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MODELING OF DESTRUCTION PROCESSES DURING RECYCLING OF RUBBER-TECHNICAL WASTE USING THE TECHNOLOGY OF MULTI-CONTOUR CIRCULATION PYROLYSIS

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Сформована математична модель процесу термічної утилізації гумо-технічних відходів за технологією багатоконтурного циркуляційного піролізу, яка включає повний механізм деструкції та кінетику паралельно-послідовних реакцій піролізу. Запропонована модель дозволяє розрахувати концентрації отриманих продуктів деструкції, а відтак дає можливість наближено визначити склад цільових кінцевих продуктів. Застосування даної моделі необхідне при оптимізації температурних режимів устаткування

Ключові слова: термічна деструкція, утилізація гумо-технічних відходів, матеріальний баланс, концентрація парогазової суміші

Сформирована математическая модель процесса термической утилизации резино-технических отходов по технологии многоконтурного циркуляционного пиролиза, которая включает полный механизм деструкции и кинетику параллельно-последовательных реакций пиролиза. Предложенная модель позволяет рассчитать концентрации полученных продуктов деструкции, а затем дает возможность приближенно определить состав целевых конечных продуктов. Применение данной модели необходимо при оптимизации температурных режимов установки

Ключевые слова: термическая деструкция, утилизация резино-технических отходов, материальный баланс, концентрация парогазовой смеси

1. Introduction

In order to recycle rubber-technical wastes (RTW) using the technology of multi-contour circulation pyrolysis (MCP) [1], methods of mathematical modeling are employed. Development of mathematical systems is based on determining the values of main factors that affect the process of recycling of rubber-technical wastes.

Prediction of the output of products of pyrolysis by chemical and physico-chemical characteristics of raw materials is becoming increasingly important for selecting optimal parameters for the implementation of the process.

The study of the process of thermal recycling in line with the MCP technology is carried out to determine intensifying factors and, based on it, the improvement of technological processes and equipment is performed.

Results of the research come down to determining the quantities of products of the thermal decomposition of rubber waste, in particular, carbon residue, condensed and non-condensed volatile products (resins, pyrolytic gas) depending on temperature and duration of the process. Therefore, the optimization of conditions of the pyrolysis, creation of new technological solutions to this process is an extremely relevant task.

It is possible to solve this problem by describing the processes of thermal destruction by a mathematical model, which is defined by the depth of knowledge about the mechanism of thermal transformation of wastes, in particular conditions of thermodynamic equilibrium and quantitative kinetic regularities.

2. Literature review and problem statement

At present, the problem of recycling RTW in line with the pyrolysis technology is being explored by many scientists and inventors. The method of pyrolysis makes it possible not only to protect the environment from serious problems of waste accumulation, but also to receive valuable energy products.

Thus, paper [2] gives a broad overview of technologies of pyrolysis of worn tires as the methods for obtaining alternative fuel. Termogravimetric method was used to determine the optimum temperatures to conduct the process, along with it, kinetic parameters were defined. However, there is a need to study the impact of the process implementation on the output of major products during pyrolysis of natural rubber with worn tires, in particular the composition and amount of gas output, enhancing the possibility of obtaining

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more valuable chemical components from the liquid fraction, an analysis of the amount of sulfur content in the liquid fraction, research into the quality of semicoke compared with commercial soot.

Article [3] introduced a method for the production of pyrolysis oil from used automobile tires, based on the effect of microwave oven. The properties of the resulting alternative fuel, which is suitable for the diesel engine, were explored. Results of the study showed that heat-generating capacity of the resulting liquid fuel is 40.4 MJ/kg. The paper does not provide other characteristics compared to traditional diesel fuel, which does not allow us to talk about the high potential of fuel replacement.

In the study [4], a new approach to a heating system with the use of liquid products of pyrolysis of waste tires was presented. Fuel properties of pyrolysis liquids, such as density, viscosity, the content of carbon and hydrogen, are almost comparable with commercial automobile diesel fuels. The problem is the high sulfur content and the lower flash point.

Authors [5] considered pyrolysis of worn tires with an immobile layer in the reactor with vacuum and with the use of catalytic additives, such as Na_2CO_3, NaOH. As a result of the performed studies, they draw a conclusion on the feasibility of using NaOH as it is possible to achieve a decrease in the temperature of the process without changing the output of the liquid fraction (pyrolysis oil). The use of Na_2CO_3 did not essentially change the course of the reaction. It was proved that vacuum pyrolysis has advantages over atmospheric pyrolysis.

Scientists in paper [6] examined properties of the liquid fraction, obtained as a result of pyrolysis of worn tires, compared with diesel fuel. As a result, they made conclusions about the possibility of subsequent use of pyrolysis oil because its properties are similar to those of diesel fuel and are able to replace it in a small engine. Certain mixtures were taken for examination, and it was defined in conclusion that the mixture DTPO 25 demonstrated better results than DTPO 50 and DTRO 75.

