OBTAINING KINETIC CHARACTERISTICS OF COMBUSTION OF THE COKE FROM SOLID BIOFUELS

Purpose. Obtaining the kinetic constants of the interaction of coke residues of different types of solid biomass with air oxygen to calculate the burn-out time of biofuel particles of different sizes in a wide range of temperatures.

Methodology. The initial data on carbon decrease over time at varying temperatures was obtained experimentally. The coke-ash residue was prepared in two stages, by placing and holding the initial biomass in an inert medium at temperatures of 750 and 900 °C. The values of the activation energy and the chemical constant of the reaction rate were calculated by the method of least squares. The kinetic constants are calculated from the first-order reaction model in the Arrhenius approximation.

Findings. It is found that the dependence of the specific per initial mass burning rate of coke residues at constant temperature has a segment of constant rate within the conversion range from 0.15 to 0.8, at a particle temperature of 600 °C, and decreases with increase in particle temperature. Based on the obtained kinetic constants, the temperature dependence was constructed of the specific burning rate of coke-ash residues of pine pellets, wheat straw and sunflower husks in the range of 600–1600 °C. It was found that under the same combustion conditions the burning rate of coke-ash residue of wheat straw pellets is the highest, and pine pellets is the lowest.

Originality. For the first time, the kinetic constants were obtained of the interaction of coke-ash residues of pine pellets, wheat straw and sunflower husks of Ukrainian origin with air oxygen in the conditions of fast heating.

Practical value. The proposed method for calculating specific rate of coke residues combustion with the obtained kinetic constants can be used to calculate the burning time for biofuel particles of different size in the furnaces of thermal installation in a wide range of temperatures, as well as to select the optimal biomass particles size for co-firing and separate combustion.

Keywords: kinetic constants, coke-ash residue, biomass

Introduction. According to the latest guidelines of the Ministry of Energy of Ukraine (the so-called “green transition” concept), the New Energy Strategy until 2035, the commitments made by the state as a member of the Energy Community and a participant to the Paris Agreement, the share of renewable energy in Ukraine’s energy balance has to increase steadily and rapidly. Therefore, the search for new alternative energy sources for Ukrainian fossil fuel TPPs and CHPs becomes especially important.

In recent decades in Ukraine, the interest has increased to solid biofuels as a substitute for traditional fossil fuels. Due to a significant increase in the price of imported natural gas, in the early 2000s the gas started being replaced with biomass. In recent years, due to the blockade in Ukraine of the supplies of anthracite coal group to TPPs, which burn anthracite and lean coals, there has been a shortage of supply of the designed coal to half of thermal power plants. This deficit can be partially covered through a full or partial re-equipment of the boilers to solid biomass combustion.

Solid biomass has certain advantages over coal. In addition to lower cost, biofuels have a lower content of ash, sulphur and nitrogen, which leads to much less impact on the environment. In European countries, the introduction of biomass combustion is primarily driven by environmental factors. Biofuels are produced from waste from the woodworking industry and agriculture, thus solving another environmental problem, waste disposal.

Today in our country, the use of biomass remains insufficient, compared to the world trends. In the energy mix of primary energy sources in Ukraine, renewable energy sources account for 4.4 %, against almost 14 % on average in the world [1]. Of all renewable sources, solid biomass amounts to approximately 75 %. According to the IEA and the Bioenergy Association of Ukraine, the annual biomass potential in Ukraine is estimated at 30 million tons of equivalent fuel (equivalent fuel is fuel with LHV = 7000 kcal/kg), or 23 % of primary energy consumption in the country. In addition to wood pellets (mainly pine), the pellets are produced in large quantities from sunflower husks and straw from various crops. That is the reason why for the study in this article the pellets of pine, wheat straw and sunflower husks were selected as being promising for use as fuel.

The elemental composition and burning characteristics of biomass vary widely and depend on the sort and cultivation conditions.

