Petroleum and Coal

Non-Stationary Computer-Aided Simulation of gasoline Fraction Pyrolysis

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Abstract

Pyrolysis of hydrocarbons is one of the main processes in petro-chemistry due to the high demand for products derived from light alkenes such as ethene and propene. The process is performed with lack of oxygen and extreme temperatures. Thus, heavier hydrocarbons decay into lighter alkenes. Although, side reactions of these obtained alkenes polymerization with further polycondensation result in coke deposition. Therefore, crossection area of tube decreases as well as residence time. And yield of target products decreases under these conditions, i.e. the process becomes inefficient. The given paper discusses the mechanism of the pyrolysis process, presents the model itself and discusses the influence of main technological parameters on the process efficiency.

Keywords: *Pyrolysis; Non-stationary simulation; Coke deposition; Optimum performance.*

1. Introduction

Almost all objects commonly used by people every day are made of various polymer materials nowadays. The most common ones include, for example: polyethylene, polypropylene, PVC, PET, polystyrene and many others. Alkenes, such as ethylene and propylene, are feed for most of manufacturing processes of these polymers due to their double bonds which makes possible polymerization reactions [1-3]. Thus, there is high and yet increasing demand for ethylene and propylene in the petroleum product market. It imposes severe requirements not only on the quality of these semi-finished products, but also, more importantly, on their quantity [4-5].

Pyrolysis, therefore, is the main method for producing of these monomers [6-7]. It is performed in the absence of oxygen inside tube furnaces which are the most common type of apparatus for this purpose. Furnaces usually consist of two sections. The first is at the top and is called convection section. Feed is supplied to the device there and is heated by the heat of the flue gases, thus being evaporated and mixed with water vapor, which is supplied there as well. So, the mixture is heated to a decay reactions temperature – usually it is about 825°C. Water vapor supply is a necessity, because it reduces the rate of side reactions by decreasing hydrocarbons partial pressure [8-10]. Thus reactions with an increase in volume are much more likely to occur than ones with decrease of volume, which are side reactions of polymerization and polycondensation. The other section is called radiant and is located under the radiant one. Heat of furnace fuel combustion in the burners in this section is needed to maintain the course of hydrocarbon decay reactions. However, it is the section where side reactions occur leading to coke deposition and consecutive efficiency decrease.

Process efficiency is determined by composition of the feedstock and by the thermodynamic parameters of the process. However, it inevitably decreases due to formation of coke deposits. These deposits are the result of said side reactions and form on the inner walls of the furnace tube. Thus, its cross-section decreases and, in turn, the pressure drop between the pipe ends increases. Therefore, yield of target products drops as well as overall efficiency. In addition, the deposits are areas of significant thermal stress. This may result in burnouts on tube, which is an emergency situation requiring replacement of the entire tube [11-14].

There are two main directions for improving the process. First one is modernization of the technology itself. Within this approach towards efficiency increase, burners are being modernized, research of process initiation, as well as development of more efficient catalysts. The second direction is creation of mathematical models and simulation with them in order to find optimal technological modes. In course of this approach deterministic as well as stochastic models are developed with further application [15-16].

There is a large number of the pyrolysis process studies. They are conducted mainly about chemical, kinetic, thermodynamic and hydrodynamic laws and patterns, as well as various mathematical models are being developed and improved. However, these works do not usually discuss processes with coke in tube during different stages of process: its occurrence as result of side reactions, formation of clusters with their further sedimentation on tube walls and, finally, coke deposits burning when tube surface is being regenerated. Since Division for Chemical Engineering has extensive experience in simulation of non-stationary processes, such model of hydrocarbons pyrolysis is being developed with aim of further monitoring and optimizing the process as well as predicting its operational conditions. This is based on the analysis of the pyrolysis process and the presented kinetic model, which contains reaction scheme of benzene fraction pyrolysis. Thus, it allows to calculate concentrations of main components of a given hydrocarbon mixture in a wide temperature range. Therefore, the novelty of the research lies in the development of a non-stationary mathematical model of the pyrolysis process - similar models of the pyrolysis process have not yet been presented in the literature. This model takes into account coke deposits on the inner surface of the tube. The rate of coke deposition depends on the composition of the feedstock, temperature and pressure, as well as on the flow pattern in the apparatus [17-23].

