MATHEMATICAL MODELLING OF PYROLYSIS OF GASOLENE FRACTION

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Pyrolysis is one of the main processes for generation of feed stock for various plants in the petrochemical industry. To improve efficiency of the process, creation of deterministic models is of great interest, since they allow to create the best optimization strategy through multilateral analysis [1].

The developed model is based on the kinetic model proposed by Zhorov Yu.M., Vasilieva N.I. and Panchenkov G.M., which consists of 7 reactions, where 12 components are involved [2]. In this model, the reaction of formation of coke from secondary polymers is also added.

$$C_2H_6 \rightarrow 0.47C_2H_4 + 0.53CH_4$$

$$C_3H_8 \rightarrow 0.32C_2H_4 + 0.34C_2H_6 + 0.16C_3H_6 + 0.18CH_4$$

$$C_4H_{10} \rightarrow 0.10C_4H_6 + 0.32C_2H_4 + 0.27C_3H_6 + 0.15C_2H_6 + 0.16CH_4$$

$$C_5H_{12} \rightarrow 0.16C_3H_6 + 0.37C_2H_6 + 0.35C_2H_4 + 0.12CH_4$$

$$C_2H_4 \rightarrow 0.15C_2H_2 + 0.85H_2$$

$$C_2H_4 \rightarrow \text{polymers}$$

$$C_3H_6 \rightarrow \text{polymers}$$

$$\text{Polymers} \rightarrow \text{coke}$$

Thus, the mathematical model of the pyrolysis process consists of two parts. The first one is a system of 7 exponential equations for calculating the rate constants of the above reactions [1]:

$$K_j = K_{0j} \cdot P_0 \cdot \exp\left(\frac{-E_j}{RT}\right), j \in \{1, ..., 7\},$$

Here K_j is reaction j rate constant, s^{-1}, K_{0j} is its preexponential factor, s^{-1}, P_0 is the process pressure, atm, E_j is reaction j activation energy, J/mol, T is the process temperature, °K.

The second part consists of 11 differential equations. They describe the changes in the concentrations of the components included in the mixture of hydrocarbons throughout the time [1]:

$$\frac{dC_k}{d\tau} = \sum a_{i,j} \cdot K_j \cdot C_i$$

Here C_i, C_k are concentrations of components i, k, mol/L, τ is the contact time, s, $a_{i,j}$ is the stoichiometric coefficient of component i in reaction j. The obtained system of equations is solved by the first-order Runge-Kutta method.

The model a well takes into account the non-stationary nature of the process. That is, the parameters of the system change over astronomical time. This allows calculating the coke concentration using the formula below and, accordingly, the thickness of its deposits on the walls of the furnace pipes [3].

$$\frac{dC_{coke}}{d\tau} = K_8 C_{coke} - \exp(0{,}023 \cdot C_{coke} - 1) \cdot \cdot G^{0,8} \cdot (D - 2 \cdot \delta)^{-1,8}$$

Here G is the mass flow of raw materials, kg/s, D is the tube diameter, mm, δ is the thickness of the coke deposits, mm.

Figure 1 shows the result obtained using the model over a short period of time, describing the accumulation of a coke layer on the walls of the pipes of the pyrolysis furnace.

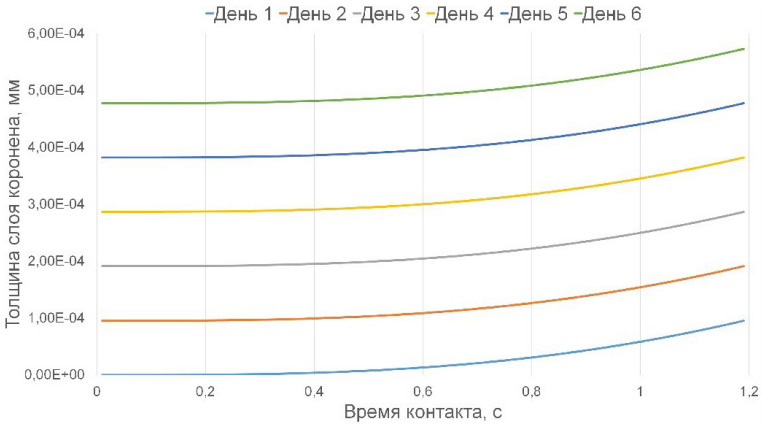

Fig. 1. *The growth of the coke layer on the walls of the tube for 6 days*

References

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DEVELOPMENT A FORMALIZED SCHEME OF SUBSTANCES CONVERSION IN THE ZEOFORMING PROCESS OF STABLE GAS CONDENSATE

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The growing demand of automobile fuels leads to the development and search of new technologies for their production. The problem of rational use of associated petroleum gas and stable gas condensate is also growing every year. The combined solution to these problems is the use of stable gas condensate as a feedstock for the production of high-octane motor fuels components.

Stable gas condensates (SGC) are liquid products consisting mainly of C_{5+} hydrocarbons, which produced at oil, gas and gas condensate fields as by-products of natural gas preparation [1].

One of the most promising directions in terms of production the high-octane components of automobile gasoline is the processing SGC on zeolite catalysts – zeoforming process. The catalysts used in this process – zeolites, have acidic properties that provide a deep conversion of paraffins and olefins, as well as incomplete conversion of mono-methylparaffins and naphthenes [2].

The high-octane component of automobile gasoline obtained in the zeoforming process is characterized by a certain group composition and an octane number. These characteristics depend on the feedstock composition and may differ significantly at the processing of SGC obtained from different fields.

The aim of this work is to develop formalized scheme of substances conversion in the zeoforming process of SGC.

To achieve this goal, chromatograms of SGC and products of its processing on zeolite at a temperature of 375, 400, 425 °C, a pressure of 0.25 MPa, and a volume feed rate of 2 h^{-1}, were analyzed [2].

As a result of the analysis of chromatograms, lists of substances whose content in feedstock and products exceeds 1 % by weight were compiled. The resulting list for feedstock includes 19 substances, including 11 paraffins, 1 olefin, 7 naphthenes; for products, it includes 34 substances, including 18 paraffins, 4 olefins, 6 naphthenes, 6 aromatic hydrocarbons.

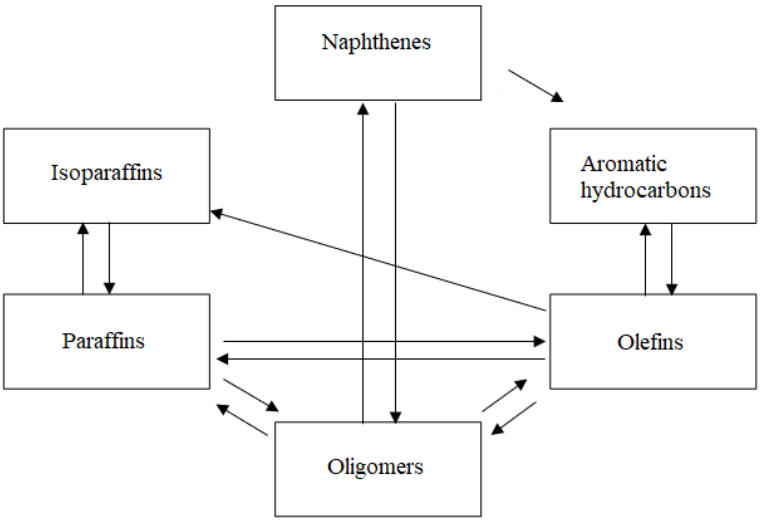

Fig. 1. *Scheme of SGC hydrocarbons conversion on the zeolite catalysts*