DEVELOPMENT OF APPROACH TO SIMULATION OF OIL REFINING PROCESSES ON EXAMPLE OF BENZENE ALKYLATION WITH ETHYLENE

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Abstract

On the example of the synthesis of ethylbenzene, an approach to reaction network formalization was proposed. This approach consists in grouping the components according to their reactivity their reactivity with respect to a specific reaction. The values of compensation degrees of reactions as an indicator of components reactivity were calculated. The kinetic model of alkylation of benzene with ethylene and heavy alkylates transalkylation was developed. The proposed approach is promising for development of mathematical modeling of multi-component processes of oil refining and petrochemical industries.

Keywords: ethylbenzene; reaction network; degree of compensation; kinetic model.

1. Introduction

Alkylation of benzene with ethylene is the main direction of consumption of benzene (50% of total supply). The resulting ethylbenzene is an intermediate for organic synthesis, especially in the production of styrene and synthetic rubber. It is used as a solvent or diluent, a component of automotive and aviation fuels, as well as for cellulose acetate production.

One of the ways of ethylbenzene obtaining is zeolite technology, including consistently flowing stages of benzene alkylation with ethylene to produce ethylbenzene and heavy alkylates transalkylation to monoethylbenzene. Both processes are carried out on zeolite catalysts.

The scale of ethylbenzene production and the possibility of its widespread use makes the need to improve resource efficiency of production. Achieving such a result is possible through integration of plant and computer simulation, that is, through introduction of computer modeling into enterprise systems. Such models have been already designed for number of refining and petrochemical processes [1,2], are successfully used in manufacturing for monitoring and forecasting of industrial plants, as simulators for engineering and technical personnel, and differ from existing analogues by taking physical and chemical nature occurring in contact apparatus and process, catalyst deactivation due poisoning and coking into account. For process of ethylbenzene production such computer modeling system is not yet developed.

Significance and predictive ability of the mathematical model is largely dependent on reaction network laid down in its foundation, which should be fairly simple, but at the same time sufficiently detailed. The aim of this study is to develop an approach to modeling of multicomponent chemical processes on the example of alkylation of benzene with ethylene.

2. Experimental

After analyzing of raw materials and products flows composition and existing ideas about chemistry of benzene with ethylene alkylation process [3], a full list of reactions in the alkylation reactor was developed (tab. 1). The thermodynamic possibility of their occurrence was confirmed by calculation of isobaric-isothermal parameter ΔG – change in Gibbs energy of reaction. The calculation was performed using the Gaussian-98 program.

Table 1 ∆G values for reactions occurring in alkylation process (T=510 K, P=3.4 MPa)

Reaction	ΔG, kJ/mole
Benzene+ethylene=ethylbenzene	-43.4
Ethylbenzene + ethylene = diethylbenzene	-46.3
Diethylbenzene + ethylene = triethylbenzene	-40.3
Triethylbenzene + ethylene =tetraethylbenzene	-38.3
Tetraethylbenzene + ethylene = pentaethylbenzene	-38.6
Pentaethylbenzene + ethylene =hexaethylbenzene	-17.4
2benzene+ ethylene =diphenylethane+ hydrogen	-147.6
Ethylene + ethylene = butylene	-64.7
Benzene + butylene =butylbenzene	-12.8
Benzene + propylene =n-propylbenzene	-23.6
Benzene + propylene =cymene	-25.7
Benzene + ethylene = o-xylol	-61.2
Benzene + ethylene = m-xylol	-61.8
Benzene + ethylene =p-xylol	-62.0
Cymene+ ethylene =ethylcymene	-27.2
Ethylbenzene + propylene = ethylcymene	-9.5
Butylbenzene + ethylene = ethylbutylbenzene	-32.1
Ethylbenzene + butylene = ethylbutylbenzene	-1.5
Toluene + ethylene =ethyltoluene	-9.0
6 benzene = coronene + hydrogen	-1375.4
Butylene =z-butane	0.2
Z-butane + z-butane =dicycle+hydrogen	-177.5