Therefore, the purpose of this study is to predict unit performance under changing conditions: operational modes, composition of feed and amount of coke.

To solve the problems described, it is needed to achieve several goals:
1) study the mechanism of the pyrolysis process itself and the mechanism of coke deposition;
2) analyze thermodynamic patterns of the process;
3) create formalized reaction scheme according to their mechanism;
4) create a kinetic model of pyrolysis;
5) create a non-stationary mathematical model of reactions in pyrolysis taking into account coke deposition;
6) supplement the system of equations with additional one to simulate accumulation of coke layer and the pressure of the reaction medium along the length of the tube with the course of astronomical time;
7) solve the inverse kinetic problem;
8) test the model;
9) make predictive calculations of the duration of the inter-regeneration cycle of the furnace;
10) carry out calculations to obtain the maximum degree of conversion, selectivity and duration of the inter-regeneration cycle.

2. Materials and methods

The object of this research is pyrolysis of the benzene fraction of varying composition and under dynamic thermodynamic conditions. The reaction scheme is presented in Fig.1.

The first part of the model is a system of exponential equations which are used for calculating the rate constants for each of the corresponding reactions according to Arrhenius law:

$$K_i = K_{0i} \cdot \frac{P_0^2}{T} \cdot \exp\left(\frac{-E_i}{RT}\right), i \in \{1, \dots, 172\}, \tag{1}$$

where K_i – reaction rate constant, s^{-1}; K_{0i} – pre-exponential coefficient, s^{-1}; P_0 – pressure, atm.; E_i – activation energy of reaction, J/mole; T – temperature, °K.

The second part consists of system of differential equations. They are meant to calculate concentrations changes of each component during the pyrolysis process along the tube which is expressed by residence time. Thus, the system is solved with the fourth-order Runge-Kutta method. That is:

$$A_{1,k} = \sum a_{k,j} \cdot K_j \cdot \prod C_i{}^{\beta_{i,j}}, \tag{2}$$

$$A_{2,k} = \sum a_{k,j} \cdot K_j \cdot \prod (C_i + \frac{h}{2} \cdot A_{1,k})^{\beta_{i,j}}, \tag{3}$$

$$A_{3,k} = \sum a_{k,j} \cdot K_j \cdot \prod (C_i + \frac{h}{2} \cdot A_{2,k})^{\beta_{i,j}}, , \tag{4}$$

$$A_{4,k} = \sum a_{k,j} \cdot K_j \cdot \prod (C_i + h \cdot A_{3,k})^{\beta_{i,j}}, , \tag{5}$$

where $A_{\{1..4\},k}$ – Runge-Kutta method summands for k-component; C_i – concentrations, mole/l; τ – residence time, s; $a_{k,j}$ – stochiometric coefficient of k-component in reaction j; $\beta_{i,j}$ – stochiometric coefficient of i-reagent in reaction j; h – residence time integration step, s.
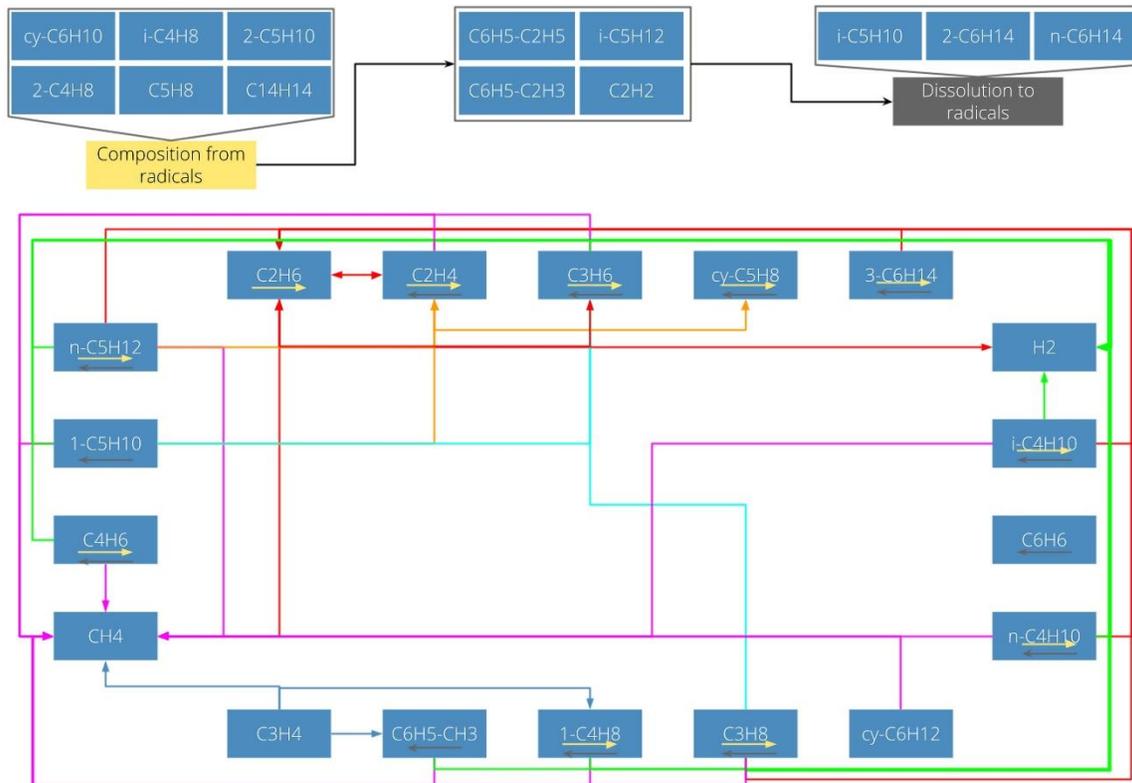

