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DEVELOPMENT OF THE UNIFIED MODEL FOR IDENTIFICATION OF COMPOSITION OF PRODUCTS FROM INCINERATION, GASIFICATION, AND SLOW PYROLYSIS

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Розглянуто процеси спалювання, газифікації та повільного піролізу. Загальноприйнятий підхід передбачає використання індивідуальних моделей для опису окремих процесів. При набутті параметрами значень близьких до межевих процесів точність опису розглянутих явищ знижується. Зазначені процеси не мають між собою різких меж і можуть плавно переходити з одного в інший при зміні зовнішніх впливів. При схожості фізико-хімічних процесів, склад продуктів реакцій, які визначаються на межах з використанням суміжних моделей, різняться. У найбільш загальному вигляді завдання, пов'язані зі спалюванням, газифікацією і повільним пиролизом, вирішуються на основі єдиної моделі. Рішення ускладнюється можливістю непередбачуваної зміни складу вихідних речовин. Крім того, вони можуть знаходиться в різних фазових станах: газоподібному, рідкому, твердому.

За основу єдиної моделі прийнята розроблена раніше система рівнянь, що описує процес спалювання органічного палива невідомого складу. Параметрами моделі, які визначаються, є парціальні тиски продуктів реакції. При такому підході їхній стан вважається газоподібним. Особливістю єдиної моделі, яка пропонується, є можливість урахування в продуктах реакції конденсованої фази (вуглистого залишку), характерного для повільного піролізу.

Для єдиної моделі, яка описує процеси спалювання, газифікації та піролізу, процеси розрахунків мають відмінності. При дослідженні процесів спалювання та газифікації визначається температура продуктів реакції спираючись на рівність їх ентальпії та ентальпії вихідних речовин. При дослідженні процесу піролізу температура реакції і, відповідно, її продуктів задається. Знайдений склад продуктів і задана температура дозволяють розрахувати їх ентальпію. По різниці між знайденою ентальпією і ентальпією вихідних речовин може бути розраховано необхідну кількість енергії у формі тепла для забезпечення реакції піролізу.

Для підтвердження адекватності моделі проведено розрахунки випадків спалювання і газифікації газоподібних (метан), рідких (етиловий спирт) і твердих (деревина сосни) речовин. Для деревини сосни виконаний розрахунок повільного піролізу. Збіг результатів з наявними в літературі даними довів допустимі для інженерних розрахунків відносні похибки.

На основі спільного використання моделі і розробленого раніше способу визначення складу суміші газів в процесі її спалювання запропонований метод ідентифікації в режимі реального часу складу вуглеводневих сполук горючих речовин в різних агрегатних станах

Ключові слова: вуглеводнева сировина, спалювання, газифікація, піроліз, єдина модель, ідентифікація складу продуктів

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1. Introduction

A wide range of problems associated with the conversion of raw materials into products are solved based on thermo-chemical transformations. The processes of utilization of organic waste are based on such transformations. The possibility of organization of optimal control and prediction of the results of technological processes is ensured by using adequate mathematical models. At present, there are four directions of thermo-chemical transformations: incineration, gasification, pyrolysis, and thermal modification. Pyrolysis, in turn, is divided into slow and fast. As a rule, independent research is conducted and different mathematical models are used for each direction. In many cases, this approach is due to objective reasons. However, there are situations where a series of the above processes can be realized using one or the same type of equipment. For example, the gasification process should be considered as an incineration process with a deep lack of oxidant (air). At the same time, like during incineration, a definite, albeit significantly smaller, amount of energy in the form of heat is released. As a rule, enough energy is released to maintain the gasification process. At a further decrease in the amount of oxidant, the process turns into slow pyrolysis. Its implementation requires external energy supply (at least at the initial stage). However, pyrolysis in terms of chemistry is similar both to gasification and to incineration. Moreover, pyrolytic processes are their initial stage. Thus, the development and use of a unified model to describe a group of processes (incineration, gasification, and slow pyrolysis) is sound and relevant.