The dehydration is considered the initial stage of combustion of solid biofuels, preceding the next stage of the ignition of...
volatile substances released as a result of its thermal destruction. The most durational of all stages of fuel particle combustion is the burning time of coke residue. It is crucial for calculating the burning time of biomass fuel [2]. The kinetic characteristics of the stages of biomass combustion of Ukrainian origin have not been studied sufficiently, so the authors paid special attention to the study of the kinetic characteristics of the reaction of the coke residue with oxygen of the air for selected biofuels.

The dynamics of coke residue combustion depends on the ratio of oxygen diffusion rate to the reacting surface of the solid particle and the rate of heterogeneous carbon reaction, which, in its turn, depends on the process temperature.

One of the most common ways to describe the combustion of coke residue is the Arrhenius equation in the first-order reaction model, and the specific burning rate \( W_m \) per carbon mass, 1/s, is described by the expression \([3, 4]\)

\[
W_m = k_0 \cdot \exp\left(\frac{-E_a}{RT}\right),
\]

where \( k_0 \) is the pre-exponential factor, 1/s; \( E_a \) is effective value of activation energy, J/mol; \( R \) is universal gas constant; \( R = 8.314 \text{ J/(mol} \cdot \text{K}) \).

Pre-exponential factor is defined by

\[
k_0 = k_0' \cdot C_m,
\]

where \( k_0' \) is the constant of the heterogeneous reaction rate, \( m^3/(kg \cdot s) \); \( C_m \) is the concentration of oxygen in the flow in which the coke residue particle burns, kg/m\(^3\).

The constant of the heterogeneous reaction rate, \( m^3/(kg \cdot s) \), is given by

\[
k_0' = \beta \cdot S_p \cdot k_0'',
\]

where \( \beta \) is the stoichiometric conversion factor of the mass of reacted oxygen toward the mass of reacted carbon; \( S_p \) is the specific (per unit mass) particle area, \( m^2/kg \); \( k_0'' \) is the constant of the chemical reaction rate, m/s.

When such kinetic constants as activation energy, heterogeneous reaction rate constant and chemical reaction rate constant that account for the external diffusion constraint are obtained, it is possible to calculate the specific combustion rate of coke residue for selected solid biomass, based on which the burning time of biofuel particle of a given size at given temperature could be calculated.

**Literature review.** The diversity of types of solid biomass suitable for combustion, and the interest in finding ecologically harmless energy sources worldwide, has led to an increase in the number of publications on the study of biomass fuel characteristics. Currently, the creation is in progress of the national databases on kinetic constants of fuel resources which are necessary for the designing of combustion devices [5]. The results of the studies published mainly consider the plants being exotic or such that do not have great prospects for energy use in Ukraine [6].

Most studies related to the kinetics of biofuel combustion stages use the method of thermogravimetric analysis (TGA) [7–11]. This method has a number of advantages, including the availability and versatility of equipment, high accuracy of measurement compared to other methods and the ability to study all stages of combustion at one fuel sample. The disadvantages include the low heating rate of the test sample, usually below 20 K/s (in case of modification – up to 100 K/s). Another disadvantage is that the fuel particles reside in a stationary dense layer, which hampers the access of oxygen to the particles inside the layer. The methods for conducting experiments on TGA in an oxidizing environment by different research groups vary only slightly, and the scientific novelty mainly lies in the development of methods for mathematical description and processing of primary data.

In [8], to define \( E_c \) of oxidative pyrolysis, for processing of the original TGA data five isosconversion methods were used:

KAS, FWO, Starink, Vyazovkin and Friedman. The activation energy profiles obtained using these calculation methods practically coincide, within the values of the degree of conversion of samples, from 10 to 90 %, at three heating rates (5, 10 and 20 K/min). The obtained values of activation energy are specific to conditions of the experiment (a certain heating rate of the sample and a state of the stationary layer), which makes the use of these kinetic characteristics more complicated for calculation of the dynamics of biofuel particles burnout in the combustion equipment.