Article [7] proposed a number of engineering solutions to intensify the process of pyrolysis of shredded tires by the technology EnresTec Inc. (Taiwan). A special feature of this method of recycling is the postcombustion of tailgas with vapor wastes. Paper [8] shows the heat and mass exchange balances and calculations for enhancing energy efficiency and economic component. Calculation-analytical substantiations are undoubtedly an important contribution into the study of thermal processes of recycling worn tires. However, the main results of these studies are determining the quantitative characteristics of finished products. The composition and quality of resulting products of the pyrolysis with the use of technical solutions, proposed by the authors, were not studied.

Scientists in [9] described kinetics and thermodynamics of reactions of pyrolysis of polyethylene terephthalate. Activation energy, pre-exponent, heat of reaction and the constant of rate of reactions were determined. For the pyrolysis, the authors propose using a bubbling reactor or a reactor circulating in a pseudo-liquefied layer as the most appropriate. The influence of the reactor type on the quality of the original products was not established since the examination of pilot reactors is still going on. Due to this fact, kinetic parameters of the process, which influence the rate of destruction and the output of pyrolytic products, will change, and this will require additional research.

A distinctive feature of the above paperss is discrepancies in the description of the total kinetics of the process of thermal decomposition. In the actual process of waste destruction, the number of reactions cannot be limited to a three-component calculation scheme. The accuracy of calculation can be enhanced through the use of a multi-component calculation scheme.

The performed overview of papers, related to the subject matter, revealed a great variety of technologies for recycling rubber-technical waste around the world. However, we failed to find studies on research into deep processes of destruction and thermal transformations in a pyrolysis reactor and technological equipment. Therefore, the optimization of conditions of pyrolysis for any technological solutions is possible through creation of a mathematical model for a complex process of thermal RTW recycling.

3. Research goal and objectives

The goal of present study is to develop a mathematical model of the process of thermal recycling of rubber-technical waste in line with the technology of multi-contour circulation pyrolysis. This will make it possible to solve the following tasks:

– to develop a scheme of destructive transformations of the original mass of waste, taking into account kinetics of the process of thermal decomposition of rubber and material flows of the formed phases in equipment;

– to compile a mathematical record of kinetic regularities and rate of destruction of rubber-technical waste depending on the concentration of original and resulting components;

– to calculate the concentrations of the main components of vapor and gas mixture during recycling of rubber-technical waste.

4. Materials and methods of examining a mathematical model of the process of thermal recycling of rubber-technical waste

Development of a mathematical model of the process of thermal recycling of RTW by the MCP technology implies construction of the system of equations that are expressed by the laws of conservation of mass and energy. The model includes material balances on separate chemical substances, heat balances and kinetic equations of rates of reactions.

MCP reactor is an idealized model of continuously operating displacement machines, in which a continuously released vapor and gas mixture enters a multi-contour circulation system (MCS) during thermal destruction in the reactor.

We developed a general principal scheme of the process of thermal recycling of wastes (Fig. 1), which demonstrates material flows of the process and output of end products.

Original data for the calculation are the chemical composition of original raw materials of rubber waste $C_{440,4}H_{634,9}O_{58,1}N_{57,2}S$ given in [10]. Index i designates a separate component in the initial composition of waste.

Functioning of MCP lies in achieving full conversion of the original mixture of waste C_i, M_i due to thermal destruction and recirculation of primary vapor and gas mixtures (VGM) C_{VGMi}, m_{VGMi} in MCP. As a result of recycling, we obtain the final components with a specified degree of purity, in particular high-powered pyrolytic gas C_{PGi}, m_{PGi} and low-molecular liquid fuel C_{LFi}, m_{LFi}.

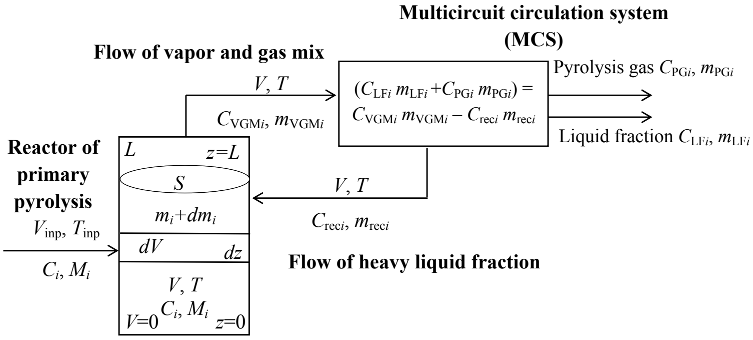

Fig. 1. Principal scheme of material flows of the process of multi-contour circulation: C_i is the molar concentration of the original composition of the mixture of waste; M_i is the molar flow of the amount of original composition of the mixture of waste; m_i+dm_i is the increase in the flow of formation and accumulation of the products of reaction over time; C_{VGMi}, m_{VGMi} is the molar concentration and molar flow of vapor and gas mixture (VGM); C_{reci}, m_{reci} is the molar concentration and molar flow of heavy liquid fraction (HLF); C_{LFi}, m_{LFi} is the molar concentration and molar flow of liquid fraction; C_{PGi}, m_{PGi} is the molar concentration and molar flow of pyrolysis gas; T_{inp}, °C is the temperature of conduction of the process (input); V_{inp} is the volume of the system (input); z, L, S are the parameters of the reactor

It is possible to make MCP technology environmentally friendly due to the presence of MCS. Because, as a result of forced condensation and recirculation, condensed high-molecular products of primary pyrolysis C_{reci}, m_{reci} return to the reactor, providing secondary deep thermal decomposition.