2. Literature review and problem statement

Historically, the study of issues related to research into combustion, gasification, and pyrolysis, began at different times and was carried out by different groups of researchers. In each case, various substances were used as source substances and various aims were set. Thus, during incineration, one looks for opportunity to maximize heat release by excluding insufficient burning or excess air. In contrast, during gasification, the aim is to decrease energy loss by reaction with simultaneous obtaining a mix of combustible gases with a maximum calorific value. In the process of pyrolysis, as opposed to the previous two cases, energy supply in the form of heat is required. Coaly residue, condensed and non-condensed gases act as products of the process. The search in each area is carried out based on different approaches and models. From these positions, the last review [1] displays the contribution of the leading group of European and American researchers within different specified areas. But in this paper, such an approach contradicts to the unified classification of the processes and source substances in their studies as "thermo-chemical treatment of biomass".

The combustion process is traditionally considered to be simple to research and control in the list of thermochemical transformations, but on one condition: the fuel composition must be known. In the absence of such knowledge, to reduce harmful emissions, it is necessary to organize the incineration process when the excess of oxidizer is known in advance. For gaseous flammable (casing-head gases), it happens in flare devices. Conversion of methane, contained in casing-head gases, into the equal amount of carbon dioxide decreases the load on the environment by tens of times. However, the impact is large and is not accompanied by the production of useful energy. Associated energy losses in the planetary scale commensurate with the needs of an entire continent [2].

One of the main ways of disposing of an increasing amount of solid household waste is their incineration. Before entering incinerators, they are sorted, also to stabilize their composition. But even in countries where there is a well-developed system of garbage collection and incineration (Sweden), there is a problem of its sorting [3]. The composition of even sorted garbage may vary, depending on the region of its collection or the season. In such circumstances, the possibilities to control incineration process are limited or non-existent. The problem can be solved by designing a model for determining the composition of household waste (biomass) during its thermo-chemical recycling. The same solution can be also applied for combustion of by-product gases. Paper [4] proposed the model of determining the composition of an unknown fuel in the combustion process and article [5] offered the method of identification of its composition. However, the proposed method and model are applicable only for gaseous fuel. They cannot be used to determine the composition of liquid, solid fuel, and household waste.

As a rule, gasification is considered as a separate process of thermo-chemical transformations. This approach is accompanied by the use of special methods [6]. This paper underlines the existence of heterophase interactions and accompanying problems of process modeling. However, as in most other works, modeling is carried out for the known composition of the source substance (wood biomass) and only for the studied gasification process.

In article [7], an attempt to consider the gasification process as a particular case of the incineration process is made. This proves the thesis that was put forward earlier about the possibility of using a unified model for describing various processes of thermal recycling of biomass. It is necessary only to vary the coefficient of excessive oxidizer. But because of the similarity of the processes, the problems are similar too – the research is conducted for substances albeit different, but with the known composition.

Pyrolysis as a process of thermo-chemical decomposition of hydrocarbon material has a series of advantages over gasification and incineration:

– lower temperature of the process and, consequently, lower emissions of contaminants into the atmosphere [8];

– more flexible scale of plants [9] and greater flexibility in the composition of products only by changing the operating parameters [10], for example, temperature;

– the ability to simplify calculations by decomposition of the original substance (at least, of vegetable origin) into separate components (hemicellulose, cellulose, lignin) and consideration of their individual pyrolysis [11].

Flexibility of the composition of reaction products can be further increased through the operation of pyrolysis plants in the presence of a small amount of air [8]. This process is called "quasi-pyrolysis". Different processes can the implemented on the same equipment when using identical raw materials. In this case, there is a conflict between applied models of pyrolysis and gasification. It becomes difficult to solve at some uncontrolled changes in the composition of the original raw material or the amount of air (inflow).

