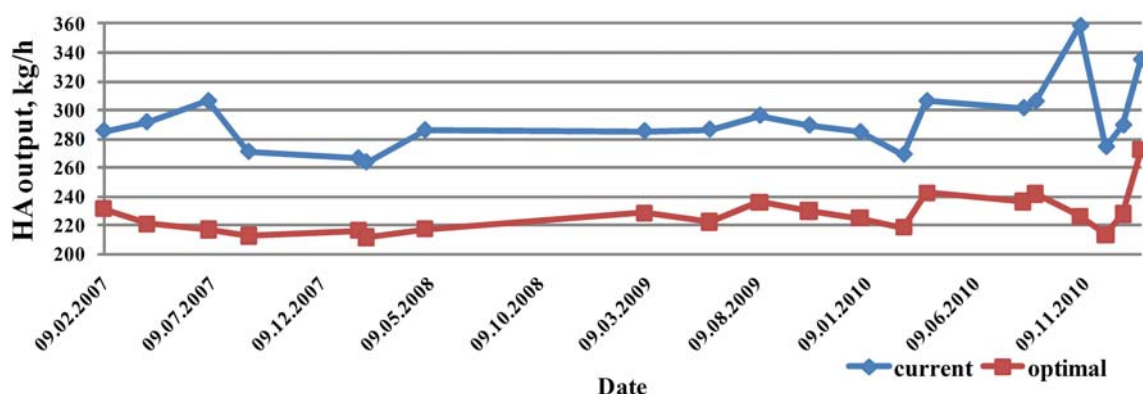


Fig. 7. HA yield under current and optimal technological conditions

According to the results, maintaining of optimal technological regime allows yield of LAB increasing on 81 kg/hour and yield of LAB decreasing on 65 kg/hour.

4. Conclusion

Used as a base of alkylation process modeling system is detailed enough to provide sensitivity to raw materials composition but, nevertheless, it does not complicate the calculations because of the aggregation of components in the groups according to their reactivity.

Proposed and implemented a methodic of the kinetic parameters identification simplifies greatly the process of inverse kinetic problem solving.

The computer program allows material and heat balances calculation and redetermination; yield of target and by-products determination; LAB quality indicators such as bromine index, content of 2-phenylalcanes and linear isomers in product flow evaluation.

Proposed and implemented algorithm of alkylation and catalyst regeneration processes optimization involves the sequential variation independent parameters. The effect of recommended process conditions maintenance is selectivity on target product increasing; bromine number of products within an acceptable range increasing (LAB quality); growth of refinery annual income.

List of symbols

X_{uns} – mass fraction of the unsaturated compound in the product, %;
 160 – molar mass of Br₂, g/mole;
 M_{uns} – molar mass of unsaturated compound, g/mole;
 ΔG – change in Gibbs energy of reaction, kJ/mole;
 ΔH – change in Gibbs energy of reaction, kJ/mole;
 t – time, sec;
 C_i – concentration of i -th component, mole/m³;
 τ – contact time, sec;
 W_i – rate of i -th component concentration while chemical reactions change, mole/(m³·sec).
 $(-\Delta H_j)$ – heat of j -th chemical reaction, J/mole;
 W_j – rate of j -th chemical reaction, mole/(m³·sec);
 C_p – heat capacity of reacting mixture, J/(mole·K);
 ρ – density of reacting mixture, kg/m³;
 T – temperature, K.
 k – reaction rate constant;
 E_a – activation energy, kJ/mole;
 R – universal gaseous constant, J/(mole·K);
 k – Boltzmann constant, J/K;
 h – Plank constant, J·sec;
 χ – transmission coefficient;
 ΔS^\ddagger – entropy change during transition complex formation, J/(mole·K);
 ΔH^\ddagger – enthalpy change during transition complex formation, J/mole;
 ΔG^\ddagger – Gibbs energy change during transition complex formation, J/mole.

References

- [1] Bannov P.G.: Petroleum refining processes. 2001, 625.
- [2] Philips C. Survey of Industrial Chemistry. 2002, p. 469-470.
- [3] Yadav G. D., Doshi N. S.: Synthesis of Linear Phenyldecanes by the Alkylation of Benzene with 1-Dodecene over Non-Zeolitic Catalyst, Org. Proc. Res. Dev., 2002, 6 (3), pp 263–272.
- [4] Anslyn E.V., Dougherty D.A. : Modern physical organic chemistry. 2006, 1995.
- [5] Reutov O. A., Kurtz A.L., Butin K.P. : Organic chemistry. 2009, Part 2, p. 544.