In [9], the kinetic characteristics were studied of olive tree leaves and wood in TGA with a heating rate up to 100 K/s. The results demonstrate effect of the heating rate over the shape of the mass loss curve, the position of maximums of the mass loss rate and on the location of the maximum temperature peaks. As the heating rate increases, the curves shift in the direction of increasing temperature, i.e. the value of the temperature at which the maximum mass loss is observed increases. This effect may be due to a stronger thermal shock, and a larger temperature gradient between the inner and outer layers of the particle, which does not facilitate release of the volatile matter. Given the heating rate of the fuel particle in the pulverized coal boiler of about \( 10^4 \text{ K/s} \), to obtain the kinetic characteristics of solid fuel combustion it is important to conduct research with the maximum heating rate.

The influence of particle size of solid biofuel on the kinetic characteristics of fuel combustion on an example of the crushed straw is given in [10]. The results of the TGA study in the air showed that at the same heating rate of 20 K/s the position of the peaks of the rate of mass loss for particles of different sizes did not change. Slight difference between the positions of the curves is explained by different mineral content and distribution of the fixed carbon.

In [11], results are presented of the study on the kinetics of combustion process stages with pure biomass and in a mixture with anthracite using TGA method in an oxidized medium of air with a heating rate of 20 °C/min. The kinetic constants of all stages of combustion were obtained: dehydration and yield of volatile substances by the Coats-Redfern method; the combustion of the coke residue by the Senum-Young method. It is shown that for high-temperature processes (combustion of coke residue) the combined method of Coats-Redfern and Senum-Young with iterative approximation should be used. The obtained kinetic constants allow calculating quite accurately the dynamics of mass losses of the studied fuels in determining the duration of stages of their thermal destruction, but their application for calculation of the specific combustion rate and burnout time of fuel particles at real conditions requires development and validation of calculation models.

The research method presented in this article has a significant advantage, specifically in that the speed of heating of the particle is \( \tau_v = 10^4 \text{ K/s} \). Another important advantage is the study of the preliminary prepared biomass coke sample, without residue of complex hydrocarbons which in the case of TGA studies on the same single sample remain unreleased.

**Unresolved aspects of the problem.** To date, insufficiency is observed in the data on the combustion kinetics of coke residues of solid biofuels of Ukrainian origin, suitable for energy use.

**Purpose.** Determination of kinetic constants of the reaction of carbon in coke residue of pine pellets, wheat straw and sunflower husk with air oxygen under fast heating.

**Methods.** Experiments to determine the kinetic characteristics of coke residue of three biomass samples were conducted at the installation “Pyrolysis-M”. The installation represents a quartz glass reactor placed in a tubular electrically heated furnace. Air is supplied to the bottom part of the reactor, and in the upper part the systems are placed for introducing a sample of the investigated material and exhaust gases sampling. The air is gradually heated to a given temperature passing through the backfill layer of MgO. The test material in the reactor re-
Results. Three types of biofuels were selected for the study: wood pellets, sunflower husk and wheat straw. Their technical analysis is presented in Table 1, and the elemental composition in Table 2. The ash content of the formed coke residue was determined by the calculation method on the basis of elemental analysis and directly by the analysis of the ash content in the formed coke. The difference between the values of ash content obtained in these two ways ranged from 10 to 15 %. The nature of this discrepancy requires a separate study and may be related to the specifics of the method for laboratory determination of volatile matter in biomass. For further calculations, the values of ash content obtained from the laboratory analysis were taken as the most accurate, equalling 1.9, 26.0 and 12.3 % for coke pellets of pine, wheat straw and sunflower husk, respectively.

Technical analysis of biofuel samples shows that biomass has a very low ash content, especially in pine pellets, which in combination with low chlorine content makes them perhaps the best choice when converting gas boilers to biomass combustion with minimal reconstruction.

Based on the composition of combustion products obtained during the experiment and their volumetric flow rate, the specific combustion rate per unit time was determined

\[ W_{m} = \frac{\Delta m}{AT} \]

where \( W_{m} \) is specific burning rate for the initial mass of carbon, kg/(kg \cdot s); \( \Delta m/AT \) is the carbon mass decrease per unit time (determined on the basis of measuring the mass flow of CO and CO\(_2\) by the gross reaction of C + O\(_2\)), kg/s; \( m_0 \) is initial mass of carbon, kg.

