

Kinetics of biomass low-temperature pyrolysis by coats–redfern method

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Abstract. Energy is one of the main sources of environmental pollution. In this regard, the world scientific community seeks to reduce its negative impact on human health and nature. To do this, some of the organic raw materials, which are fuel for power plants, are gradually replaced by renewable resources, in particular - biomass. The combustion of biomass by traditional methods is accompanied by high operating costs, which leads to the conclusion that it is necessary to process it into energy-valuable products. The development of one of the most promising such directions - thermal processing - requires studying the thermophysical properties of biomass and studying its kinetics of decomposition. The aim of this work is to estimate the activation energy of thermal decomposition of biomass by the method of Coats-Redfern.

1 Introduction

As is known [1], the power engineering is one of the main sources of environmental pollution. In which connection, the power stations, used coal and brown coals, anthracites as fuel, are cause damage to the environment. According to the World Health Organization [1, 2], air pollution leads to premature deaths of several million people per year, what is comparable to the size of a large metropolis.

In this regard, developed and developing countries (for example, the USA, Finland, France, Canada, etc. [3]) announced a policy by gradually fossil organic fuels use reducing for energy production. Replacement of organic fuel should be carried out by increasing the share of renewable energy sources (RES), such as sun, wind, biomass, etc. The use of RES will increase the ecological purity of energy production; will reduce the external energy dependence of countries, which not have own fuel resources; will stimulates the development of local and regional production; will contribute to the development of the agro-industrial complex and creation of new jobs [4]. In 2015, 7.1% of electricity was generated on the basis of renewable energy (excluding hydropower) [5]. At the same time, the share of such output will increase to 20% by 2020 at the plan of the European Union [6].

Biomass is considered as one of the most important and promising RES, what is due to its ubiquity and large volumes of formation. It is recognized that biomass is neutral in the carbon dioxide circulation: when burning biomass, the same amount of carbon dioxide is

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formed, which was absorbed during her life as a result of photosynthesis. The sulfur is practically absent in biomass content, what ensures the low SO_x emissions at the time of its burning [7]. At present time, the share of biomass in the world fuel and energy balance is about 9.7% [5].

However, the burning of biomass by traditional methods is accompanied by a number of problems, which prevent its wide using in the energy sector. For example, the biomass in a natural state has a high humidity, which reaches to 30.4-79.7% [8], what leads to a low calorific value in terms of the operating state. In addition, such a high humidity of biomass leads to its caking, sticking during a transportation, and in winter – to freezing, what additionally complicates the process of transportation and unloading of raw materials [9]. Some types of biomass (for example, bran) are prone to slagging of heating surfaces during combustion [10], as a result of which the service life of the fuel-burning equipment is reduced and the cost of repair works is increased. The heterogeneous fractional composition of the biomass leads to a high value of the failure through the grate at layer combustion, increasing the losses with mechanical underburning (q_4) and thereby reducing the overall boiler efficiency. Thus, the energy use of biomass by traditional methods of combustion is accompanied by high operating costs, which prevents its widespread use as fuel.

The previous studies [11] are shown the prospects for thermal processing of biomass into energy-valuable products, such as high-calorific solid fuel, liquid biofuels or flammable gas. The combustion of these products, even by traditional methods, is highly efficient and requires significantly less cost than using of raw materials in their natural state.

The various studies of biomass thermal processing by physical experiment is a labour-intensive process required a large time and material resources. The construction of a mathematical model and the conduction on its basis of numerical studies is contributed to increasing of productivity and study economy. The development of model for thermal processing is required of study a large number of physical and chemical quantities, which necessary to obtain of reliable and adequate results, in particular the activation energy.

In this regard, the purpose of this paper is evaluation of biomass thermal decomposition activation energy by Coats-Redfern method.

2 Material and methods

Several samples of biomass were considered in this work: straw, chips from various types of wood and low-lying peat (Sukhovskoe deposit, Tomsk region). The samples were previously dried to air-dry state (Table 1).

Table 1. The humidity of researched biomass samples

Biomass	Straw	Chips	Peat
Humidity W ^a , %	8.5	8.5	11.5

The differential thermal (DTA) and thermogravimetric (TGA) analyzes with thermal analyzer STA 449C Jupiter (Netzsch, Germany) were performed to evaluation of the activation energy. The samples were heated at a rate of 10°C per minute (averaged heating rate according to the generally accepted standard of fuels semi-coking of ISO 647-74), the temperature range of the experiment was from 20°C to 600°C. The weight of samples was 50 mg. Analyzes were performed in an inert medium (helium) in order to exclude the influence of oxidative reactions on the results of the study.