Obtaining of the target products is carried out due to the mass and energy exchange between the flows of primary VGM and recirculation flow of heavy liquid fraction, circulating in MCP. This is achieved under condition of setting the equilibrium state of circulating flows, resulting in reduced molecular weight of the final product and achievement of environmental safety of substances.

A full mathematical description of the process is represented by the componentwise material balance of elementary cell with volume dV for a small period of time dt since parameters of the flow change by height of MCP equipment and over time.

When modeling, we accept the following assumptions: each element of the flow in a certain cross section of the apparatus moves along the axis at the same linear velocity. Given this, we assume the lack of losses of pressure on the friction of flow against the walls of reactor, as well as the lack of diffusion phenomena of longitudinal, reverse agitation.

Thermal recycling of vulcanized rubber is characterized by depolymerization reactions as a result of the rupture of transverse bonds and main chains of rubber grid, with the formation of destruction products, the ratio between which depends on the conditions of the process. Thus, products of destruction, obtained in the process of pyrolysis, are divided into phases: gas phase, condensed liquid phase (formed as a result of condensation reactions of substances), and single-component phases, in the condensed solid state.

Representation of thermodynamic MCP system [11] in the form of totality of the phases does not impose restrictions on the distribution of mass of chemical elements, both between individual subsystems and between their components. The exact determining of parameters of the flows of phases inside the plant is a necessary condition for the analysis and optimization of process efficiency.

Fig. 2 shows the scheme of destructive transformations of the initial mass of waste by the MCP technology.

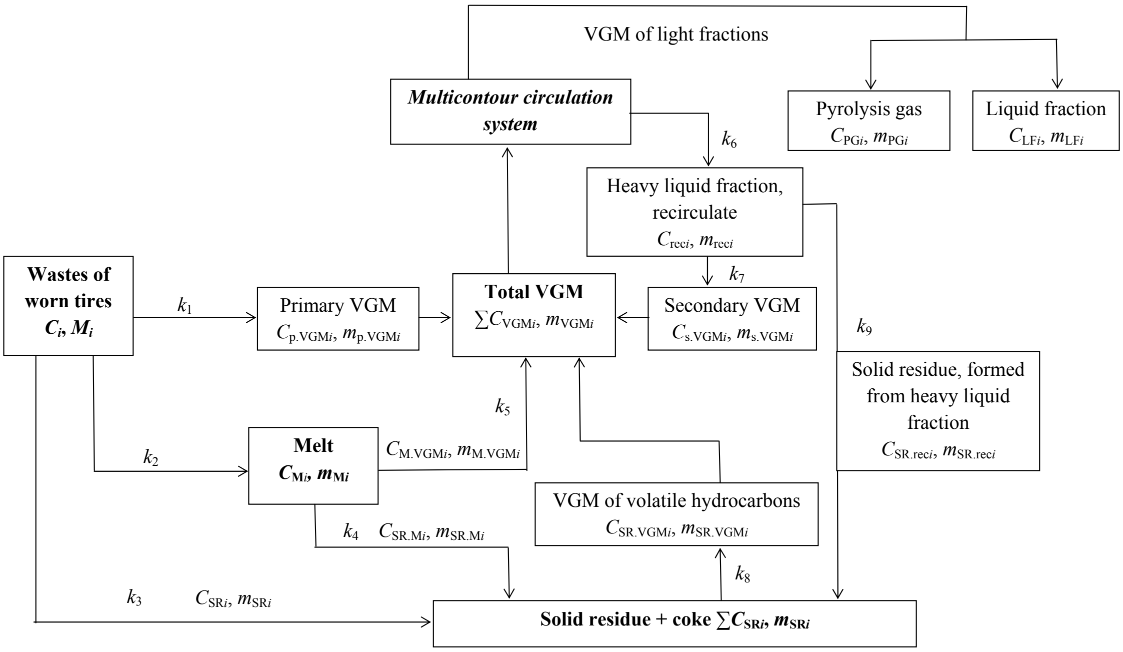

Fig. 2. Kinetic scheme of thermal transformation of rubber waste in line with the technology of multi-contour circulation pyrolysis