Figure 1. Pyrolysis reaction scheme

In the equation above it should be noted that if certain k-component is a reagent in reaction j, then its stoichiometric coefficient, α is negative (e.g. in reaction A + B = C coefficient of A is -1). And vice versa for component being the product of reaction.

Thus, changes in concentration after each small step is calculated as:

$$\frac{dC_k}{d\tau} = \frac{\sum A_{l,k}}{6}, \tag{6}$$

$$C_{k,\tau} = C_{k,\tau-h} + \frac{dC_k}{d\tau}, \tag{7}$$

While changes in coke concentration are calculated for each step as:

$$\frac{dC_{12}}{d\tau} = K_8 C_{12} - \exp(0.023 \cdot C_{12} - 1) \cdot G^{0.8} \cdot (D - 2 \cdot \delta)^{-1.8}, \tag{8}$$

where G – feed mass flow, kg/s; D – tube diameter, mm; δ – coke deposition thickness, mm.

Since the main goal of this research is to control furnace operating mode and optimize process taking into account changing composition of feed, the process is assumed to be isothermal in order to speed up the calculations.

According to operational manual of pyrolysis installation from one of oil refineries, the moment to stop the process in order to burn accumulated coke in tube is chosen according to pressure drop between two ends of furnace tube. Regeneration is performed when the drop

reaches certain value. Therefore, a function to calculate pressure loses along the tube was implemented:

$$\Delta P = \lambda \frac{L}{d_e} \cdot \frac{\omega^2 \rho}{2} ,$$ (9)

where ΔP – pressure drop, Pa; λ – coefficient of friction between hydrocarbons mixture and tube; L – tube length, m; d_e – effective diameter of tube, m; ω – flow speed, m/s; ρ - hydrocarbon mixture density, kg/m^3.

3. Experimental

Therefore, the model was tested with set of data presented in Table 1 which describes composition of the feed.

Table 1. Feedstock composition used to test the model

Component	Concentration, mol/L	Component	Concentration, mol/L
i-C_4H_{10}	0.04	1-C_6H_{12}	0.11
i-C_5H_{12}	1.0	cyclo-C_6H_{12}	1.13
n-C_6H_{14}	3.60	i-C_4H_8	0.20
CH_3-$CH(CH_3)$-C_3H_7	1.78	2-C_4H_8	0.20
C_2H_5-$CH(CH_3)$-C_2H_5	1.08	cyclo-C_5H_8	0.51
1-C_5H_{10}	0.16		

Since the main objective is to predict coke deposition growth and accumulation it may be reasonable to check the model`s adequacy by this parameter. As there is no specific number for coke deposit daily growth provided, it has been decided to calculate it via several different ways. The first one is estimation of pressure drop. It is said in plant schedule that coke must be burned in tube if pressure drop value reaches 0.265 MPa as coke deposition, i.e. it`s thickness, becomes big enough. Thus, the difference is caused by a pressure loss due to friction against the pipe wall and the coke layer and pressure drop of 0.265 MPa is simply the ΔP in the equation (9). According to the same schedule provided, the heat exchange area is 176 m^2. However, this is the total value for 4 parallel tubes, so with a tube inner diameter of 100 mm:

$$L = \frac{S_{HE}}{\pi d} = \frac{\left(\frac{176}{4}\right)}{\pi \cdot 0.1} = 140.13 \, m ,$$ (5)

