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Quantum-chemical modeling of benzene with ethylene alkylation reactions using liquid-phase catalyst

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Abstract

The article describes the results of thermodynamic and kinetic parameters determination of benzene with ethylene alkylation reactions in the presence of liquid-phase catalyst. During the process a list of reactions was considered, activation energy and reaction rate constants are determined. These parameters were used as the basis for the mathematical model development in benzene with ethylene alkylation.

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Keywords: alkylation; mathematical modeling; thermodynamics, quantum chemistry.

1. Introduction

One of the most dynamically developing areas of petrochemical industry is the ethylbenzene production (EB), which is widely used as an intermediate in styrene production, the raw material for polystyrene, ABS - plastic and synthetic rubber productions. Usually ethylbenzene is prepared by benzene with ethylene alkylation and a small amount of ethylbenzene can be obtained by C_8 aromatic hydrocarbons superfractionating. The alkylation reaction can occur in both liquid and gas phases [1-7].

In Russia, the total production capacity of EB is 849 000 tons per year, which in turn is 2.4% of the world capacity. Given the growth in demand for polystyrene and styrene-butadiene rubber, in the next few years EB production will continue growing by 5-7% per year [8].

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The purpose of this work is to define thermodynamic parameters and kinetics of benzene with ethylene alkylation using liquid-phase catalyst and to develope mathematical model of alkylation unit for one of the Russian petrochemical plants.

2. Study subject

The most important step in mathematical model development of alkylation is to define a list of possible process reaction, as well as consideration of physical and chemical laws (kinetic and thermodynamic) of reactions occurrence. The calculations accuracy, the mathematical model adequacy of the real process, the complexity of mathematical description and computer realization largely depend on the degree of chemical reactions specification [9-13].

The list of reactions was compiled on the base of component composition of the input and output streams in alkylator. The used data are the results of the reactor block monitoring at one of the Russian petrochemical plants. The list of reactions is shown in Table 1. Table 2 shows the component composition of input and output streams in the alkylator.

Table 1. The list of reactions in alkylation.

№	Reaction
1	$C_6H_6 + C_2H_4 \rightarrow C_6H_5C_2H_5$
2	$C_6H_5C_2H_5 + C_2H_4 \rightarrow C_6H_4(C_2H_5)_2$
3	$C_6H_6 + C_6H_4(C_2H_5)_2 \rightarrow 2C_6H_5C_2H_5$
	$C_2H_4 + C_2H_4 \rightarrow C_2H_4C_2H_4$
5	$C_6H_6 + C_2H_4C_2H_4 \rightarrow C_6H_5C_2H_4C_2H_5$
6	$C_6H_6 + C_3H_6 \rightarrow C_6H_5C_3H_7$
7	$C_6H_4CH_3 + C_2H_4 \rightarrow C_6H_3CH_3(C_2H_5)$
8	$2\,C_6H_6 + C_2H_4 \rightarrow 2C_6H_4CH_3$
9	$C_6H_4CH_3 + 2C_2H_4 \rightarrow C_6H_5C_2H_5 + C_3H_6$

For the most of hydrocarbons in this process thermodynamic properties are not defined in literature data. So it made necessary to determine the thermodynamic characteristics of alkylation reactions using quantum chemistry methods.

Table 2. Composition of raw and product mixture in alkylation.

Component	Concentration, mol %
Raw	
benzene	76
ethylene	16
PAB*	8
Product	
benzene	61.09
toluene	3.28
ethylbenzene	30.01
iso-propylbenzene	0.95