Schematic in Fig. 2 considers causal-logical connections of kinetics of the process of rubber and material flows of phases, formed during thermal decomposition, in perticular: $C_{p.VGMi}$, $m_{p.\,VGMi}$ are the molar concentration and molar flow of primary vapor and gas mixture; C_{Pi}, m_{Pi} are the molar concentration and molar flow of waste melt; C_{SRi}, m_{SRi} are the molar concentration and molar flow of solid residue, formed from original composition of waste; $C_{SR.Mi}$, $m_{SR.Mi}$ are the molar concentration and molar flow of solid residue, formed of waste melt; $C_{M.VGMi}$, $m_{M.VGMi}$ are the molar concentration and molar flow of primary vapor and gas mixture, formed from waste melt; ΣC_{VGMi}, m_{VGMi} are the molar concentration and molar flow of total vapor and gas mixture; $C_{s.VGMi}$, $m_{s.VGMi}$ are the molar concentration and molar flow of secondary vapor and gas mixture, formed as a result of destruction of heavy liquid fraction; $C_{SR.reci}$, $m_{SR.reci}$ are the molar concentration and molar flow of solid residue, formed from heavy liquid fraction; ΣC_{SRi}, m_{SRi} are the molar concentration and molar flow of total amount of solid residue, accumulated in the reactor; $C_{SR.VGMi}$, $m_{SR.VGMi}$ are the molar concentration and molar flow of vapor and gas mixture of volatile hydrocarbons, released as a result of destruction of solid residue; $k_{1\text{-}9}$ is the constant of rate of correspondent reactions.

Description of the mechanism of thermal transformations defines the main stable phases [12], as well as the intermediate and end products of the process of recycling as a whole. Kinetic schematic (Fig. 2) is the basis for modeling the kinetic regularities and for determining the rate of destruction of rubber-technical waste in line with the MCP technology.

Mathematical record of the kinetic model is represented by a system of equations (1). The model correlates the rate of decomposition of primary components of rubber waste and the rate of transformation of intermediate destruction products depending on concentration and kinetic parameters of destruction.

$$\begin{cases} r_1 = \dfrac{dC_{p.VGM_i}(t)}{dt} = -k_1C_i, \\ r_2 = \dfrac{dC_{M_i}(t)}{dt} = -k_2C_i, \\ r_3 = \dfrac{dC_{SR_i}(t)}{dt} = -k_3C_i, \\ r_4 = \dfrac{dC_{SR.M_i}(t)}{dt} = -k_4C_{M_i}, \\ r_5 = \dfrac{dC_{M.VGM_i}(t)}{dt} = -k_5C_{M_i}, \\ r_6 = \dfrac{dC_{rec_i}(t)}{dt} = -k_6C_{\Sigma VGM_i}, \\ r_7 = \dfrac{dC_{s.VGM_i}(t)}{dt} = -k_7C_{rec_i}, \\ r_8 = \dfrac{dC_{SR.VGM_i}(t)}{dt} = -k_8C_{\Sigma SR_i}, \\ r_9 = \dfrac{dC_{SR.rec_i}(t)}{dt} = -k_9C_{rec_i}, \end{cases} \tag{1}$$

where r is the rate of progress of destruction reactions; $k_{1\text{-}9}$ is the rate constant of of corresponding reactions:

1 – formation of primary vapor and gas mixture;

2 – formation of waste melt;

3 – formation of solid residue from the original component of waste;

4 – formation of solid residue from waste melt;

5 – formation of primary vapor and gas mixture from waste melt;

6 – formation of recirculate;

7 – formation of secondary vapor and gas mixture from heavy liquid fraction;

8 – formation of vapor and gas mixture of volatile hydrocarbons from solid residue;

9 – formation of solid residue of heavy liquid fraction.

To calculate the rate of each intermediate reaction of destruction, it is necessary to know the values of kinetic and activation parameters [13]. Constants of rates of reactions were determined based on a thermogravimetric analysis. Theoretical calculations were proved by experimental research when measuring a decrease in the mass of waste over time [14]. The value of activation energy was accepted according to data of experimental research into thermal destruction of rubber [11].

In accordance with the kinetic diagram (Fig. 2), destruction is characterized by the progress of reactions in four directions. A system of differential equations (2) represents the rates of thermal transfromation of rubber waste, as a result of which the main products (phases) are formed in the reactor.

$$\begin{cases} R = r_1 + r_2 + r_3 = -(k_1 + k_2 + k_3)C_i, \\ R_{\Sigma M_i} = r_2 - (r_4 + r_5) = -\left(k_2C_i - (k_4 + k_5)C_{M_i}\right), \\ R_{\Sigma VGM_i} = r_1 + r_5 + r_7 + r_8 = -\left(k_1C_i + k_5C_{M_i} + k_7C_{rec_i} + k_8C_{\Sigma SR_i}\right), \\ R_{\Sigma SR_i} = r_3 + r_4 + r_9 - r_8 = -\left(k_3C_i + k_4C_{M_i} + k_9C_{rec_i} - k_8C_{\Sigma SR_i}\right), \\ R_{rec_i} = r_6 - (r_7 + r_9) = -\left(k_6C_{\Sigma VGM_i} - (k_7 + k_9)C_{rec_i}\right). \end{cases} \tag{2}$$

System of equations (2) describes a change in the rate of destruction of each phase:

R is the rate of primary reaction of destruction of original composition of waste;

$R_{\Sigma P}$ is the general rate of accumulation of melt of organic mass of rubber waste;

$R_{\Sigma VGM}$ is the total rate of formation of vapor and gas mixture;

$R_{\Sigma SR}$ is the rate of accumulation of solid carbon residue;

$R_{\Sigma rec}$ is the rate of formation of condensed fraction, recirculate.