According to this list of reactions, a detailed reaction network will look like following (fig. 1).
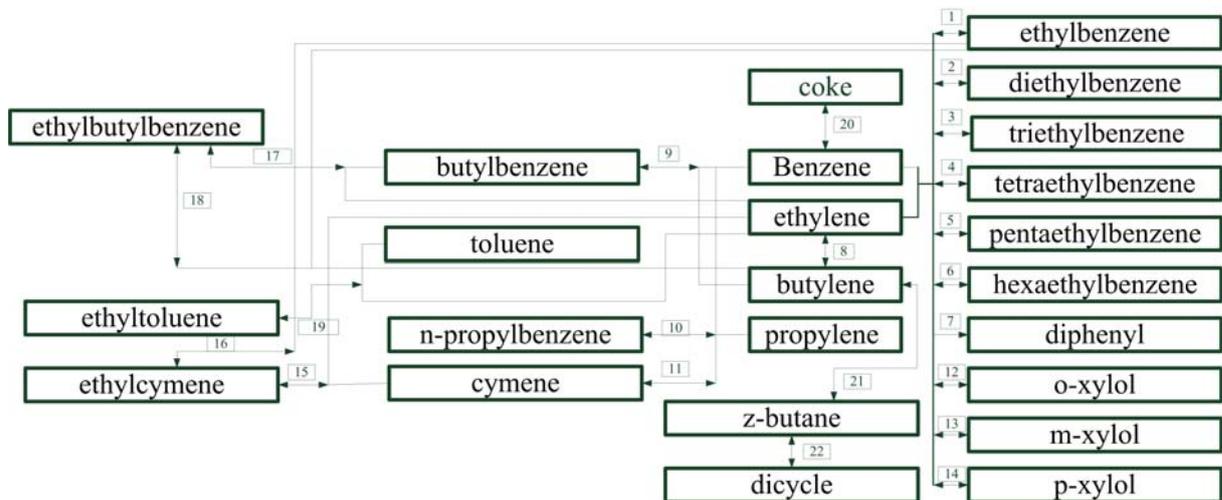
Figure 1. The detailed reaction network of benzene with ethylene alkylation process

Reaction network is necessary to formalize, that is to combine individual substances with close reactivity in particular reaction into pseudo components. Essential help in solving the problems of catalytic action prediction provides degree of compensation, which characterizes partial compensation of energy expended to break old bonds by energy of new bonds formation while moving along the path of reaction [4].

Therefore, further research step is calculation of degree of compensation of reactions from drawn up list.

$$H = \frac{\sum D_i - E_{à}}{\sum D_i} \cdot 100\%$$

The main problem in calculating of degree of compensation is determination of activation energies of reactions. As a first approximation activation energy was calculated with use of Polanyi-Semenov expression for exothermic reactions [4].

$$E_a = 48.185 + 1.05 \cdot \Delta H$$

Heat effects of reactions were calculated with use of quantum-chemical methods for calculating of thermodynamic functions. Values of ΔH and E_a are given in tab. 2.

Table 2 Values of ΔH and E_a of reactions occurring in alkylation process (T=510 K, P=3.4 MPa)

