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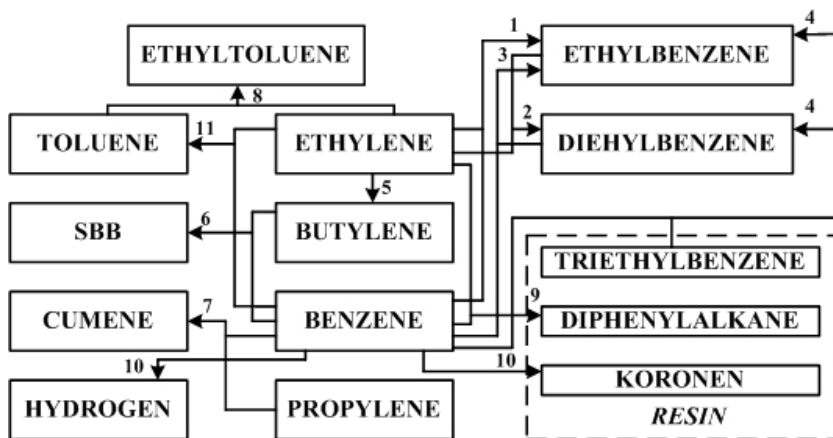
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RESOURCE SAVING IN ETHYLBENZENE PRODUCTION

Evergrowing demand on output of oil-refining and petrochemical industries issues the challenge of increase the efficiency of oil-refining and petrochemical processes [1]. This problem can be solved using mathematical modeling method. Mathematical modeling of benzene alkylation with ethylene in presence of chloric-alumina catalyst is the object of the present work.

The first stage of model development is creation of hydrocarbons transformation scheme. According to the material balance, feed flow is plural-component. After the analysis of this flow and theoretical knowledge about chemism of benzene alkylation the list of reactions was formed. Thermodynamic probability was confirmed by calculation of isobaric-isothermal figure – change of Gibbs energy ΔG . Calculation was realized in program Gaussian by PM3 quantum chemical method with taking into account technological conditions: temperature 395 K, pressure 1,5 MPa.

According to the obtained thermodynamic analysis formalized conversion scheme is presented on the pic. 1.



Formalized conversion scheme. Picture 1.

On the base of developed conversion scheme the kinetic model was created. Expressions of reactions rates was wrote according to the law of mass action.

Taking into account hydrodynamic regime [2], material balance of reactor is:

$$\begin{aligned}
 \frac{dC_{Benzene}}{d\tau} &= -k_1 \cdot C_{Benzene} \cdot C_{Ethylene} - k_4 \cdot C_{Benzene} \cdot C_{Diethylbenzene} - k_5 \cdot C_{Benzene} \cdot C_{Resin} - \\
 &- k_7 \cdot C_{Benzene} \cdot C_{Butylene} - k_8 \cdot C_{Benzene} \cdot C_{Propylene} - 2k_{10} \cdot C_{Benzene}^2 \cdot C_{Ethylene} - \\
 &- 6k_{11} \cdot C_{Benzene}^6 - 2k_{12} \cdot C_{Benzene}^2 \cdot C_{Ethylene} \\
 \frac{dC_{Ethylene}}{d\tau} &= -k_1 \cdot C_{Benzene} \cdot C_{Ethylene} - k_2 \cdot C_{Ethylbenzene} \cdot C_{Ethylene} - k_3 \cdot C_{Diethylbenzene} \cdot C_{Ethylene} - \\
 &- 2k_6 \cdot C_{Ethylene}^2 - k_9 \cdot C_{Toluene} \cdot C_{Ethylene} - k_{10} \cdot C_{Benzene}^2 \cdot C_{Ethylene} - k_{12} \cdot C_{Benzene}^2 \cdot C_{Ethylene} - \\
 &- k_{13} \cdot C_{Ethylene} \cdot C_{Hydrogen} \\
 \frac{dC_{Ethylbenzene}}{d\tau} &= k_1 \cdot C_{Benzene} \cdot C_{Ethylene} - k_2 \cdot C_{Ethylbenzene} \cdot C_{Ethylene} + 2k_4 \cdot C_{Benzene} \cdot C_{Diethylbenzene} + \\
 &+ k_5 \cdot C_{Benzene} \cdot C_{Resin} \\
 \frac{dC_{Diethylbenzene}}{d\tau} &= k_2 \cdot C_{Ethylbenzene} \cdot C_{Ethylene} - k_3 \cdot C_{Diethylbenzene} \cdot C_{Ethylene} - \\
 &- k_4 \cdot C_{Benzene} \cdot C_{Diethylbenzene} + k_5 \cdot C_{Benzene} \cdot C_{Resin} \\
 \frac{dC_{Butylene}}{d\tau} &= k_6 \cdot C_{Ethylene}^2 - k_7 \cdot C_{Benzene} \cdot C_{Butylene} \\
 \frac{dC_{SRB}}{d\tau} &= k_7 \cdot C_{Benzene} \cdot C_{Butylene} \\
 \frac{dC_{Propylene}}{d\tau} &= -k_8 \cdot C_{Benzene} \cdot C_{Propylene} \\
 \frac{dC_{Cumene}}{d\tau} &= k_8 \cdot C_{Benzene} \cdot C_{Propylene} \\
 \frac{dC_{Toluene}}{d\tau} &= -k_9 \cdot C_{Toluene} \cdot C_{Ethylene} + 2k_{12} \cdot C_{Benzene}^2 \cdot C_{Ethylene} \\
 \frac{dC_{Ethyltoluene}}{d\tau} &= k_9 \cdot C_{Toluene} \cdot C_{Ethylene} \\
 \frac{dC_{Hydrogen}}{d\tau} &= 12k_{11} \cdot C_{Benzene}^6 - k_{13} \cdot C_{Ethylene} \cdot C_{Hydrogen} \\
 \frac{dC_{Resin}}{d\tau} &= k_3 \cdot C_{Diethylbenzene} \cdot C_{Ethylene} + k_{10} \cdot C_{Benzene}^2 \cdot C_{Ethylene} + k_{11} \cdot C_{Benzene}^6
 \end{aligned}$$

Initial conditions: $\tau = 0$, $C_i(0) = C_{i0}$, where i – corresponding hydrocarbon.

The thermal balance looks:

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

Then kinetic parameters of the model was determined, using the theory of activated complex. According to the literary data [3] the activation energy can be calculated through the change of Gibbs energy in process of transient state formation. For the bimolecular reaction:

$$E_a = \Delta G^\ddagger + RT,$$

It is accepted that limitative stage in mechanism of aromatic electron-seeking substitution is the stage of σ -complex formation [4].

After determination of kinetic constants the developed mathematical model was checked up on the adequacy to the real process. Because of the model is appropriate, the optimal technological conditions of alkylation was found (the temperature is 130 °C, molar ratio «benzene:olefins» is 14:1).

Thus, the carrying out process of benzene alkylation at optimal technological conditions allows to utilize natural resource and resource of plants and industrial power, that, certainly, will given more positive economical effect.

Literature

1. Fetisova V.A. Increase of efficiency the process of benzene alkylation by high olefins, using mathematical modeling method. Dissertation of competition the candidate of science degree. – Tomsk, 2012. – 144 p.
2. Beskov V.S., Flokk V. The modeling of catalytic processes and reactors. M.: Chimiya, 1991. – 256 p.
3. Emanuel N.M., Knorre D.G. The course of chemical kinetics. M.:Vyssh. shk., 1984. – 463 p.
4. Organic chemistry. Part 2. / O.A. Reutov, A.L. Kurc, K.P. Butin – M.:Binom. the laboratory of knowelege., 2009. – 544