Given the material flows of main products and the rates of their formation, we constructed a full mathematical model of rubber waste destruction in line with the MCP technology. It is based on the componentwise material balances for each phase by general equation:

$$\frac{1}{t}\cdot\left(C_{inp} - C_i\right) + R_{\Sigma_i} = 0,$$

$$\begin{cases} \dfrac{dC_{M_i}(t)}{dt} = \dfrac{1}{t}\cdot\left(C_i - C_{M_i}\right) + R_{\Sigma M_i}, \\ \dfrac{dC_{VGM_i}(t)}{dt} = \dfrac{1}{t}\cdot\left(C_i - C_{VGM_i}\right) + R_{\Sigma VGM_i}, \\ \dfrac{dC_{SR_i}(t)}{dt} = \dfrac{1}{t}\cdot\left(C_i - C_{SR_i}\right) + R_{\Sigma SR_i}, \\ \dfrac{dC_{rec_i}(t)}{dt} = \dfrac{1}{t}\cdot\left(C_{VGM_i} - C_{rec_i}\right) + R_{rec_i}. \end{cases} \tag{3}$$

Solution to system (3) is the system of equations (4) that expresses concentrations of the components of the reaction mixture at the outlet of the reactor:

$$\begin{cases} C_{M_i} = \dfrac{C_i + R_{\Sigma M_i} \cdot C_i \cdot t}{1+\left(R_{\Sigma M_i} - \left(R_{\Sigma VGM_i} + R_{\Sigma SR_i}\right)\right)\cdot t}, \\ C_{VGM_i} = C_{M_i} + R_{\Sigma VGM_i} \cdot C_i \cdot t, \\ C_{SR_i} = C_{M_i} + R_{\Sigma SR_i} \cdot C_i \cdot t, \\ C_{rec_i} = C_{VGM_i} - R_{rec_i} \cdot C_{VGM_i} \cdot t, \\ k_j = k_j^0 \cdot e^{\frac{E_i}{RT}}, j = 1,2,3..., \\ t = \dfrac{Vr}{V}. \end{cases} \tag{4}$$

For quantitative measurement of components, that is, determining the values of molar shares of products and flows, we compiled componentwise material balances for an elementary cell of the reactor (Fig. 3). For this purpose, we use the calculated values of concentration and of the rate of reactions as a result of thermal transformation.

Record of material balance in mathematical form:

1. Arrival of a substance with flow m_i dt:

$$m_i \cdot dt = V_{inp} \cdot C_i \cdot dt = u \cdot S \cdot C_i \cdot dt.$$

2. Consumption of a substance with the flow (m_i+dm_i) dt:

$$\left(m_i + dm_i\right)\cdot dt = \left(V_{inp} \cdot C_i \cdot d\left(V_{inp} \cdot C_i\right)\right)\cdot dt.$$

3. Change of a substance in chemical reaction $dV \cdot r_i \cdot dt$.

4. Accumulation of a substance dM_i:

$$dM_i = dC_i \cdot dV,$$

$$m_i \cdot dm - \left(m_i + dm_i\right)\cdot dt + dV \cdot r_i \cdot dt = dC_i \cdot dV,$$

where r_i is the rate of change in the concentration of substance i as a result of chemical transformation, mol/($m^3 \cdot s$).

5. Mole flow of substance i:

$$m_i = V_{inp} \cdot C_i = u \cdot S \cdot C_i, \ \text{mol/s}.$$

6. Linear velocity of flow u, m/s.

When all the members of the equation are divided by (dV·dt), the final form of the equation of the componentwise material balance of the reactor of ideal displacement for substance i in dimensionality mol/($m^3 \cdot s$) takes the form:

$$\frac{dC_i}{dt} = \frac{dm_i}{dV} + r_i. \tag{5}$$

According to the scheme of flows, the total material balance of reaction mixture M_i, mol in the reactor is determined from equation of the componentwise material balance:

$$\frac{dM_i}{dt} = M_i - m_{p.VGM_i} + m_{rec_i} - m_{s.VGM_i} - m_{SR_i}.$$

Material balance of the vapor and gas phase at the outlet of the reactor, that is, the total VGM (primary VGM, secondary VGM of heavy liquid fraction and VGM of volatile products of solid residue) takes the form:

$$\frac{dM_{VGM_i}C_{VGM_i}}{dt} = R_{\Sigma VGM_i} + m_{p.VGM_i}C_{p.VGM_i} + \\ + m_{M.VGM_i}C_{M.VGM_i} + m_{s.VGM_i}C_{s.VGM_i} + m_{SR.VGM_i}C_{SR.VGM_i}.$$

Material balance of the liquid phase, that is, the formation of melt of reaction mass of waste in MCP, in accordance with the scheme of flows, will be written as:

$$\frac{dM_{M_i}C_{M_i}}{dt} = R_{\Sigma M_i} + m_{rec_i}C_{rec_i}.$$

Material balance of the formation of solid residue during destruction of the original mass of waste:

$$\frac{dM_{SR_i}C_{SR_i}}{dt} = R_{\Sigma SR_i} + m_{SR_i}C_{SR_i} + m_{SR.M_i}C_{SR.M_i} + m_{SR.rec_i}C_{SR.rec_i}.$$