Reaction	ΔH, kJ/mole	E_a, kJ/mole (Polanyi-Semenov expression)
Benzene+ethylene=ethylbenzene	-117.9	18.7
Ethylbenzene + ethylene = diethylbenzene	-110.6	20.5
Diethylbenzene + ethylene = triethylbenzene	-106.3	21.6
Triethylbenzene + ethylene =tetraethylbenzene	-112.3	20.1
Tetraethylbenzene + ethylene = pentaethylbenzene	-111.9	20.2
Pentaethylbenzene + ethylene =hexaethylbenzene	-103.8	22.2
2benzene+ ethylene =diphenylethane+ hydrogen	-282.3	22.4
Ethylene + ethylene = butylene	-118.7	18.5
Benzene + butylene =butylbenzene	-91.8	25.2
Benzene + propylene =n-propylbenzene	-98.2	23.6
Benzene + propylene =cymene	-90.1	25.7
Benzene + ethylene = o-xylol	-132.1	15.2
Benzene + ethylene = m-xylol	-140.3	13.1
Benzene + ethylene =p-xylol	-140.4	13.1
Cymene+ ethylene =ethylcymene	-102.7	22.5
Ethylbenzene + propylene = ethylcymene	-75.0	29.4
Butylbenzene + ethylene = ethylbutylbenzene	-104.2	22.1
Ethylbenzene + butylene = ethylbutylbenzene	-78.1	28.7
Toluene + ethylene =ethyltoluene	-89.7	25.8
6 benzene = coronene + hydrogen	-1316.3	280.9
Butylene =z-butane	-18.3	43.6
Z-butane + z-butane =dicycle+hydrogen	-351.0	39.6

The obtained values of the heat effects of reactions agree with literary data [5]. The values of activation energies were determined without taking catalytic action into. In reference [6] the values of kinetic parameters are given for alkylation process occurring on zeolite catalyst under similar technological conditions. According to this source, the activation energy of the target reaction of benzene alkylation with ethylene to ethylbenzene is 63.4 kJ/mole, and for the reaction of diethylbenzene formation – 47.03 kJ/mole.

For connection establishing between literary and calculated from the Polanyi-Semenov expression values of activation energies, linear correlation equation describing the dependence of activation energies literature values on values calculated from the Polanyi-Semenov equation was determined, fig.2.
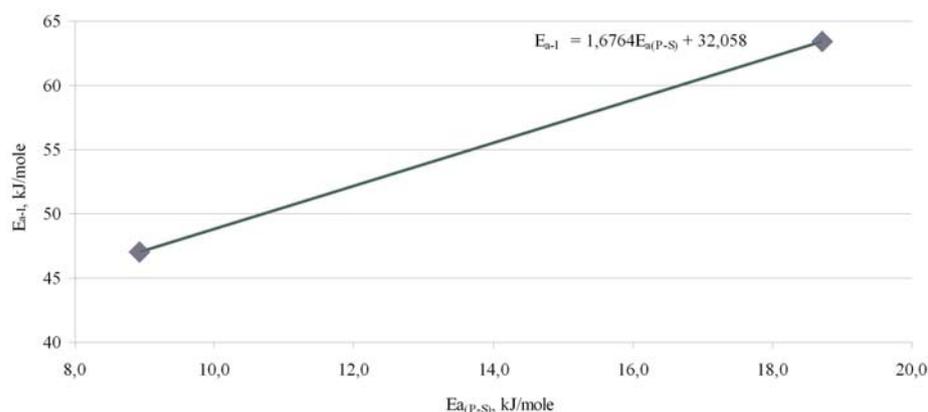
Figure 2. Connection between literary and calculated from the Polanyi-Semenov expression values of activation energies

With use of obtained dependence activation energy values for the other reactions were determined. The next step in determining the degree of compensation is reaction energy

of broken bonds calculation. Let us consider methodology of calculation on the example of target reaction.

Formation of ethylbenzene requires breaking of two bonds: bond C-H in benzene molecule and the bond C-H in molecule of ethylene. Energies of these bonds were calculated on the Gaussian program.

The energy of first connection amounted 433.8 kJ/mole, the second - 215.5 kJ/mole. The energy of broken bonds is equal to 649.3 kJ/mole. Likewise we calculated energies of broken bonds for other reactions and then the degree of compensation. The results are presented in tab. 3. They also show the literature values of bond energies [7,8] and their comparison with the calculated values.