Therefore, tube cross-section area is:

$$S_{cs} = \frac{\pi d^2}{4} = \frac{\pi \cdot 0.1^2}{4} = 0.00785 \, m^2 ,$$ (6)

Density was calculated using the Mendeleev-Clapeyron formula. It should be noted that a certain simplification was used: mean value of pressures at both ends of the tube was taken as the pressure value:

$$\rho = \frac{p \cdot M_{cp}}{RT} = \frac{0.36 \cdot 10^6 \cdot 64 \cdot 10^{-3}}{8.314 \cdot 1098} = 2.52 \, {kg}/{m^3} ,$$ (7)

Thus, the linear flow rate can be calculated:

$$\omega = \frac{G}{S_{cs} \cdot \rho \cdot 3600} = \frac{4730}{0.00785 \cdot 2.52 \cdot 3600} = 66.32 \, {m}/{s} ,$$ (8)

And respective effective diameter value would be:

$$d_e = \lambda \frac{L}{\Delta p} \cdot \frac{\omega^2 \rho}{2} = 0.03431 \cdot \frac{140.13}{0.27 \cdot 10^6} \cdot \frac{66.32^2 \cdot 2.52}{2} = 0.09983 \, м = 98.83 \, mm ,$$ (9)

Coke layer thickness, therefore:

$$\delta = \frac{(d - d_e)}{2} = \frac{(100 - 98.83)}{2} = 0.59 \, mm ,$$ (10)

Then the deposition rate during the inter-regeneration cycle will be:

$${\delta}/{t} = \frac{0.59}{48} = 0.012 \, {mm}/{day} .$$ (11)

Another way to check whether the model is adequate enough in terms of coke thickness is based on stoichiometry of coke burning. It was assumed that the main component of coke is coronene, thus the reaction looks like:

$C_{24}H_{12} + 27O_2 = 24CO_2 + 6H_2O$
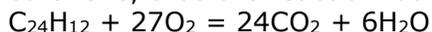
Process air is used for burning and it`s mass flow rate varies according to measuring elements logs as it is shown in Table 2.

Table 2. Various stages of burning durations and respective mass flow rates

Duration, h	Mass flow rate, kg/h	Duration, h	Mass flow rate, kg/h
9.25	50	0.875	315
0.5	100	5.75	100
0.25	150	5.25	315
0.25	200	3.625	90
0.25	250	Air intake, total, kg	3493.125

In utilized process air oxygen content is 2.5% wt. Thus, oxygen mass is:

$$m_{O_2} = \omega_{O_2} \cdot m_{air} = 0.025 \cdot 3494.125 = 87.33 \ kg \tag{12}$$

Which corresponds to:

$$v_{O_2} = \frac{m_{O_2}}{M_{O_2}} = \frac{87.33}{32} = 2.73 \ kmoles \tag{13}$$

Which means that 0.1 kmoles of coke was burned. Therefore, mass of burnt coke is:

$$m_{coke} = M_{coke} \cdot v_{coke} = 300 \cdot 0.1 = 30.32 \ kg \tag{14}$$

Coke density is 1493 kg/m^3, therefore deposit volume is:

$$V_{coke} = \frac{m_{coke}}{\rho_{coke}} = \frac{30.32}{1493} = 0.203 \ m^3. \tag{15}$$

According to engineering specification tube length is 140 meters with inner diameter of 100 mm. Thus, overall thickness in the end of inter-regeneration cycle is:

$$\delta = \frac{d - \sqrt{d^2 - \frac{4V_{coke}}{L \cdot \pi}}}{2} = \frac{0.1 - \sqrt{0.1^2 - \frac{4 \cdot 0.2}{\pi \cdot 140.13}}}{2} = 0.00046 \ \text{м} = 0.46 \ mm. \tag{16}$$