A general form of material balance by all the phases, formed in the reactor during thermal recycling of organic wastes in line with the MCP technology, is represented by system of equations (6).

$$\begin{cases} \dfrac{dM_i}{dt} = M_i - m_{p.VGM_i} + m_{rec_i} - m_{s.VGM_i} - m_{SR_i}, \\ \dfrac{dM_{VGM_i}C_{VGM_i}}{dt} = R_{\Sigma VGM_i} + m_{p.VGM_i}C_{p.VGM_i} + \\ + m_{M.VGM_i}C_{M.VGM_i} + m_{s.VGM_i}C_{s.VGM_i} + m_{SR.VGM_i}C_{SR.VGM_i}, \\ \dfrac{dM_{M_i}C_{M_i}}{dt} = R_{\Sigma M_i} + m_{rec_i}C_{rec_i}, \\ \dfrac{dM_{SR_i}C_{SR_i}}{dt} = R_{\Sigma SR_i} + m_{SR_i}C_{SR_i} + \\ + m_{SR.M_i}C_{SR.M_i} + m_{SR.rec_i}C_{SR.rec_i}. \end{cases} \tag{6}$$

In MCP reactor, vapor and gas mixture and melt of organic wastes are in equillibrium; however, they have different composition. For any component, the relationship between its content in the vapor and gas phase C_{VGMi} and the composition in melt C_{Pi} is expressed by a simplified relation, based on the Raoult law:

$$PC_i = C_{P_i} f_i(T),$$

where PC_i is the partial pressure of the i-th component in the vapor and gas phase; function $f_i(T)$ expresses relationship between pressure and temperature of boiling of pure i-th component; P is the total pressure in the system.

[Rate of accumulation of the reaction mixture]=[content of substances in the original mass of waste (M)]–
–[output of the primary vapor and gas mixture ($m_{p.VGM}$)]+[return of recirculation flow of reverse heavy liquid fractions (m_{rec})]–
–[formation of secondary VGM of light fractions during deep destruction of reverse heavy liquid fractions ($m_{s.VGM}$)]–
–[solid residue formed during deep destruction of reverse heavy liquid fractions (m_{SR})].

$$\left\{\begin{matrix}\text{Accumulation of substance}\\ \text{in volume dV}\end{matrix}\right\}=\left\{\begin{matrix}\text{Arrival of substance i}\\ \text{in elementary cell}\end{matrix}\right\}-\left\{\begin{matrix}\text{Consumption of substance i}\\ \text{in elementary cell}\end{matrix}\right\}+\left\{\begin{matrix}\text{Change in the amount}\\ \text{of substance i in reaction}\end{matrix}\right\},\ \text{mol}$$

Fig. 3. Material balance of an elementary cell of the reactor of multi-contour circulation pyrolysis

Thus, the composition of vapor and gas phase (in mole fractions) $\sum C_{VGMi}$ follows from the equations of equilibrium vapor-fluid for each component (Fig. 4).

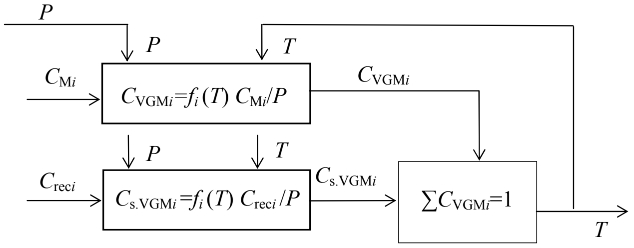

Fig. 4. Use of equations of vapor and gas equilibrium for finding the composition of vapor and gas mixture in the reactor of multi-contour circulation pyrolysis

Thus, given the fact that the mixture is multi-component, the combined scheme of vapor-liquid equilibrium allows us to determine the composition of the primary VGM, arriving to MCS. The VGM composition ($\sum C_{VGM}$) is introduced into equations that model material flows in MCS.

Multi-contour circulation system is considered based on the equation of equilibrium $\sum C_{VGM}=1$, which determines the fraction of vapor of heavy condensed hydrocarbons, in particular:

$$\sum C_{VGM_i}=1\rightarrow m_{rec_i}.$$

From equations (6), describing material flows in MCS, we shall receive the composition of heavy liquid fraction (C_{rec}), the composition of total vapor and gas mixture (C_{VGM}), as well as the amount of VGM (m_{VGM}) and the amount of HLF (m_{rec}).

Incorporation of above mentioned equations in a mathematical model, taking into account causal relations in the process of construction of models of each transformation stage, is given in Fig. 5.

The scheme in Fig. 5 incorporates equation of kinetic model, equation of material balance, as well as equations of vapor-and-liquid equilibrium that is established in MCP reactor between VGM and the melt for any component.

5. Results of research, obtained when modeling destructive transformations of rubber waste

As a result of theoretical calculations, we obtained the concentrations of gaseous and condensed substances – products of thermal decomposition of the original mass of waste, formed at a certain temperature (as it increases). The dynamics of the main VGM constituents depending on temperature was explored by components (Table 1).

