MATHEMATICAL MODELING OF THE PYROLYSIS PROCESS

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For a wide range of processes used in the petrochemical industry, the pyrolysis of hydrocarbons is one of the main large-capacity processes that form their raw material base. Today, developments aimed at improving the pyrolysis process are carried out in two main directions [1]. Firstly, the pyrolysis technology itself is being modernized — technical re-equipment of existing plants and the design of new ones using new developments are being carried out. Secondly, mathematical models are created to search for optimal modes of the process. In this case, the creation of deterministic models is of greatest interest, since they allow a multilateral analysis of the process, which will help to form a certain optimization strategy. [1].

The analysis of the process of pyrolysis of hydrocarbons was performed using the kinetic model proposed by Y. Zhorov, N. Vasilieva and G. Panchenkov. [3]. Thus, the kinetics model of the pyrolysis process consists of 8 reactions, listed below, in which 12 components are involved.

$$C_2H_6 \rightarrow 0.47C_2H_4 + 0.53CH_4$$
$$C_3H_8 \rightarrow 0.32C_2H_4 + 0.34C_2H_6 + 0.16C_3H_6 + 0.18CH_4$$
$$C_4H_{10} \rightarrow 0.10C_4H_6 + 0.32C_2H_4 + 0.27C_3H_6 + 0.15C_2H_6 + 0.16CH_4$$
$$C_5H_{12} \rightarrow 0.16C_3H_6 + 0.37C_2H_6 + 0.35C_2H_4 + 0.12CH_4$$
$$C_2H_4 \rightarrow 0.15C_2H_2 + 0.85H_2$$
$$C_2H_4 \rightarrow \text{polymers}$$
$$C_3H_6 \rightarrow \text{polymers}$$
$$\text{Polymers} \rightarrow \text{coronene}$$

Despite the fact that the obtained model is based on a rather simplified reaction scheme, it nevertheless makes it possible to obtain calculated data on the concentrations of the main components of the hydrocarbon mixture in question over a wide temperature range.

Accordingly, the mathematical model of the kinetics of pyrolysis includes, firstly, a system of 7 exponential algebraic equations for calculating the rate constants of the corresponding reactions [4]:

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

where K_j is the rate constant for reaction j, s^{-1}, K_{j0} is the preexponential factor, s^{-1}, P_0 is the process pressure, atm, E_j is the activation energy for reaction j, J/mol, T is the process temperature, ° K.

Secondly, another 11 equations are differential and are necessary for describing changes in the concentrations of each component of a hydrocarbon mixture during the pyrolysis process [4]:

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

where C_i, C_k are the concentrations of component i, k respectively, mol/l, τ is the residence 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 according to the algorithm shown in the figure 1, which is implemented by Python3.

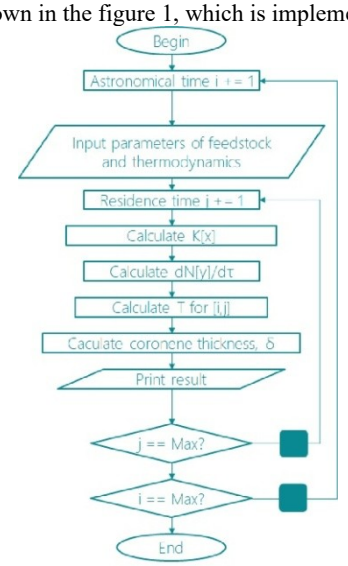

Fig. 1. The algorithm of the mathematical model of pyrolysis

As can be seen from the proposed algorithm, the process takes into account the non-stationarity of the process - each time passing a nested cycle that searches for the residence time, which, in turn, is necessary to describe the behavior of the hydrocarbon mixture along the coil tube of the pyrolysis reactor, the astronomical time iterator increases its value. Taking astronomical time into account is necessary because it allows you to expand the model and add to it the calculation of coke concentration using the formula below and, accordingly, the thickness of its deposits on the walls of the reactor pipes [2].

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

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

The operation of the pyrolysis model obtained in this way was tested using a set of input data on the propane-butane fraction presented in Table.

Table

Propane-butane fraction input for model

The composition of the hydrocarbon mixture,% mass.							Temperature, °K
Methane	Ethane	Ethylene	Propane	Propylene	Butane	Butadiene	
10,1	9,6	17,2	18,2	11,5	30,4	3	825

As a result of the model working for 6 days (6 external cycle passes), calculations were obtained that describe the accumulation of a coronene layer on the walls of the pyrolysis reactor pipes, presented in Figure 2.

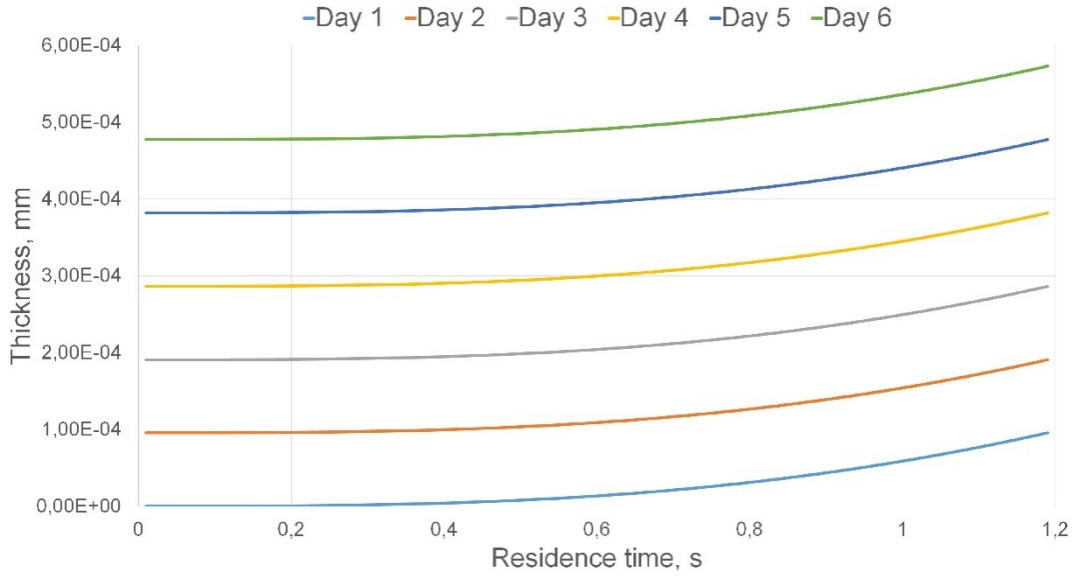

Fig. 2. The growth of the coronene layer on the walls of the tube for 6 days

Thus, a prototype model of the pyrolysis process was obtained. The further progress of the work consists in scaling the transformation scheme - it is proposed to increase the number of substances under consideration and, accordingly, reactions with their participation. Then, it is also necessary to compose, in addition to the kinetic, hydrodynamic, energy, and thermal models of the process. Another important aspect during development is the receipt of relevant data from existing production. And, finally, it requires the creation of a graphical shell for the model being developed for its implementation as software.

References

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