Table 3 Results of compensation energies calculation

Reaction	E_a, kJ/mole	$\sum D_i$, kJ/mole	$\sum D_i$, kJ/mole; (literature)	H, %
Benzene+ethylene=ethylbenzene	63.4	649.3	715.0	90.2
Ethylbenzene + ethylene = diethylbenzene	47.0	633.5	715.0	92.6
Diethylbenzene + ethylene = triethylbenzene	68.3	617.7	715.0	88.9
Triethylbenzene + ethylene =tetraethylbenzene	65.8	602.0	715.0	89.1
Tetraethylbenzene + ethylene = pentaethylbenzene	65.9	586.2	715.0	88.8
Pentaethylbenzene + ethylene =hexaethylbenzene	69.3	570.4	715.0	87.9
2benzene+ ethylene =diphenylethane+ hydrogen	69.6	1083.2	1100.0	93.6
Ethylene + ethylene = butylene	63.1	882.2	955.0	92.8
Benzene + butylene =butylbenzene	74.3	762.9	685.0	90.3
Benzene + propylene =n-propylbenzene	71.7	788.2	685.0	90.9
Benzene + propylene =cymene	75.1	788.2	685.0	90.5
Benzene + ethylene = o-xylol	57.5	1298.7	1428.0	95.6
Benzene + ethylene = m-xylol	54.1	1298.7	1428.0	95.8
Benzene + ethylene =p-xylol	54.0	1298.7	1428.0	95.8
Cymene+ ethylene =ethylcymene	69.8	633.0	715.0	89.0
Ethylbenzene + propylene = ethylcymene	81.4	772.3	715.0	89.5
Butylbenzene + ethylene = ethylbutylbenzene	69.2	635.4	715.0	89.1
Ethylbenzene + butylene = ethylbutylbenzene	80.1	747.1	715.0	89.3
Toluene + ethylene =ethyltoluene	75.2	747.6	715.0	89.9
6 benzene = coronene + hydrogen	503.0	5206.0	4980.0	90.3
Butylene =z-butane	105.2	952.5	1014.0	89.0
Z-butane + z-butane =dicycle+hydrogen	98.4	809.6	830.0	87.8

This table shows good agreement of calculated and literary values of broken bonds energies.

3. Results and discussion

For reaction network formalization reactions with close values of degree of compensation were grouped (tab. 4). Degree of compensation of reactions in one group differs in about 1 %.
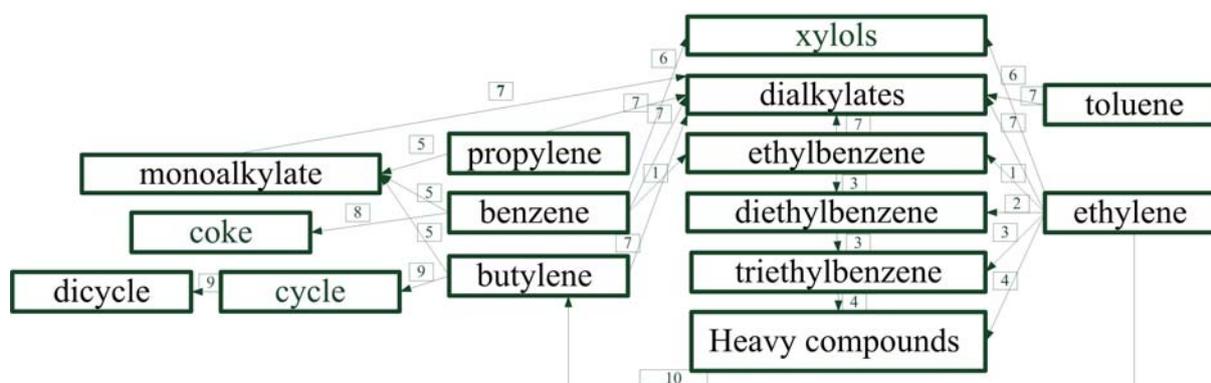
Figure 3. Formalized reaction network of benzene with ethylene alkylation process

Thus, a number of pseudo components can be identified: heavy compounds, which consist of individual components such as tetra-, penta-, gexaethylbenzene and diphenylethane; monoalkylates (butylbenzene, n-propylbenzene, cumene), dialkylates (ethylcumene,

ethylbutylbenzene), xylols (o-, m-, p-xylol), cyclic and dicyclic hydrocarbons. Built on the basis of the above the formalized reaction network was built (fig. 3).