Analysis of the sources revealed the use of different models by authors for studying the processes of incineration, gasification, and pyrolysis. At the same time, all the sources consider these procedures as the components of the integral process of thermo-chemical recycling of organic substances. A number of works mention the possibility of a smooth transition from one process to another, or implementation of different processes or even their joint realization on the same equipment. This combination implies the necessity and possibility to describe the related processes based on a single model. At the same time, this approach was not found in the analyzed sources.

The unifying feature of most specified works is consideration of different, but necessarily known original substances. In actual situation, the case of the unpredictable change in the composition of raw material during recycling process is essential. It seems important to develop the method for determining the variable composition of original substances used for recycling in real time mode. In article [4], such a method was proposed, but only for the case of gaseous substances. It is relevant to extend this method in case of using original substances in other phase states within a unified model for description of the processes of incineration, gasification, and slow pyrolysis.

3. The aim and objectives of the study

The aim of this study is to develop a unified method for identification of incineration, gasification, and slow pyrolysis of hydrocarbon substances of unknown and variable composition. This will allow the rational use of hydrocarbon substances from the technological, energy and environmental positions.

To accomplish the aim, the following tasks have been set:

– to select and adapt for the calculation of the studied processes a unified model for solution of the problems of incineration, gasification, and slow pyrolysis with the known composition of original hydrocarbon substances;

– to determine the magnitude of errors, brought in to the solution of the corresponding tasks by different perturbations;

– to develop within the selected model the method of determining the composition of the original hydrocarbon substance in different aggregation states in real time mode.

4. Method for solving problems of incineration, gasification, and slow pyrolysis of hydrocarbon substances of unknown and variable composition

4. 1. Selection and adaptation of the unified method of solution

One of the features of the processes under consideration is gaseous state of their products. In addition, in all diversity of hydrocarbon substances, the number of chemical elements in their composition is limited. They most often include carbon (C), hydrogen (H), oxygen (O) and nitrogen (N). Less often, these are sulphur (S) and phosphorus (P). Because of this, the number of resulting gases is also limited, which greatly facilitates the task.

For clarity, consider the original substance, consisting only of three elements: (C), (H) and (O). This does not fundamentally change the nature of the solution, but significantly decreases the complexity of calculations. By using selected elements as original products, one can describe:

– gaseous – saturated and non-saturated hydrocarbons and others;

– liquid – alcohols, aldehydes, organic acids, phenols, etc.;

– solid – wood, agricultural wastes (cellulose, lignin), plastic wastes, etc.

It makes no difference for pyrolysis, which of the listed elements are the components of the original substance. When developing the methods of calculation for incineration and gasification, air can be used as an oxidizer. Nitrogen in the air composition does not change the essence of the ongoing processes and serves mostly as ballast. The number of resulting nitrogen oxides is not large and does not have a fundamental impact on the ongoing processes. The existence of nitrogen in the air requires consideration of the additional chemical element (N).

In calculation results, the following gases and elements they consist of can act as products:

$$[CO], [CO_2], [H_2O], [OH], [NO], [H_2], [O_2], [N_2], [H], [O], [C], [N]. \tag{1}$$

Based on such source data and assumptions, paper [4] proposed the model to determine the unknown composition of gaseous fuel in the form of its empirical formula represented in the form of:

$$C_{bC}H_{bH}O_{bO}N_{bN}. \tag{2}$$

Here, bC, bH, bO, bN is the number of atoms of corresponding chemical elements in the empirical formula of fuel. Based on the model, in paper [5], the method for identification of the composition of fuel was proposed. In the course of the implementation of the method, the direct problem of determining the composition of combustion products at the assigned empirical formula of gaseous fuel was solved. It should be noted that the implementation of the solution of a direct problem no longer requires the use of fuel in gaseous form only. Different aggregate states can be explored.