The degree of carbon conversion at each moment was derived from the expression

\[ x_t = 1 - \frac{m_t}{m_0} \]

where \( m_t \) is the current mass of unreacted carbon, kg.

Given the significant increase in the temperature of burning particle toward the gas and the reactor wall temperatures, overheating of the particle was calculated from the heat balance, taking into account convective and radiative heat exchange, according to the formula

\[ \Delta T = T_w - T_p = \frac{Q_2}{\Delta m} \left( \frac{\rho p_d^2 d^3}{6\pi \eta D} \right) + \frac{d \delta \rho e}{N_u \eta} \left( T_m - T_p \right) \]

where \( T_p, T_w, T_m \) are temperatures of gases, particles and wall, respectively, \( K, Q \) is thermal effect of the reaction C + O\(_2\) = CO\(_2\), kJ/kg; \( \rho p_d \) is apparent particle density, kg/m\(^3\); \( d \) is equivalent particle diameter, m; \( \lambda \) is gas thermal conductivity of the; \( \delta \) is Stefan-Boltzmann constant; \( \frac{J}{m^2 \cdot s \cdot K} \) is integral degree of blackness

Due to the fact that the particle temperature at each moment of time in both parts of the equation is unknown, to solve

<table>
<thead>
<tr>
<th>Pellets</th>
<th>( W^A, % )</th>
<th>( W^F, % )</th>
<th>( A^F, % )</th>
<th>( S^F, % )</th>
<th>( V^om, % )</th>
<th>( t_{e}, °C )</th>
<th>( t_{ie}, °C )</th>
<th>( t_{ci}, °C )</th>
<th>( Q^{r}, MJ/kg )</th>
</tr>
</thead>
<tbody>
<tr>
<td>pine</td>
<td>8.43</td>
<td>8.7</td>
<td>0.4</td>
<td>0.03</td>
<td>85.9</td>
<td>1300</td>
<td>1310</td>
<td>1325</td>
<td>17.63</td>
</tr>
<tr>
<td>wheat straw</td>
<td>7.98</td>
<td>8.4</td>
<td>6.1</td>
<td>0.14</td>
<td>82.0</td>
<td>1180</td>
<td>1200</td>
<td>1225</td>
<td>15.57</td>
</tr>
<tr>
<td>sunflower husk</td>
<td>8.90</td>
<td>9.3</td>
<td>9.7</td>
<td>0.18</td>
<td>80.3</td>
<td>1100</td>
<td>1110</td>
<td>1200</td>
<td>14.81</td>
</tr>
</tbody>
</table>
it, an iterative method was used with time resolution of one second. The value of particle overheating ranged from 25 to 210 °C depending on the initial temperature in the reactor.

For each type of biomass, the studies were performed taking into account the overheating of the particle in the temperature range from 600 to 1150 °C.

The dependence of specific per initial mass conversion rate of carbon coke residues of solid biomass of three species on the degree of conversion ($X$) for four temperature levels (550, 650, 750 and 850 °C) has a flat area with deviation of $W_m^0$ at each point not greater than 10% of the average value. The value of constant specific rate lies in the range $X_0 = 0.15–0.8$ at a particle temperature of 600 °C and tends to narrow with increasing temperature. The dependence of specific per initial mass conversion rate of carbon coke residue for the three types of fuel at the initial temperature of 650 °C is shown in Fig. 2.

Presence of a segment of constant specific per initial mass carbon burning rate in a wide range of conversion allowed using its average values and temperature values to construct the dependence $W_m = f(T)$.

The specific combustion rate for a wide range of temperatures includes kinetic ($W_k$, 1/s) and diffusion ($W_d$, 1/s) components and has the form

$$W_m = \frac{1}{W_k} + \frac{1}{W_d}.$$  
(5)

The specific burning rate in the external diffusion region was determined by the formula

$$W_d = \frac{\beta \cdot S_p \cdot C_0 \cdot N_{ad}^{0.5} \cdot D_{p}}{d_p},$$  
(6)

where $N_{ad}^{0.5}$ is the Nusselt diffusion criterion; $D$ is the molecular diffusion coefficient, m²/s.