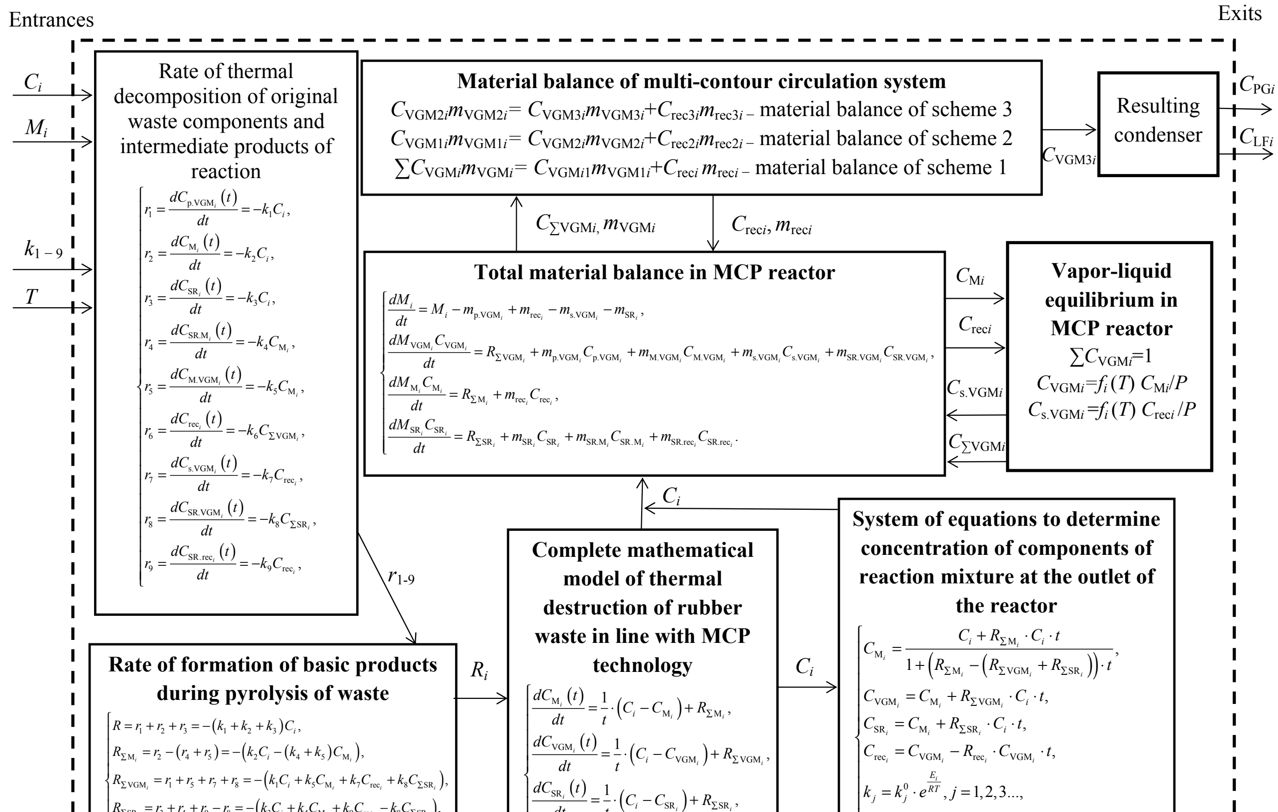

Fig. 5. Combined scheme of mathematical model of material balance in the reactor of multi-contour circulation pyrolysis

Table 1

Concentrations of main components of vapor and gas mixture during recycling rubber-technical waste in line with the technology of multi-contour circulation pyrolysis

	Components of vapor and gas mixture										
T, ºC	CO	H_2	CH_4	CO_2	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}	N_2	H_2S	C
450	0.11792	0.9366	13.778	0.64081	13.208 E(-5)	6.7198E(-09)	4.41530000 E(-13)	2.07410 E(-17)	3.9317	0.13758	41.14
470	0.18205	11.148	12.964	0.68616	13.484 E(-5)	7.1469E(-09)	4.86360000 E(-13)	2.32100 E(-17)	3.9317	0.13755	41.844
490	0.27508	13.097	12.082	0.73178	13.469 E(-5)	7.3643E(-09)	5.14230000 E(-13)	2.57920 E(-17)	3.9318	0.13752	42.588
510	0.40692	15.19	11.146	0.7757	13.161 E(-5)	7.3521E(-09)	5.21940000 E(-13)	2.66710 E(-17)	3.9319	0.13748	43.348
530	0.58921	17.394	10.175	0.81501	12.582 E(-5)	7.1142E(-09)	5.08890000 E(-13)	2.62550 E(-17)	3.93321	0.13743	44.098
550	0.83449	19.671	9.1897	0.84574	11.773 E(-5)	6.6783E(-09)	4.77240000 E(-13)	2.46440 E(-17)	3.93324	0.13738	44.807
560	0.98456	20.825	8.699	0.85644	11.299 E(-5)	6.3997E(-09)	4.55700000 E(-13)	2.34700 E(-17)	3.9325	0.13734	45.136
570	1.1547	21.98	8.2134	0.86317	10.791 E(-5)	6.0897E(-09)	4.31250000 E(-13)	2.21080 E(-17)	3.9326	0.13731	45.445
580	1.3458	23.132	7.7353	0.86634	10.255 E(-5)	5.7555E(-09)	4.04590000 E(-13)	2.06070 E(-17)	3.9328	0.13727	45.573
600	1.7929	25.407	6.8119	0.8538	9.1351 E(-5)	5.0436E(-09)	3.47540000 E(-13)	1.73810 E(-17)	3.9331	0.1372	46.218