Table 4 Grouping of reactions occurring in alkylation process in accordance with degree of compensation value

Reaction group	Medium H, % for reaction group
1. Ethylbenzene forming	90.2
Benzene+ethylene=ethylbenzene	
2. Dithylbenzene forming	92.6
Ethylbenzene + ethylene = diethylbenzene	
3. Triethylbenzene forming	88.9
Diethylbenzene + ethylene = triethylbenzene	
4. Heavy compounds forming	89.8
Triethylbenzene + ethylene = polyethylbenzene	
2benzne+ ethylene =diphenyletan + hydrogen	
5. Other monoalkylates forming	90.6
Benzene + butylene = monoalkylate	
Benzene + propylene = monoalkylate	
6. Xylols forming	95.7
Benzene + ethylene = o-xylol	
7. Other dialkylates forming	89.4
Ethylbenzene + butylene = Dialkylate	
Ethylbenzene + butylene = Dialkylate	
Monoalkylates+ ethylene = Dialkylate	
Toluene + ethylene = Dialkylate	
8. Coke forming	90.3
6 benzene = coke + hydrogen	
9. Cycles and dicycles forming	88.4
Butylene =z-butane	
Z-butane + z-butane =dicycle+hydrogen	
10. Butylene forming	92.8
Ethylene + ethylene = butylene	

According to the law of mass action [9], expressions for rates of chemical reactions occurring in alkylation and transalkylation processes should be written as follows (tab. 5).
Kinetic model of alkylation process can be written as follows.

$$\frac{dC_{benzene}}{dt} = -W_1 - 2W_{4.2} - W_{5.1} - W_{5.2} - W_6 - 6W_8$$

$$\frac{dC_{ethylene}}{dt} = -W_1 - W_2 - W_3 - W_{4.1} - W_{4.2} - W_6 - W_{7..3} - W_{7.4} - 2W_{10}$$

$$\frac{dC_{butylene}}{dt} = -W_{5.1} - W_{7.2} - W_{9.1} + W_{10}$$

$$\frac{dC_{propylene}}{dt} = -W_{5.2} - W_{7.1}$$

$$\frac{dC_{z-butane}}{dt} = W_{9.1} - 2W_{9.2}$$

$$\frac{dC_{dicycle}}{dt} = W_{9.2}$$

$$\frac{dC_{hydrogen}}{dt} = W_8 + W_{4.2} + W_{9.2}$$

$$\frac{dC_{ethylbenzene}}{dt} = W_1 - W_2 - W_{7.1} - W_{7.2}$$

$$\frac{dC_{diethulbenzene}}{dt} = W_2 - W_3$$

$$\frac{dC_{triethylbenzene}}{dt} = W_3 - W_4$$

$$\frac{dC_{heavy\ compounds}}{dt} = W_{4.1} + W_{4.2}$$

$$\frac{dC_{monoalkylates}}{dt} = W_{5.1} + W_{5.2} - W_{7.3}$$

$$\frac{dC_{dialkylates}}{dt} = W_{7.1} + W_{7.2} + W_{7.3} + W_{7.4}$$

$$\frac{dC_{xylols}}{dt} = W_6$$

$$\frac{dC_{toluene}}{dt} = -W_{7.4}$$

$$\frac{dC_{coke}}{dt} = W_8$$

Initial conditions: t = 0, $C_i = C_{0i}$, where i - the corresponding hydrocarbon.

The presented kinetic model will be the basis for development of computer modeling system of ethylbenzene manufacturing.