The value of the apparent particle density of the coke residue, which is necessary to know to determine $S_p$, was assumed for the three types of biomass to be equal to 877 kg/m³. This value was obtained by calculation based on the published data for pine wood and its coke residue and the known value of the apparent density of pellets. Having calculated diffusion velocity component and experimentally obtained total specific combustion rate the value $W_k$ was derived from equation (5). Dependence of the total, kinetic and diffusion specific burning rates of coke residues for pine pellets, wheat straw and sunflower husk on the inverse temperature is shown in Figs. 3–5.

The values of the activation energy and the constant of the chemical reaction rate were calculated by the method of least squares from the dependence $W_k = f(T)$ and are presented in Table 3.

The obtained kinetic constants were used in equations (1–6) to calculate dependence of the total specific rate of com-

Table 2

<table>
<thead>
<tr>
<th>Pellets</th>
<th>C_{d, %}</th>
<th>C_{daf, %}</th>
<th>H_{daf, %}</th>
<th>O_{daf, %}</th>
<th>N_{daf, %}</th>
<th>S_{daf, %}</th>
</tr>
</thead>
<tbody>
<tr>
<td>pine</td>
<td>0.04</td>
<td>51.9</td>
<td>6.33</td>
<td>41.6</td>
<td>0.14</td>
<td>0.03</td>
</tr>
<tr>
<td>wheat straw</td>
<td>0.27</td>
<td>50.3</td>
<td>6.21</td>
<td>42.8</td>
<td>0.53</td>
<td>0.15</td>
</tr>
<tr>
<td>sunflower husk</td>
<td>0.42</td>
<td>49.4</td>
<td>6.2</td>
<td>43.4</td>
<td>0.89</td>
<td>0.21</td>
</tr>
</tbody>
</table>
bustion of coke residues on the temperature in a wide range, taking into account the external diffusion constraints. Fig. 6 shows the dependence of the specific burning rate of coals of three types of biomass and of anthracite coal from the Donetsk basin on temperature (600–1600 °C), d = 1–1.6 mm.

The analysis of the obtained results showed that the burning rates of coke-ash residue of wheat straw pellets are the highest, pine pellets are the lowest, and the values for sunflower husk are in between of the two another rates at the same combustion conditions. Compared to the combustion rate of coke-ash residue of particles of the same size, biomass particles burn out much faster. These results indicate possibility of using a coarser grinding for biomass compared to coal when converting combustion plant to co-firing coal with biomass or to pure biomass combustion.

The presented calculation method and the obtained kinetic characteristics allow determining the specific conversion rates of coke-ash residue of the investigated fuels for a wide range of particle sizes and temperatures.

**Conclusions.** Experiments on the study of the kinetic characteristics of coke-ash residues of three samples of solid biofuels demonstrated the existence of a segment of constant combustion rate in a wide range of carbon conversion at constant temperature, which allows obtaining the dependence of specific combustion rate on temperature to determine kinetic constants.

The obtained kinetic characteristics of combustion of coke residues can be used, in particular with the aid of specialized software, to calculate the burning rate of pellets in the boiler combustion chamber.

The dependence of the specific burning rate on temperature constructed using the obtained kinetic characteristics showed that under the same combustion conditions the burning rate of coke-ash residue of wheat straw pellets is the highest, of pine pellets is the lowest, and sunflower husk pellets burning rate lies somewhere in between.

**Acknowledgements.** The authors of the article thank Serhii Hryhorovych Duliyenko for conducting experiments on the Pyrolysis-M installation.

### Table 3

<table>
<thead>
<tr>
<th>Coke residue (pellets)</th>
<th>$k_o$, $m^3/(kg \cdot s)$</th>
<th>$k_o''$, m/s</th>
<th>$E_a$, kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>pine</td>
<td>406.0</td>
<td>709.4</td>
<td>80.06</td>
</tr>
<tr>
<td>wheat straw</td>
<td>619.1</td>
<td>1248.2</td>
<td>77.62</td>
</tr>
<tr>
<td>sunflower husk</td>
<td>623.7</td>
<td>1089.8</td>
<td>80.48</td>
</tr>
</tbody>
</table>

**References.**


**Визначення кінетичних характеристик горіння коксозольних залишків твердого біопалива**

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Мета. Отримання кінетичних констант взаємодії коксозольних залишків різних видів твердої біомаси з киснем повітря для розрахунку часу вигоряння частинок біопалива різного розміру в широкому діапазоні температур.