The empirical formula of fuel in the form of (2) is determined from the appropriate formulas of fuel and oxidizer using coefficient of excessive oxidizer α. Including the case when $\alpha<1$. In other words, the model shown in [4], when solving a direct problem can be used to describe incineration and gasification processes. There is a constraint for the case of gasification. In accordance with the proposed model, temperature and quantitative composition of products of incineration (gasification) are determined based on the equality of their enthalpy and the enthalpy of the original fuel. This implies that the energy released at the final stage of gasification is enough for self-maintaining of the process. This condition may be violated, for example, at elevated moisture content of the gasified substances. The possibility of solving the problem at supplying extra energy is explored below.

The model described in [4], after correction can be also used when solving the problem of slow pyrolysis. Consider the types of equations in the model [4].

The law of mass action. For the first eight substances from (1) on the example of CO_2 through partial pressures of corresponding components, the equations are written down in the form:

$$K_{CO_2}(T)=\frac{P_C\cdot P_O^2}{P_{CO_2}}, \tag{3}$$

where $K_{CO_2}(T)$ is the constant of chemical balance at the temperature of combustion products T for reaction of formation of CO_2 from elements C and O (tabular magnitude); P_{CO_2}, P_C, P_O are the partial pressures of corresponding components in the mix of combustion products. Equation (3) was written down with the use of partial pressures instead of concentrations for convenience of further transformations. For gas mixtures, it is possible to achieve the numerical equality of concentrations of components to their partial pressures. This is possible when considering a certain number of moles of fuel M_T (2) instead of the one mole. Magnitude M_T is an additional unknown magnitude and is to be determined.

The law of conservation of matter. The equations are written down for the last four elements from (1) with regard to MT moles of fuel. As an example, the equation for (C) takes the form:

$$M_T\cdot bC=P_{CO}+P_{CO_2}+P_C. \tag{4}$$

The number of carbon atoms in fuel (2) is displayed in the left-hand side of the equation. The number of carbon atoms in combustion products is displayed in the right part of the equation. Like in (3), partial pressures act as concentrations.

Dalton Law. It is written for completing the system of equations taking into account additional magnitude MT:

$$P_{\Sigma}=\sum_i P_i. \tag{5}$$

Here P_{Σ} is the pressure in the incineration chamber (furnace); P_i is the partial pressures of components of combustion products.

In such scheme of recording, partial pressures of combustion products can differ among themselves by 15–20 orders of magnitude. To reduce the range of a change of magnitudes, all equations of the model are logarithmized. As a result, we have the system of nonlinear algebraic equations. In the process of linearization, derivatives are determined not by the corresponding arguments, but rather by their logarithms:

$$\frac{d\sum_i\left\{\ln\left[f(P_i)\right]\right\}}{d\left[\ln(P_i)\right]}=\frac{\sum_i d\left\{\ln\left[f(P_i)\right]\right\}}{d\left[\ln(P_i)\right]}. \tag{6}$$

When solving the problems of pyrolysis, there occurs the need to take into account an additional component of the mixture of reaction products – coaly residue in the form of condensed phase. Designate its concentration through P_U. To close the system, write down another equation of form (3) for the reaction of formation of coaly residue:

$$K_U(T)=\frac{P_{\mathrm{C}}}{P_U}. \tag{7}$$

After taking logarithm, equation (7) will take the form:

$$\ln(P_{\mathrm{C}})-\ln(P_U)-\ln\left[K_U(T)\right]=0. \tag{8}$$

One of the peculiarities of the model is demonstrated during linearization of equation (8). Concentration P_U for assigned temperature does not change. The derivative of the corresponding member of equation (8), unlike other kinds of equations (3), is equal to zero. The linearized equation takes the form:

$$1\cdot\Delta\left[\ln(P_C)\right]=(-1)\cdot\left\{\ln(P_C)-\ln(P_U)-\ln\left[K_U(T)\right]\right\}^{*}. \tag{9}$$

In this expression, sign (*) represents the initial approximation, and corresponding initial approximations P_{C} and P_U or magnitudes from the previous calculation step are used in the right side.

