NON-STATIONARY SIMULATION OF GASOLINE FRACTION PYROLYSIS

Bunaev A.A., Dolganova I.O., Dolganov I.M., Chernyshov M.N.
Scientific advisor scientific researcher Dolganova I.O.
National Research Tomsk Polytechnic University, Tomsk, Russia

Currently, the process of pyrolysis of hydrocarbons is most often carried out in tube furnaces. The efficiency of the process in these devices depends both on the composition of the raw material and on the thermodynamic parameters. However, it decreases during the operating cycle of the installation, since coke accumulates in the furnace tubes as the result of side processes. Under the conditions of high temperatures, raw hydrocarbons decompose into lighter olefins, which undergo polymerization reactions with the formation of high molecular weight compounds. These compounds, in turn, enter into polycondensation reactions with each other, as a result of which coke is obtained, which settles on the inner surface of the tubes of the pyrolysis furnace.

Thus, the tube diameter decreases, and it leads to an increase in the pressure drop. In addition, the residence time increases, due to which the yield of the target products of the process decreases. Also, the deposition of coke leads to occurrence of thermal stress areas on the tubes of the furnace. Burnout may occur in these places, which will require to stop production and replace the entire tube.

The improvement of the process of pyrolysis of hydrocarbons today occurs in two directions. First, the process technology itself is being modernized. That is, the burner devices are being improved, the processes that initiate pyrolysis are being investigated, more efficient catalysts are being sought, and a number of other improvements are being developed. Secondly, the search for optimal operating modes of the installation is carried out using computer simulation methods. Within this direction, deterministic and stochastic models of the process are being developed. In this case, deterministic models are of greater interest, since by virtue of the mathematical apparatus, which is based on physicochemical and chemical laws, they make it possible to determine the influence of certain parameters on the efficiency of the process in an explicit form in order to form a strategy for its optimization.

The model is based on the reaction scheme for the gasoline fraction pyrolysis process shown in Figure 1.

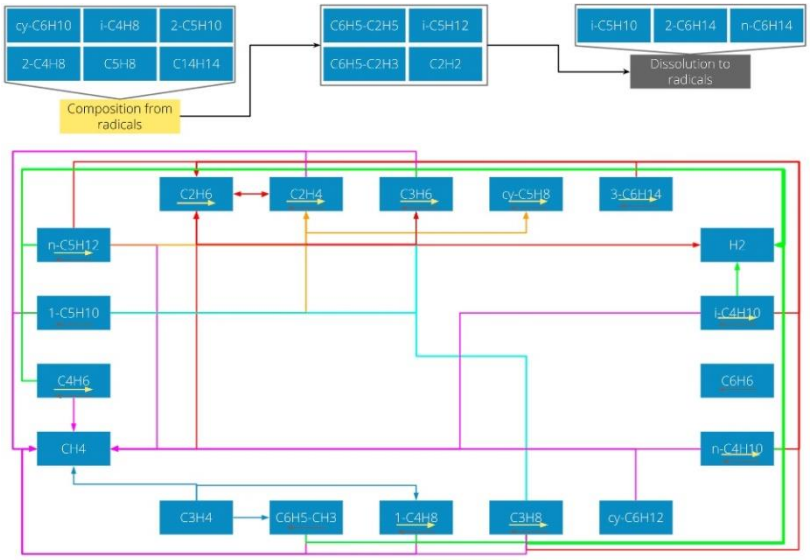

Fig.1 Pyrolysis reaction scheme

On the basis of this scheme, a mathematical model of the kinetics of the process has been compiled.

The calculation takes place in two stages. At the first, the reaction rate constants are calculated [2]:

$$K_i = K_{0i} \cdot P_0 \cdot \exp\left(\frac{-E_i}{RT}\right), i \in \{1, \dots, 62\}, \quad (1)$$

where K_i - the rate constant of reaction i, s^{-1}, K_{0i} - the preexponential factor, s^{-1}, P_0 - the process pressure, atm, E_i - the activation energy of reaction i, J./mol., T - the process temperature, °K.

Next, the changes in the concentrations of the components of the system are calculated. It performed by adding up the reaction rates in which a particular component is present. The reaction rates are multiplied by the stoichiometric coefficient of the component in given reaction [1].

$$\frac{dC_i}{d\tau} = \sum a_{i,j} \cdot K_j \cdot \prod C_i^{\alpha_{i,j}}, \quad (2)$$

where C_i - the concentration of component i, mol./l., τ - residence time, s, $a_{i,j}$ - the stoichiometric coefficient of component i in reaction j.