Table 5 Expressions for rates of chemical reactions occurring in alkylation and transalkylation process

Reaction group	Expression for reaction rate
1. Ethylbenzene forming	$W_1 = k_{0(1)} \cdot e^{-Ea(_1)/RT} \cdot C_{benzene} \cdot C_{ethylene}$
2. Dithylbenzene forming	$W_2 = k_{0(2)} \cdot e^{-Ea(2)/RT} \cdot C_{ethylbenzene} \cdot C_{ethylene}$
3. Triethylbenzene forming	$W_3 = k_{0(3)} \cdot e^{-Ea(3)/RT} \cdot C_{diethylbenzene} \cdot C_{ethylene}$
4. Heavy compounds forming	$W_{4.1} = k_{0(4)} \cdot e^{-Ea(4.1)/RT} \cdot C_{triethylbenzene} \cdot C_{ethylene}$ $W_{4.2} = k_{0(4)} \cdot e^{-Ea(4.2)/RT} \cdot C_{benzene}^2 \cdot C_{ethylene}$
5. Other monoalkylates forming	$W_{5.1} = k_{0(5)} \cdot e^{-Ea(5.1)/RT} \cdot C_{benzene} \cdot C_{butylene}$ $W_{5.2} = k_{0(5)} \cdot e^{-Ea(5.2)/RT} \cdot C_{benzene} \cdot C_{propylene}$
6. Xylols forming	$W_6 = k_{0(6)} \cdot e^{-Ea(6)/RT} \cdot C_{benzene} \cdot C_{ethylene}$
7. Other dialkylates forming	$W_{7.1} = k_{0(7)} \cdot e^{-Ea(7.1)/RT} \cdot C_{ethylbenzene} \cdot C_{propylene}$ $W_{7.2} = k_{0(7)} \cdot e^{-Ea(7.2)/RT} \cdot C_{ethylbenzene} \cdot C_{butylene}$ $W_{7.3} = k_{0(7)} \cdot e^{-Ea(7.3)/RT} \cdot C_{monoalkylates} \cdot C_{ethylene}$ $W_{7.4} = k_{0(7)} \cdot e^{-Ea(7.4)/RT} \cdot C_{toluene} \cdot C_{ethylene}$
8. Coke forming	$W_8 = k_{0(8)} \cdot e^{-Ea(8)/RT} \cdot C_{benzene}^6$
9. Cycles and dicycles forming	$W_{9.1} = k_{0(9)} \cdot e^{-Ea(9.1)/RT} \cdot C_{butylene}$ $W_{9.2} = k_{0(9)} \cdot e^{-Ea(9.2)/RT} \cdot C_{z\text{-}butane}^2$
10. Butylene forming	$W_{10} = k_{0(10)} \cdot e^{-Ea(_{10})/RT} \cdot C_{ethylene}^2$

4. Conclusions

1. With use of quantum-chemical methods of thermodynamic functions calculating thermodynamic analysis of reactions occurring in alkylation process was carried out.
2. A method of reaction network formalizing consisting in grouping components of reactivity according to value of degree of compensation in corresponding reactions. The correctness of energy of broken bonds in molecules of reactants calculation is confirmed by comparison with literature data.
3. On the basis of formalized reaction network kinetic model of benzene with ethylene alkylation processes was developed.

List of symbols

ΔG – change in Gibbs energy of reaction, kJ/mole;
H – degree of compensation, %;
ΣD_j – sum of broken bonds energies, kJ/mole;

E_a – activation energy of reaction, kJ/mole;

ΔH– change enthalpy of reaction, kJ/mole;

E_{a-l} – literary activation energy of reaction, kJ/mole;

$E_{a(P-S)}$ – calculated from the Polanyi-Semenov expression value of activation energy, kJ/mole;

W_i – rate of i-th chemical reaction, mole/l*sec;

$k_{0(i)}$ – pre-exponential factor for the i-th group of reactions;

$Ea_{(i,j)}$– activation energy of the j-th sub-group of the i-th reaction group, kJ/mole;.

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