When writing down the law of conservation of matter, magnitude P_U is taken into account in the balance of the number of carbon atoms and equation (4) takes the form:

$$M_T\cdot bC=P_{\mathrm{CO}}+P_{\mathrm{CO_2}}+P_U+P_{\mathrm{C}}. \tag{10}$$

When writing down the Dalton law (5), magnitude P_U is not taken into account due to the small specific volume.

Calculations based on the proposed model are simple for the case of pyrolysis compared with incineration and gasification. Thus, for the case of pyrolysis, the temperature of products of reaction is assigned and the iterative process of calculations is determined only by solving a nonlinear system of equations. In the calculation of processes of incineration and gasification, the temperature of combustion products is found within the external step of the iteration process.

Thus, a unified model for solving the problems of incineration, gasification and slow pyrolysis at the known composition of original hydrocarbon substances was selected and adapted. The variants of the model for calculating various processes differ by taking into consideration the existence of the condensed phase of the coaly substance. The temperature of combustion products is determined within the calculation of the process of incineration and gasification. At pyrolysis, the temperature of reaction products is assigned.

4. 2. Examples of calculation of processes of incineration and pyrolysis of hydrocarbon substances of the known composition based on the unified model

In order to decrease bulkiness without changing the commonality of presentation, model (1) to (5) was constructed for the incineration process of hydrocarbon substances in the air. To verify the workability of the used model in the study of incineration and gasification processes, the calculations of methane combustion (CH_4) [13] and ethyl alcohol (empirical formula C_2H_6O) [14] were performed earlier. The composition of the air in the amount of ~1 %, in addition to O_2 and N_2, contains impurities of other gases. They do not participate in the process of oxidation and are inert in the combustion process. To reduce complexity in calculations, they were replaced with N_2. As a result, the composition of air was accepted as: 21 % – O_2, 79 % – N_2.

Calculations were performed for various magnitudes of coefficient of excess of oxidizer α. At $\alpha=1$, the process was considered as incineration. At $\alpha<1$, it is considered as gasification. The results of the calculations on the proposed model and the data from [12] during combustion of methane [13] and ethyl alcohol [14] in the air were compared. The magnitudes of temperature T (K) and partial pressures P_i (in bar) of combustion products at the pressure in the combustion chamber (furnace) of 1 bar were presented. Comparison was conducted for different values of α by determining relative error ε of calculation of partial pressures relative to the pressure in the combustion chamber. The magnitude of minimal presented value α is conditioned by the availability of data in [12]. Based on the used model, calculations can be performed at any value of α.

The results obtained in [13] and [14] show good coincidence of calculation results based on the proposed model and shown in [12]. Relative errors of determining partial pressures during combustion of methane do not exceed 1 %, and for ethyl alcohol – 1.4 % and do not exceed the values that are permissible for engineering calculations (<5 %). The part of the obtained error may be due to using the approximate composition of the air in calculations.

Despite the diversity of experimental works, we did not manage to find any structured data to assess the reliability of the model used in solving the problem of thermo-chemical transformations of solids. The experimental values of the ranges of a change in concentrations of basic groups of products of transformations for the original wood raw materials from pine trees were used in this role. These data are contained in most available sources of various years. This determined their choice.

The composition of empirical formula and enthalpy of the original substance (pine wood), used in the calculations, were determined based on indirect data. The magnitudes of these data are close in different sources, but still not the same and are presented in a certain range. For this reason, the source of their values was not specified. It is accepted that pine wood contains: C – 49...50 %; O – 42...44 %; H – 6...7 %. In addition, wood contains ~ 0.1...1 % of N and up to 1 % of mineral components (ash content). These substances are not taken into account by virtue of the smallness of magnitudes of their concentrations at the assessment nature of calculation. As a result, $CH_{1,44}O_{0,64}$ was accepted as the empirical formula of original raw material. Heat output of absolutely dry pine wood in several sources is indicated at the level of 2,100 °C (2,370 K), which enables estimating the enthalpy of original raw material by magnitude of 68.24 kJ/mol (–2880 kJ/kg).

