Fig. 1. *Group composition of feedstock diesel fractions and products obtained by their processing, % wt.*

case is the transfer of hydrogen in olefins formed during cracking reactions. A probable method of naphthenes formation is reactions of diene synthesis, involving olefins and diolefins formed during cracking.

The predominance of diene synthesis reactions for medium-distillate fractions is supported by the significant content of naphthenes in the resulting products. Moreover, even if there are not very many naphthenes in the feedstock (Feedstock 3), the content of this hydrocarbons group in the product exceeds 20 % wt.

References

1. *ASTM D611-12(2016) Standard Test Methods for Aniline Point and Mixed Aniline Point of Petroleum Products and Hydrocarbon Solvents,* *URL: https://www.astm.org/d0611-12r16.html. Date of access 15.02.2022.*

DEVELOPMENT OF NON-STATIONARY MODEL OF PYROLYSIS

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Polymers are one of the main components of almost any industrial products, as well as consumer goods. The raw materials for the production of polymers are alkenes, which are obtained mainly by the pyrolysis of hydrocarbon feedstock. However, coke deposits in the furnace coils during this process. The formation of coke leads to a decrease in the yields of target products, and the likelihood of accidents increases.

The purpose of this work is to optimize the process by controlling the rate of coking. This requires the development of a non-stationary model. It is based on a formalized reactions scheme shown in Figure 1.

Since the process is carried out at high temperatures, decomposition reactions prevail over saturation and decyclization ones. That is, for any K_i for which K_{-i} exists, $K_i >> K_{-i}$.

The model first calculates the reaction rate constants at the current time, at the current point of the pyrolysis coil:

$$K_{j,t,l} = K_{0j} \bullet \frac{P_{0\,t,l}}{T_{t,l}^2} \bullet exp\left(\frac{-E_j}{RT_{t,l}}\right), j \in \{1...172\}$$

Next, the reaction rates are calculated at a given point in the coordinate plane, where the axes are astronomical time and distance from the entrance to the coil. Finally, the rates of change in the concentrations of the components are calculated as the sum of the corresponding reactions:
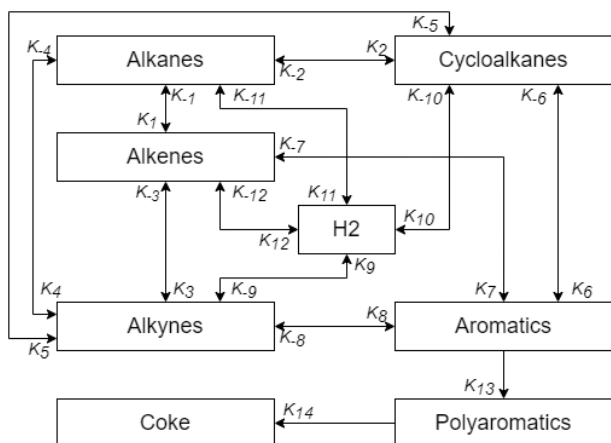
Fig. 1. *Formalized reaction scheme of the pyrolysis process*

$$\frac{dC}{dt} + \frac{dC}{dl} \bullet u = \sum a_{i,j} \bullet K_{j,t,l} \bullet \prod C_{i,t,l}^{a_{j,j}}$$

Thus, using the method of finite differences, an explicit expression is derived for calculation of the component's concentration at certain point on the mentioned coordinate plane:

$$C_{i,j} = \left(\frac{\Delta l}{u}\right) \bullet \left(\sum W - \frac{1}{\Delta t} \bullet C_{i-1,j+1} + \right.$$

$$\left. + \left(\frac{1}{\Delta t} + \frac{u}{\Delta l}\right) \bullet C_{i-1,j}\right)$$

Coke concentration is calculated as follows [1]:

$$\frac{dC}{dt} + \frac{dC}{dl} \bullet u = \sum W - R_S$$

R_S is polyaromatic components' sedimentation rate towards the wall area of the pyrolysis coil from the reaction stream:

$$R_S = \frac{0{,}023}{(0{,}25 \bullet \pi)^{0{,}8}} \bullet \left(\frac{G^{0{,}8} \bullet \mu^{0{,}2} \bullet \omega_{\text{масс.}}}{D^{1{,}8} \bullet Sc^{\frac{2}{3}} \bullet M_{\text{CM}}}\right)$$

Thus, using the implemented part of the model, changes in the concentrations during the flow through the furnace coil of ethylene and propylene were calculated. The results are shown in Figure 2. In the virtual product stream, the concentrations were 0.027 mol/l for ethylene and 0.008 mol/l for propylene. Relative errors in comparison with the real values from a certain enterprise are 10 % and 20 %, respectively.

Large errors are due to the fact that the geometric parameters of the real coil are not fully known, as well as the lack of a mechanism within the model that takes into account the effect of the coke layer on heat transfer from the burning fuel to the reaction mixture.
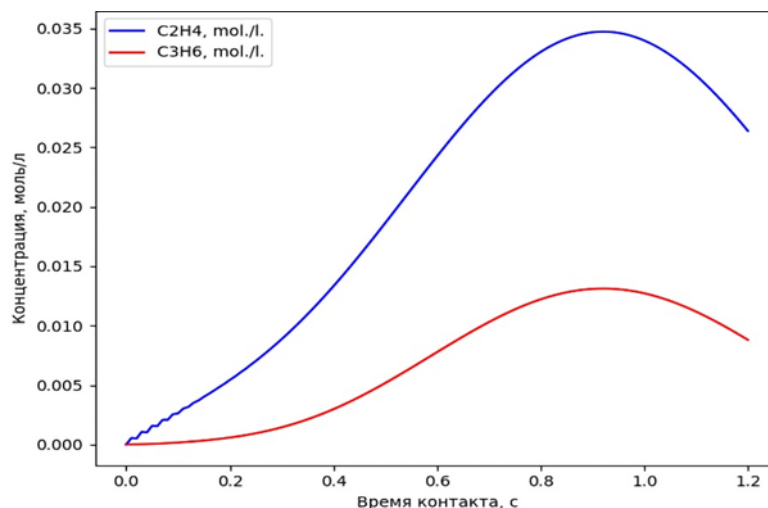

Fig. 2. *Dynamics of ethylene and propylene concentrations*

References

1. *Fernandez-Baujin J. M., Solomon S. M. New reactor design offers benefits // Oil Gas J., 1976. – V. 74. – P. 94–95.*