Daily thickness growth, therefore, is:

$$\delta/_t = \frac{0.46}{48} = 0.0097 \ mm/day. \tag{17}$$

Coke layer thickness growth calculated via pressure drop, burning stoichiometry and with the model is presented in Fig. 2. However, it is impossible to determine specific coke distribution along the tube with these two methods, thus the respective values are presented as straight lines on the graph.
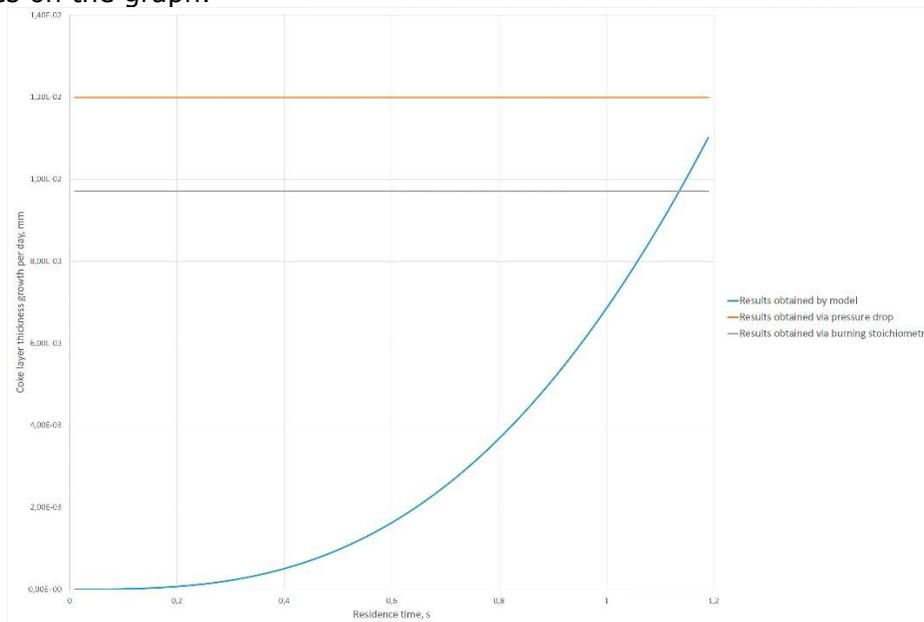

Figure 2. Coke layer thickness growth calculated via pressure drop, burning stoichiometry and with the model

Finally, it is possible to estimate mass of coke accumulated during inter-regeneration cycle and compare it with simulation results. According to equation (14), after 48 days there are 30.32 kg of coke in tube. Model-acquired coke thickness distribution may be described by the following polynomial function:

$$\delta(\tau) = 3 \cdot 10^{-9} \cdot \tau^3 + 2 \cdot 10^{-7} \cdot \tau^2 - 7 \cdot 10^{-6} \cdot \tau + 0.4516 \tag{19}$$

Thus, volume of virtual coke is:

$$
\begin{aligned}
V_{coke} &= \int_0^L \frac{\delta(l)}{1000} \cdot \pi \cdot D \, dl \\
&= \int_0^{140} \frac{(3 \cdot 10^{-9} l^3 + 2 \cdot 10^{-7} l^2 - 7 \cdot 10^{-6} l + 0.4516)}{1000} \cdot \pi \cdot 0.1 \, dl \\
&= \left(3 \cdot 10^{-9} \frac{140^4}{4} + 2 \cdot 10^{-7} \frac{140^3}{3} - 7 \cdot 10^{-6} \frac{140^2}{2} + 0.4516 l \right)/1000 \cdot \pi \cdot 0.1 \\
&= \frac{63.76}{1000} \cdot \pi \cdot 0.1 = 0.02002 \, m^3
\end{aligned}
\tag{20}
$$

Which corresponds to:

$$m_{coke} = \rho_{coke} \cdot V_{coke} = 1493 \cdot 0.02002 = 29.89 \, kg \tag{21}$$

Therefore, it may be assumed that the model is adequate enough since errors for three different ways of validation are 8.2, 13.5 and 1.4% respectively considering that reference values are not precise themselves.