We determined the concentration of the main components of pyrogas and of the condensed fraction of products of the process and their dependence on temperature in the range of 450–600 °C. It was found that with an increase in temperature the concentration of the output of main heat-generating components of pyrogas decreases, to large extent on the concentration of methane and ethane, and to a lesser extent to the concentration of propane. The output of components depends on the type of waste. The largest output of heat-generating components makes up:

– output of methane (CH_4) is within the range of 1.2–13.778 mol/kg,

– output of ethane (C_2H_6) is in the range of $1.8–13.8\times\times10^5$ mol/kg,

– output of propane (C_3H_8) is within $1–6.8\times10^{-9}$ mol/kg.

With an increase in temperature, the mass concentration of hydrogen (H_2) also increases – 0.9366––25.407 mol/kg, and so does that of sulphur oxide (SO) – 0.11792–1.7929 mol/kg, but the output of hydrogen sulfide (H_2S) decreases – 0.13758–0.1372 mol/kg.

For each substance, there is an optimal time, at which its output reaches the maximum, and with an increase in temperature this optimal value of time decreases.

Thus, an increase in the temperature of pyrolysis with a correspondent simultaneous decrease in time contributes to achieving larger output of the target products, first of all, ethylene. Given this, the industrial process of pyrolysis develops in the direction of an increase in temperature and a decrease in time.

6. Discussion of results of modeling the processes of thermal recycling of rubber-technical waste in line with the technology of multi-contour circulation pyrolysis

Advantages of the present research include a possibility to improve the understanding of physical and chemical essence of the thermal recycling of waste. The developed model makes it possible to determine chemical composition of the target products, which is the aim of the implementation of the process of waste recycling in line with the MCP technology. Application of the apparatus of mathematical modeling, when the composition of the original mass of hydrocarbon waste is known, makes it possible to approximately determine the possible yields of end products of the process of recycling.

The benefits also include the possibility to control MCS performance in order to achieve the assigned quality of end products under actual conditions. It is possible to achieve the aim by means of constant monitoring of the concentration of VGM that arrives to MCS contours.

The disadvantages of present research are the lack of calculated values of mole shares of products and flows since the article reports the procedure for calculation of quantitative measurement of components, which is the basis for compiling a material balance. Therefore, the next step in research might be to set the goal to calculate quantitative characteristics of phase flows inside the plant and to calculate material balance in MCP equipment.

The relevance of present study is beyond any doubt since the use of the developed model is the basis for the subsequent synthesis of automated control systems. Thus, the application of the model of destruction processes is a necessary aspect when implementing the technology on industrial scale.

The present study is a continuation of previous research [11, 12, 14] into destructive processes of thermal recycling of organic wastes in line with the MCP technology. In subsequent studies, it is planned to use the obtained data to model the process of repeated condensation and recirculation of heavy fractions in MCS. Investigation of dependence of temperature parameters of conducting the process in each MCS contour on the quality of end products will be carried out as well.

7. Conclusions

1. We developed a kinetic scheme of thermal decomposition of rubber waste in line with the technology of multi-contour circulation pyrolysis, which makes it possible to comprehend the mechanism of waste transformation in technological equipment. The process of recycling is schematically presented in the form of sequentially-parallel reactions of decomposition of reaction mass of waste, taking into account kinetics of the process and material flows of the formed phases and products.

2. A mathematical model of kinetic regularities and of the rate of destruction of rubber-technical wastes was constructed. Kinetic parameters and the rate of reaction are used for subsequent modeling of the recycling process and for determining the end products of waste decomposition. By using the mathematical model, we obtained the composition of primary VGM (C_{VGMi}). The basic compositional components were defined: CO, H_2, CO_2, C_2H_6, C_3H_8, C_4H_{10}, C_5H_{12}, N_2, CH_4, H_2S, C.

3. As a result of research and theoretical modeling, we performed calculations of the concentration of gaseous and condensed substances, formed in the range of 450–600 °C. It was found that as temperature increases, the concentration of the output of main heat-generating components of pyrogas decreases, in particular: methane (CH_4) – 1.2–13.778 mol/kg; ethane (C_2H_6) – 1.8–13.8×10^{-5} mol/kg; propane (C_3H_8) – 1–6.8×10^{-9} mol/kg.

The method for solving the system of differential equations that describes a change in the concentration of each component allows us to calculate parameters by the model and to compare them with experimental data. Maximum divergence from the precise solution does not exceed 7 % at the step of integrating 0002 and resulting time 1 s.

The use of methods of mathematical modeling at preparatory stages makes it possible to reduce material and technological cost due to a minimal use of energy resources for the optimization of the volume of liquid fraction as a target product.

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