The combustion process at stoichiometric ratio of fuel and oxidizer (α=1) in a simplified version is considered as a process of complete oxidation of combustible substances. For pine wood it takes the following form:

$$CH_{1,44}O_{0,64}+\underbrace{1,04\cdot O_2+3,91\cdot N_2}_{\text{air}}=$$

$$=CO_2+0,72\cdot H_2O+3,91\cdot N_2. \qquad (11)$$

The results of the calculation of this process based of the proposed model are displayed (highlighted) in the correponding row in Table 1. As above, the pressure of combustion products in the combustion chamber (furnace) was accepted as P_Σ=1 bar.

Table 1

Temperature and concentrations (partial pressures, volumetric shares) of products of pine wood combustion at different values of coefficient of excess of oxidizer α

α	T, K	Concentrations (partial pressures, bar) of reaction products							
		CO	CO_2	H_2O	OH	H_2	N_2	O_2	NO
2.5	1,409	0	0.077	0.055	0	0	0.749	0.119	0
2.2	1,530	0	0.086	0.062	0	0	0.743	0.107	0
1.9	1,681	0	0.099	0.071	0	0	0.736	0.092	0.0017
1.6	1,870	0.0001	0.116	0.083	0	0	0.723	0.071	0.0028
1.3	2,119	0.0015	0.139	0.100	0.002	0.0003	0.711	0.042	0.0043
1	2,356	0.019	0.156	0.121	0.004	0.003	0.684	0.008	0.003
0.9	2,371	0.040	0.150	0.128	0.003	0.007	0.667	0.002	0.0016
0.8	2,316	0.072	0.134	0.132	0.0015	0.015	0.644	0	0
0.6	2,071	0.153	0.093	0.125	0	0.052	0.577	0	0
0.4	1,661	0.246	0.058	0.085	0	0.134	0.476	0	0
0.3	1,348	0.303	0.043	0.048	0	0.201	0.406	0	0

The list of combustion products shown in Table 1 is wider than the similar list in (11). Nevertheless, these data can be compared, if we find the amount of H- and N-containing products per 1 mole of C-containing substances:

$$\frac{P_{H_2O}+P_{OH}+P_{H_2}}{P_{CO}+P_{CO_2}}=\frac{0,121+0,004+0,003}{0,019+0,156}=0,731, \qquad (12)$$

$$\frac{P_{N_2}+P_{NO}}{P_{CO}+P_{CO_2}}=\frac{0,684+0,003}{0,019+0,156}=3,926. \qquad (13)$$

Deviation of results (12), (13) from the magnitudes of (11) (the number of moles of H_2O и N_2) does not exceed 1.5 %. In addition, it is more informative. The calculation results (Table 1) reflect the main features of incineration and gasification processes. Thus, the temperature of reaction products is shown as higher for α=0.9, compared with α=1.0. This is due to the great influence of an increase of ballast in the form of N_2, compared with an increase of obtained energy in the form of heat. It is necessary to heat this gas, but it does not participate in the reaction. The calculation results adequately display the change in the ratio of CO, CO_2 and H_2O as α changes, when switching from incineration to gasification. An increase in the amount of nitrogen oxides at an increase in free O_2 with the growth of α was displayed. Starting with a certain value of α, the number of NO decreases despite the continuing increase in O_2 in reaction products. This is due to a decrease in their temperature.

The subsequent decrease in the value of magnitude α, in comparison to those listed in Table 1, leads to the impossibility to organize the incineration (gasification) process. At α=0 and at heating the hydrocarbon material, its dry distillation (slow pyrolysis) occurs. The results of calculation of parameters of this process based on the proposed model are shown in Table 2. The additional component – coaly residue (U) is taken into account in the composition of the reaction products.