With the feed composition given in the Table 1 and residence time of 1.2 s results shown on the Fig. 3, 4 were obtained. The respective graphs show dynamics of ethene and propene concentrations.
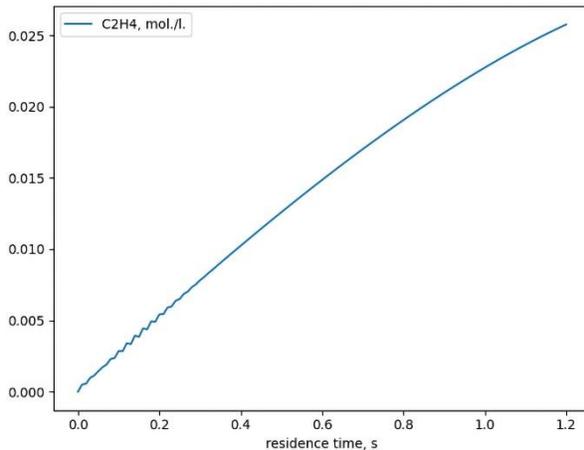

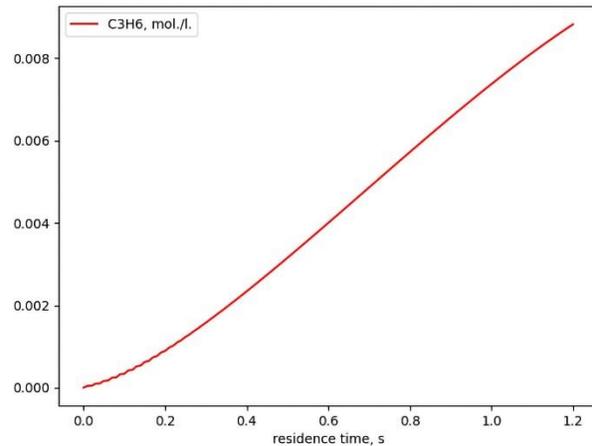Figure 3. Ethene concentration dynamics in pyrolysis process

Figure 4. Propene concentration dynamics in pyrolysis process

According to documentation yield of ethylene and propylene are 30 and 15% mass. respectively. Thus, their concentrations in product stream are:

$$C_{C2H4} = \frac{w_{C2H4} \cdot \rho}{M_{C2H4}} = \frac{0.3 \cdot 2.52}{28} = 0.027 \, mol./L \tag{22}$$

$$C_{C3H6} = \frac{w_{C3H6} \cdot \rho}{M_{C3H6}} = \frac{0.15 \cdot 2.52}{42} = 0.009 \, mol./L \tag{21}$$

The respective results obtained with the model are: 0.0258 mol/L for ethylene and 0.0088 mol/L for propylene. Therefore, errors are 4.4 and 2.2% respectively.

On a contrary, as it could be expected, concentrations of feed heavier hydrocarbons decrease towards the end which is shown on the Fig. 5, 6. In this case various hydrocarbons were sorted according to number of carbon atoms in their chain for purposes of distinctiveness.

Despite taking into account the course of astronomical time in simulation, the dynamics of hydrocarbons concentration does not change. This is due to the fact that the only component amount that changes is coke or, more specific, its layer thickness. From this point of view, at this stage of work it would be more correct to call the model as pseudo-stationary. Nevertheless, it is planned to create a mechanism for changing the concentrations of all components in real time, as well as to create functionality for predicting the state of the system based on the data accumulated during the operation of the installation.
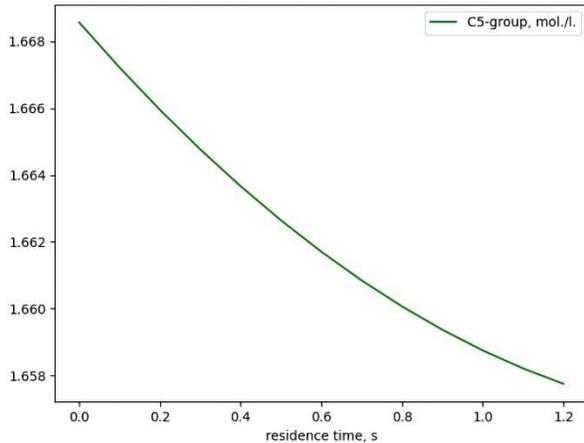