Методика. Першінні дані убутку вуглецю за часом у залежності від температури були отримані експериментальним шляхом. Коксозольний залишок отриманий у два етапи шляхом витримки вихідної біомаси в інертному середовищі за температури 750 і 900 °C. Значення енергії активації й хімічної константи швидкості реакції розраховувалися методом найдешевших квадратів. Кінетичні константи розраховані за моделлю реакції першого порядку у наближенні Арреніуса.
Результати. Встановлено, що залежність питомої на початкову масу швидкості горіння коксозольних залишків при постійній температурі мають ділянку постійної швидкості в діапазоні ступеню конверсії від 0,15 до 0,8 при температурі частиною 600 °С і зменшується зі збільшенням температури частинки. На основі отриманих кінетичних констант була побудована залежність питомої швидкості горіння коксозольних залишків пелет сосни, соломи пшениці й лущинки соняшника від температури в діапазоні 600–1600 °С. Встановлено, що швидкість горіння коксозольного залишку пелет соломи пшениці є найбільшою, а пелет сосни найменшою в однакових умовах спалювання.

Наукова новизна. Уперше отримані кінетичні константи взаємодії коксозольних залишків пелет сосни, соломи пшениці й лущинка українського походження з киснем повітря в умовах швидкісного нагрівання.

Практична значимість. Наведена у роботі методика розрахунку питомої швидкості горіння коксозольних залишків з використанням отриманих кінетичних констант може застосовуватися для розрахунку часу вигоряння частинок біотоплива різного розміру в умовах швидкісного нагрівання, а також для вибору оптимального розміру біомаси при спільному та окремому її спалюванні.

Ключові слова: кінетичні константи, коксозольний залишок, біомаса

Определение кинетических характеристик горения коксозольных остатков твердого биотоплива

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Цель. Получение кинетических констант взаимодействия коксозольных остатков различных видов твердой биомассы с кислородом воздуха для расчета времени выгорания частиц биотоплива разного размера в широком диапазоне температур.

Методика. Первичные данные убыли углерода по времени в зависимости от температуры были получены экспериментальным путем. Коксозольный остаток получен в два этапа путем выдерживания исходной биомассы в инертной среде при температуре 750 и 900 °С. Значения энергии активации и химической константы скорости реакции рассчитывались методом наименьших квадратов. Кинетические константы рассчитаны по модели реакции первого порядка в приближении Аррениуса.

Результаты. Установлено, что зависимость удельной на начальную массу скорости горения коксозольных остатков при постоянной температуре имеет участок постоянной скорости в диапазоне степени конверсии от 0,15 до 0,8 при температуре частиц 600 °С и уменьшается с увеличением температуры частицы. На основе полученных кинетических констант была построена зависимость удельной скорости горения коксозольных остатков пеллет соломы пшеницы и шелухи подсолнечника от температуры в диапазоне 600–1600 °С. Установлено, что скорость горения коксозольного остатка пеллет соломы пшеницы является наибольшей, а пеллет соломы наименьшей в одинаковых условиях сгорания.

Научная новизна. Впервые получены кинетические константы взаимодействия коксозольных остатков пеллет соломы пшеницы и шелухи подсолнечника украинского происхождения с кислородом воздуха в условиях скоростного нагрева.

Практическая значимость. Приведенная в работе методика расчета удельной скорости горения коксозольных остатков с использованием полученных кинетических констант может применяться для расчета времени выгорания частиц биотоплива разного размера в топках теплотехнического оборудования в широком диапазоне температур, а также для выбора оптимального размера биомассы при совместном и отдельном ее сгорании.

Ключевые слова: кинетические константы, коксозольный остаток, биомасса

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