The experimental research of low temperature (350–450 °C) slow pyrolysis of wood notes the formation of condensing hydrocarbon substances – pyroligneous distillate: acetic acid, resins, etc. This is the result of relatively rapid removal of decomposition products from the heating zone. High-molecular volatile hydrocarbon substances that are resistant to thermal destruction do not have enough time to degrade to simple ones. This effect is more vividly pronounced in the process of fast pyrolysis. At an increase in the temperature of slow pyrolysis or at an increase in the time when reaction products are in the heating zone, the amount of condensed substances decreases, even until complete disappearance. Table 2 gives the results from calculation of parameters of such process. For this reason, the list of reaction products does not contain hydrocarbon substances, except methane. Consideration of the proposed fast pyrolysis with the formation of a large amount of condensed substances, based on the proposed model, will be subject for additional studies. In literary sources, the composition of reaction products for slow pyrolysis is specified in mass fractions (m_i). The same magnitudes are used in Table 2 to display the results of calculations.

To assess the adequacy of the obtained results, use to basic characteristics of slow and high-temperature pyrolysis in Table 3, presented in (13).

Calculation results (Table 2) at the temperature of T=700 K correspond to slow pyrolysis. Relative error of the calculated share of coal of 34 % differs from the experimental data by not more than 3 %. Error of calculation of proportion of water is even less and makes up ~1.5 %. For high-temperature pyrolysis, the difference of calculation values is larger, but does not contradict to the nature of the data. In this case, it is necessary to take into account that experimental data are shown for a certain range of conditions. Calculation values are determined for a fixed temperature value.

Thus, results of calculations, performed with the use of the proposed unified model adequately reflect the parameters of the various processes of thermo-chemical conversion of hydrocarbon combustion products: incineration, gasification, and slow pyrolysis. Relative error of calculations does not extend beyond the allowed values for engineering calculations (<5 %).

Table 2

Mass fractions (m_i) of products of pyrolysis of pine wood at different values of temperatures (T)

T, K	CO	CO_2	H_2O	CH_4	H_2	U
700	0.003	0.288	0.246	0.112	0.005	0.34
900	0.102	0.294	0.178	0.05	0.028	0.343
1,100	0.490	0.125	0.067	0.06	0.051	0.255
1,300	0.707	0.019	0.014	0.001	0.059	0.195
1,500	0.744	0.003	0.003	0	0.060	0.184

Table 3

Characteristics of types of pyrolysis

Process	Conditions	Products, % by weight		
		Distillate	Coal	Gas
Slow pyrolysis	Low temperature (350–450 °C), lengthy process	30 (water up to 75 %)	35	35
High-temperature pyrolysis	High temperature (>600 °C)	5 (resins)	10	85

4. 3. Method for determining the composition of original hydrocarbon substance in different aggregation states under real-time mode

All the above calculation results were obtained on conditions of the known composition of original substances. At a change of the type, quality of the original raw material, this condition is violated and results lose their relevance. Without identifying the composition of original substances, it is not possible to arrange a controllable process of their thermo-chemical recycling.

Calculations in the study of all processes under consideration are based on the use of the empirical formula of the original substance. Another feature is the identity of the experimental formula of the original substance and products of reactions. These properties are the basis of the method for determining the composition of hydrocarbon substances during thermo-chemical recycling.

In (5), the method for determining the composition of combustible gas in the incineration process was proposed. The method is based on the model considered in this article. But the mixture of gases, albeit of unknown composition that can burn, can be obtained from liquid and solid hydrocarbon substances during their gasification at small values of α. Bearing in mind these comments, the process of determining the composition is implemented as follows:

– an uncontrollable process of gasification of a substance, the composition of which must be determined, is implemented in a separate small-size device. In this case, the air flow supplied for gasification is taken into account;

– in accordance with the method proposed in (5), the gas obtained at the previous stage is incinerates and its composition is determined (empirical formula);

– based on this formula and excluding the air consumed for gasification at the first stage, the empirical formula of the original substance is determined.