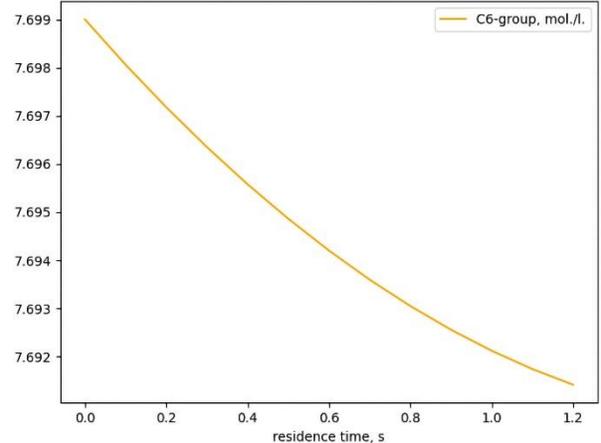Figure 5. C_5-like hydrocarbons concentration dynamics in pyrolysis process

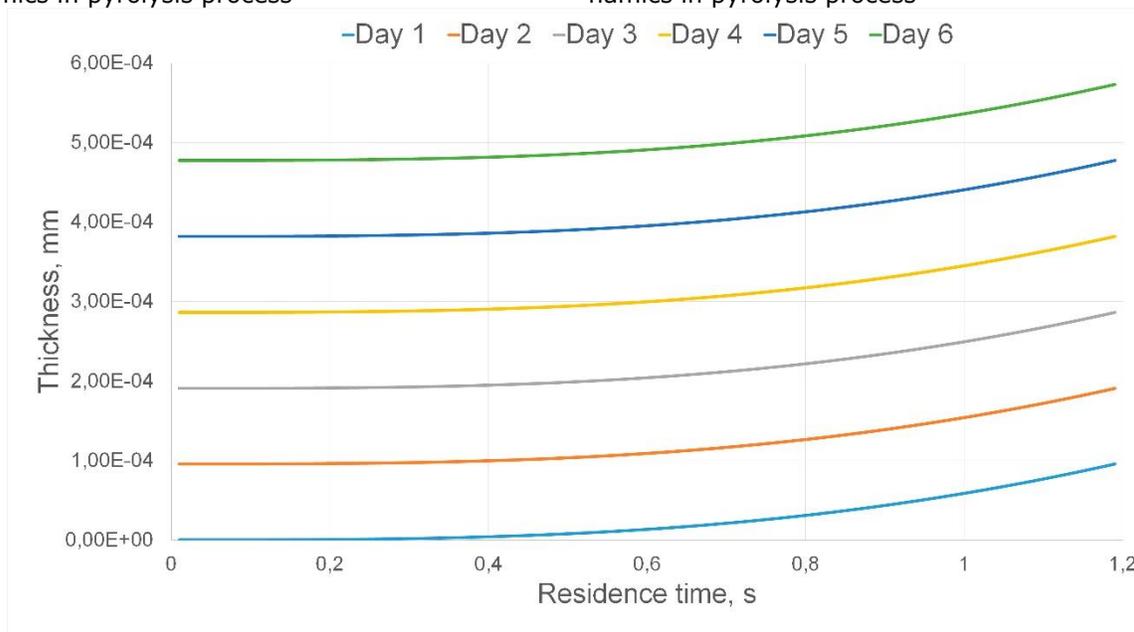Figure 6. C_6-like hydrocarbons concentration dynamics in pyrolysis process

Figure 7. Coke layer growth within a week

Fig. 7 shows the dynamics of the coke layer growth inside the tube of the furnace for a short period of time. However, the layer profile is the same every day, while in reality the distribution of coke is more random. Additionally, the model makes it possible to take into account the change in the composition of feed and operational conditions when calculating the rate of formation and deposition of coke.

4. Results and discussion

Thus, following results were yielded in course of the study above:

1) A non-stationary model of benzene fraction pyrolysis was developed. It became an instrument to study process of coke deposition along the pyrolysis tube. Thus, layer thickness increase towards the end of the tube was shown which proves uneven distribution. In its turn, it is consistent with theoretical concepts of deposition processes.

2) The rate of coke deposition along the tube was determined, taking into account the operational mode and composition of the supplied feed (the calculated value of the rate of coke deposition is 0.011 mm /day).

It is planned to develop mechanisms to simulate dynamics of components in real time. Thus, the model will be completely non-stationary. It is also planned to introduce the heat transfer equation into the general system of differential equations, taking into account the rate of heat transfers through the contaminated wall, thereby taking into account the uneven heating of the flow. It is planned to develop mechanisms for predicting the state of the system, which performs calculations based on data accumulated over the entire period of operation of the installation.

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