However, it should be noted that the calculation of the change in the concentration of coke is carried out using a different formula [3]:

$$\frac{dC_{coke}}{d\tau} = K_{172}C_{coke} - \exp(0.023 \cdot C_{coke} - 1) \cdot G^{0.8} \cdot (D - 2 \cdot \delta)^{-1.8}, \quad (3)$$

where G – mass flow rate, kg/s, D – tube diameter, mm, δ – coke layer thickness, mm.

Thus, using the obtained model, the pyrolysis of the gasoline fraction was simulated, the composition of which is presented in Table 1.

Table 1

Pyrolysis feedstock composition

Components sorted by carbon chain length	Concentrations sum, mol./l.
C_4	0.44
C_5	1.67
C_6	7.7

As a result, the dynamics of target products was obtained, presented in Figure 2.

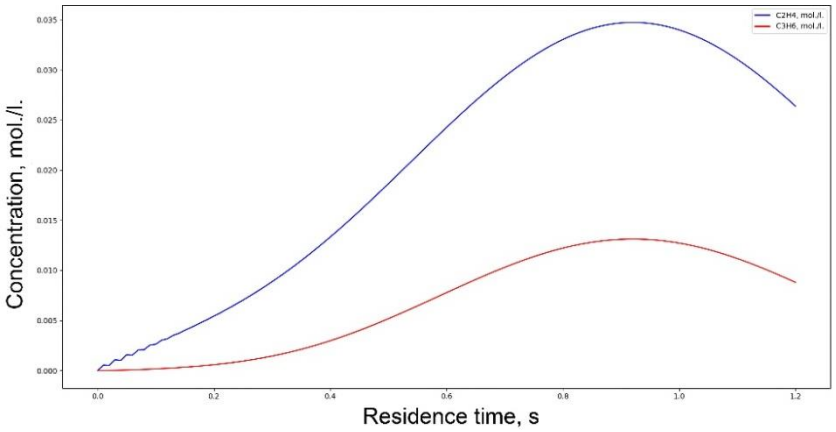

Fig.2 Ethylene and propylene concentrations dynamic

In addition, the results were obtained for the growth of the coke layer over several days, which are presented in Figure 3.

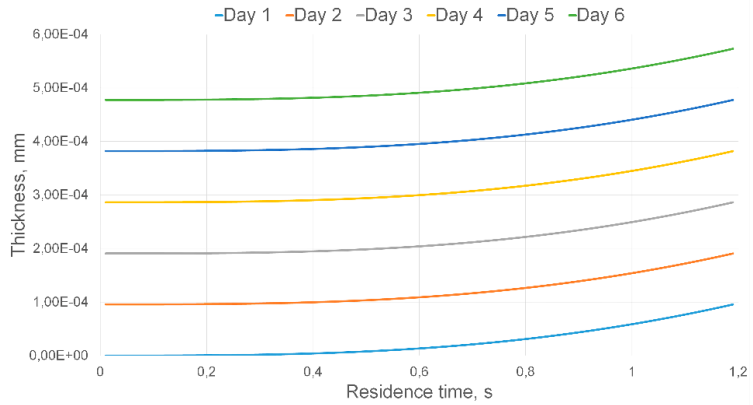

Fig.3 Coke layer accumulation within several days

However, the model is not yet complete at this stage. So, in the future, it is planned to add a mechanism for calculating the dynamics of the concentrations of all components of the system in real time. That is, it is necessary to make the model completely non-stationary, since at this stage the amount of coke, expressed in one form or another, is the only component that changes over astronomical time. In addition, it is necessary to calculate the pressure loss in the reactor tube of the furnace, since the pressure directly affects the rate constants, and, therefore, the concentration dynamics. Finally, it is also planned to introduce calculations of the thermodynamic conditions of the process.

References

1. Bituykov V.K., Tikhomirov S.G., Arapov D.V., Savvin S.S. Process modeling of pyrolysis of traight run gasoline with a help of use of genetic algorithm // Vestnik of Voronezh State University of Engineering Technologies. – Voronezh, 2015. – №3. – P. 79 – 84
2. Samedov F.A., Morozov A.Yu., Samoilov N.A., Prosochkina T.P. Mathematical modeling of nonstationary process of pyrolysis of hydrocarbons //Neftekhimiya. – Moscow, 2019. – № 2. – P. 143 – 151.
3. Fernandez-Baujin J. M., Solomon S. M. New reactor design offers benefits//Oil Gas J. – 1976. – V. 74. – P. 94-95.