Thus, based on the proposed algorithm, it is possible to implement a closed technological process of operational determining the changing composition of the mixture of hydrocarbon substances and their controllable thermo-chemical recycling.

5. Discussion of results of solving the problems of incineration, gasification, and slow pyrolysis of hydrocarbon substances

In the existing methods, substances or mixes of substances of unknown compositions are the source data for calculation. Actual mixtures can consist of their large quantity. Thus, the standard for natural gas chromatography implies determining the percentage of more than 30 separate constituent substances. The same problems of determining the compositions exist when using household, agricultural and other waste for thermo-chemical recycling. The complexity of description of the composition of substances and their mixtures significantly decreases when their empirical formulas (2) are used. The use of only four chemical elements (C), (H), (O) and (N) allows describing the composition of most organic substances. Thus, consideration of another element (S) makes it possible to describe the composition of the above-mentioned natural gas. The simplicity of formulas at the known composition of original substances allows their use for calculating various processes of thermo-chemical transformations ([13, 14], Table 1). This universality at the initial stage will form the basis for the extension of applicability of the empirical formula for calculation to the area of slow pyrolysis at the known composition of original raw material (Table 2).

Adequate results in the calculation of incineration and gasification processes were obtained due to high temperatures of occurring processes. The existence of condensed substances at pyrolysis is a consequence of low temperatures and relatively rapid removal of products from the reaction zone (heating zone). At an increase in temperature, their number decreases, which is proved by the data from Table 2.

Pyrolysis, unlike incineration and gasification, is characterized by obtaining condensed (coaly residue) and condensing (distillate) substances. Coaly residue is the product of final decomposition of hydrocarbon substances. Therefore, the considered model describes the process of its formation. Condensing substances in the reaction area are in gaseous form, but do not reach the final stage of decomposition. To describe the process of their formation, the model used in the article must be improved, which is the subject of further research.

The observed simplification of calculations when using the empirical formula is the basis of the method for determining the composition of gaseous organic substances and mixtures in the process of their incineration [4]. This universality enabled proposing the method for determining the composition of various organic substances by generally uncontrollable gasification of their small amount. Such process of gasification and determining the composition of the empirical formula can occur in real time, in parallel with the basic process of thermal recycling of substances and ensure its adjustability and controllability.

The proposed unified model for identification of composition of products of incineration, gasification and slow pyrolysis can serve as the basis for calculation of the required parameters and control of corresponding processes through them. This does not exclude the need for engineering-technological and metrological provision of corresponding processes and requires additional research.

6. Conclusions

1. The unified model for solving the problems of incineration, gasification, and slow pyrolysis at the known composition of original hydrocarbon substances was selected and adapted. The model uses partial pressures of the reaction products as determined magnitudes. Such approach implies their gaseous state. The specific feature of the model under consideration is the possibility of taking into account the condensed phase when making calculations. In the present case, it is coaly residue at pyrolysis.

2. The results of calculations based on a unified model of the composition of products of slow pyrolysis were presented. Their relative error does not exceed the permissible magnitude for engineering calculations (<5 %). This corresponds to accuracy of calculations of incineration and gasification processes, for which the adapted model was originally developed. Feature, which allowed performing the calculations based on the unified model for substances that are diverse in composition and aggregate state, is their unified empirical formula (2). Changing down to zero the values of corresponding magnitudes b_C, b_H, b_O, b_N, it is possible to obtain descriptions of all used and many other substances. This applies to both separate substances, and their mixtures. Using the formula of this type, it is possible to describe a mixture of original substances with the air at any magnitude α.

3. We developed the method for determining in real-time the composition of the hydrocarbon component of combustible substances in different aggregation states by the unified proposed model, which is a further development of the model proposed in [5]. The method is based on the specific feature of the unity of the empirical formula of the hydrocarbon component of original substances and products of reaction of the processes under consideration.

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