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Developing of the mathematical model for controlling the operation of alkane dehydrogenation catalyst in production of linear alkyl benzene

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HIGHLIGHTS

- Process model dehydrogenation of alkanes is predicting the deactivation of catalyst.
- The influence of raw material for the catalyst lifetime was obtained.
- The optimum working parameters for different Pt-catalysts were determined.
- The optimum flow rate of water in the reactor has been found.

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ABSTRACT

The main results are presented on the modeling of the industrial process of catalytic dehydrogenation of C_9–C_{14} *n*-alkanes which is one of the technological stages in the production of linear alkyl benzene used in the synthesis of synthetic detergents. Application of the developed mathematical model in evaluating the influence of the raw material composition on the target product yield is considered. The calculation results are given for the optimal technological modes with different dehydrogenation Pt-catalysts and also for prediction of catalysts lifetime duration.

1. Introduction

The dehydrogenation of hydrocarbons is one of the most important processes in the organic synthesis. The process of dehydrogenation of C_9–C_{14} *n*-alkanes into alkenes is used in the production of linear alkyl benzene (LAB) that are the intermediate products in the synthesis of synthetic detergents and surfactants [1]. In an industrial reactor, this process is usually performed at the pressure of 0.2 MPa, and the temperature of 465–495 °C. Different catalysts are used, usually containing platinum deposited on alumina or zeolite. A rather high selectivity of ~90% is obtained at a relatively low conversion of approx. 10–11%. The average catalyst operating cycle duration is 5–8 months. Even a slight increase in the selectivity, activity or stability of Pt-catalysts used in the alkane dehydrogenation can substantially influence the cost and the quality of the LAB produced [2–5]. Thus, the urgency of solving the problems related to the abovementioned changes is obvious.

The modernization of this technology is not limited to the development and the improvement of Pt-catalysts. The computer assistance for industrial processes aimed at optimizing the operating modes is also of a great importance [6,7]. The application of the process simulation systems determines a new level of operational efficiency of processes related, and allows optimizing the operating modes of catalysts.

Therefore, our aim was to develop an intelligent system controlling the operation of the alkane dehydrogenation catalyst in the LAB production, and allowing the increase in the operational efficiency of an industrial unit.

2. Brief description of the technology

The LAB production complex includes five interconnected units: PAREX unit, preliminary fractionation facility, dehydrogenation plant for converting alkanes into alkenes, unit for selective hydrogenation of side products of dehydrogenation, and the alkylation plant, where the LAB is produced from the alkenes and benzene (Fig. 1).

3. The mathematical model

The system for controlling the operation of gasoline reforming Pt catalysts was recently developed, based on the hierarchical

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Symbols

H	enthalpy (kJ/mol)	T_0	start temperature (temperature of an environment) (K)
S	entropy (J/mol K)	T_{in}	temperature of an input in a reactor (K)
C_i	concentration of ith hydrocarbon (mol/m^3)	C_{in}	entrance concentration of hydrocarbon (mol/m^3)
ε	pore volume of catalyst layer	V	volume of catalyst (m^3)
r_i	rate of reaction (mol/m^3 h)	G	hour expenditure of raw material (m^3/h)
w_j	rate of jth component in ith reaction transformation (mol/m^3 h)	t	time (h)
T	temperature of the process (K)	z	total volume of the processed raw material (m^3)
ΔH_j	thermal effect of reaction (J/mol)	ω	mass concentration of substance in hydrocarbons (mass%)
C_p	thermal capacity of a mixture (J/mol K)	x	molar fraction of substance in hydrocarbons (mol/l)
ρ	density of a mixture (kg/m^3)	Mr	molar weight (kg/mol).

approach, at the Department of Chemistry of Fuels and Chemical Cybernetics in Tomsk Polytechnic University. It was then successfully applied in the industry [8,9]. The mathematical formulation of the process of C_9–C_{14} alkane dehydrogenation is based on the same approach. The mixture of *n*-alkanes with the difference of 1–4 carbon atoms in their carbon chains, e.g. C_{10}–C_{13} or C_{11}–C_{14}, is used as a raw material for dehydrogenation. In this case, the C_{10}–C_{14} fraction is unsuitable. The restriction is dictated by the necessity to convert the light *n*-alkanes without boosting the cracking of the heavier alkanes. Results of studies of the reactivity of the given homologous group show that these hydrocarbons have substantially different relative rates of dehydrogenation [10]: the lighter hydrocarbons are much more slowly dehydrogenated than the heavier ones. Thus, in order to avoid a high yield of gases in the cracking of heavier hydrocarbons and high losses of the target product, it is necessary to provide the required number of carbon atoms. Nevertheless, the raw material contains C_9 and C_{14} *n*-alkanes (0.01–0.50 wt.%) that are taken into account in the mathematical formulation of the process. The mathematical model we developed for the *n*-alkane dehydrogenation on Pt-catalysts is sensitive to the changes in the chemical composition of raw materials [11]. For the *i*th component, the material balance can be written with the differential equation:

$$G\frac{\partial C_i}{\partial z} + G\frac{\partial C_i}{\partial V} = (1-\varepsilon)\sum_{j=1}^{N} r_j, \quad i = 1 \ldots M, \quad j = 1 \ldots N, \tag{1}$$

where G is the raw material flow rate, m^3/h; C_i is the ith hydrocarbon concentration, mol/m^3; V is the catalyst volume, m^3; ε = 0–1 is the catalyst layer porosity; r_j is the jth reaction rate, mol/(m^3 h); $z = G \cdot t$ is the total volume of raw material processed after catalyst regeneration, m^3; t is the time, h; M is the number of components, and N is the number of reactions. The heat balance can also be written with the differential equation:

$$G\frac{\partial T}{\partial z} + G\frac{\partial T}{\partial V} = -(1-\varepsilon)\frac{\sum_{j=1}^{N}(\Delta H_j r_j)}{C_p}, \tag{2}$$

where T is the process temperature, K; ΔH_j is the reaction heat, J/mol; C is the heat capacity of the mixture, J/(kg K); ρ is the raw material density, kg/m^3.

The initial and boundary conditions are the following:

$$z = 0 : C_i = 0,\ T = T_0;$$
$$V = 0 : C_i = C_{i,\text{in}}, T = T_{\text{in}}.$$

The basis for the considered mathematical model is the formalized hydrocarbon conversion scheme that takes the hydrocarbon reaction abilities under dehydrogenation conditions into account (Fig. 2).

Known conceptions [12] of the dehydrogenation mechanism allowed forming the presumable transformation scheme of the process. We used the Gaussian program package with PM3 procedure of NDDO (Neglect of Diatomic Differential Overlap) method based on quantum-chemistry modeling to calculate the electron molecule structures, and to estimate the thermodynamic characteristics (ΔG_r, ΔH_r, ΔS) for the reactions conducted under 753 K and 0.2 MPa. The method under consideration takes into account oscillatory and rotator movements of atoms, electron orbit patterns, effects of double bonds conjugation, and reproduces the structure and energy hyper valence compounds with high validity, providing adequate accuracy for high-quality reproduction of molecule physiochemical characteristics [13,14]. The results are illustrated in Table 1.

The calculated data on the component structures involved in the dehydrogenation process is compared with the experimental data [15]. In the absence of extensive information on higher alkanes, the comparison is made on the basis of entropy and heat

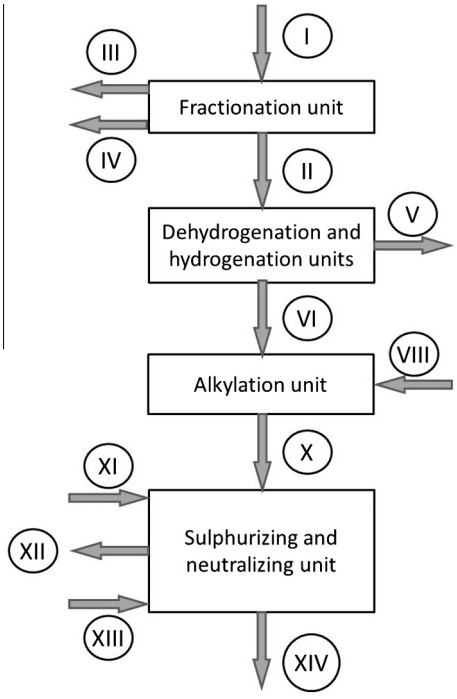

Fig. 1. LAB production flow chart: (I) n-alkanes from Parex unit; (II) *n*-alkanes C10–C13; (III) *n*-alkanes C14–C17; (IV) *n*-alkanes C18 and higher; (V) hydrogenous gas; (VI) mixture of *n*-alkanes and monoalkenes; (VII) recycling *n*-alkanes; (VIII) benzene from benzene reforming installation; (IX) alkylate bottom; (X) alkyl benzene; (XI) sulfur from the elemental sulfur installation; (XII) LAB sulfonate; (XIII) alkali; and (XIV) sodium LAB sulfonate.