The activation energy was calculated by the method of A. Coats and J. Redfern [12]. The method is based on the hypothesis about that the single-stage first-order reactions, submitted to the Arrhenius laws occur, are proceed at the time of solid fuels thermal

decomposition. The activation energy equation according to Coats-Redfern has the following form:

$$\ln \left[\frac{-\ln(1-\alpha)}{T^2} \right] = \ln \left[\frac{AR}{\beta E_a} \left(1 - \frac{2RT}{E_a} \right) \right] - \frac{E_a}{RT} \quad (1)$$

where $\alpha = \frac{m_0 - m_i}{m_0 - m_k}$

- m_0 – mass of reaction start, kg;
- m_k – mass of reaction finish, kg;
- m_i – mass in the period of i , kg;
- α – conversion level;
- T – temperature of heating, K;
- A – pre-exponential coefficient;
- R – gas constant, J/(mole·K);
- E_a – activation energy, kJ/mole;
- β – reaction rate, K/min.

Further, the dependency diagram $\ln(-\ln(1-\alpha)/T^2)$ from $1/T$ is constructed in accordance with the formula for the first-order reaction, its result is a straight line, the slope of this line is E_a/R , and the intersection point of this line with the axis $\ln(-\ln(1-\alpha)/T^2)$ is equal to $\ln(AR/\beta E_a)$.

3 Results and discussion

The results of DTA and TGA for researched samples are shown in Fig. 1. It can be seen that during heating from 20 to 140-150°C there occurs moisture evaporation from the samples, which was accompanied by an endothermic peak. The thermal decomposition of biomass starts at a temperature of 160-180°C and accompanied by its mass decrease (Fig. 1, TG curve). The temperature 240°C was the beginning for main exothermic reactions, terminating at 580°C, for straw and chips. With the thermal decomposition of peat samples, two exothermic peaks were observed: first – 200-330°C, second – 380-560°C.

The graphical construction of the Coats-Redfern equation is shown in Fig. 2. It can be seen that the biomass samples decomposition proceeds in two stages. The calculation of the activation energy for each stage on dependence of biomass type is given in Table 2.

Table 2. Activation energy of thermal decomposition

Biomass	Activation energy E_a , kJ/mole		Start of decomposition t_0 , °C	Transition temperature t_i , °C	Finish of decomposition t_k , °C	Pre-exponential coefficient, c^{-1}	
	I	II				I	II
straw	74.2	29.1	162	350	595	5919	8213333
chips	85.0	11.7	180	366	575	61773	5480814
peat	68.9	18.9	180	340	565	2537	3629208

The analysis of obtained data (Table 2) is shown that the activation energy for the first stage have a greatest value for the sample of chips, a smallest – for sample of peat. At the second stage, the straw has a greatest value of the activation energy, and the chips – a smallest. Considering that the activation energy is the energy, which necessary for breaking bonds between molecules, the most energy-consuming raw material for processing (including both stages) is straw, and less energy-consuming – peat.

The obtained data are accorded with the results of previous studies by other authors [13].

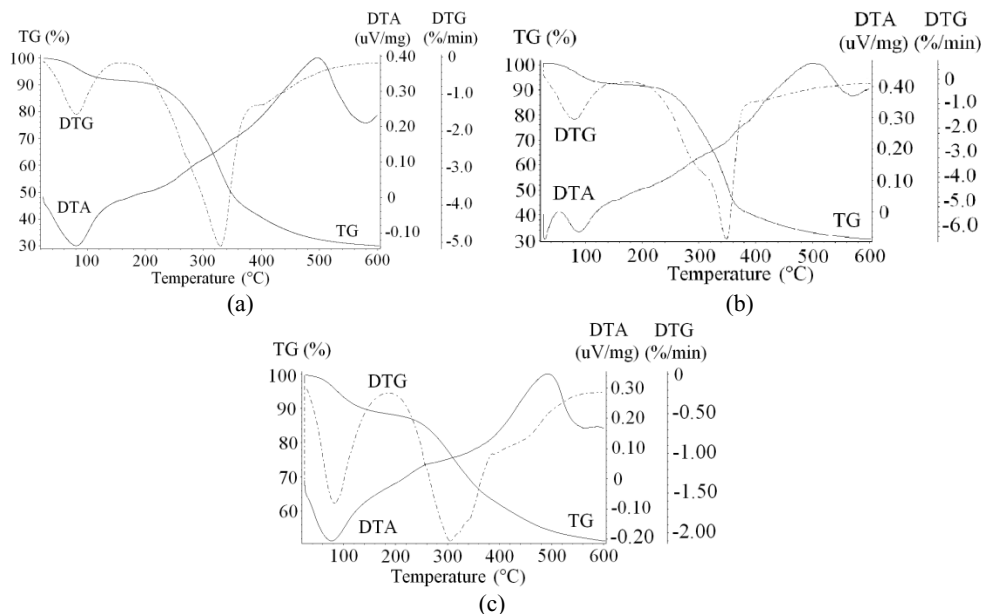


Fig. 1. Curves of DTA analysis: a – straw, b – chips, c – peat.

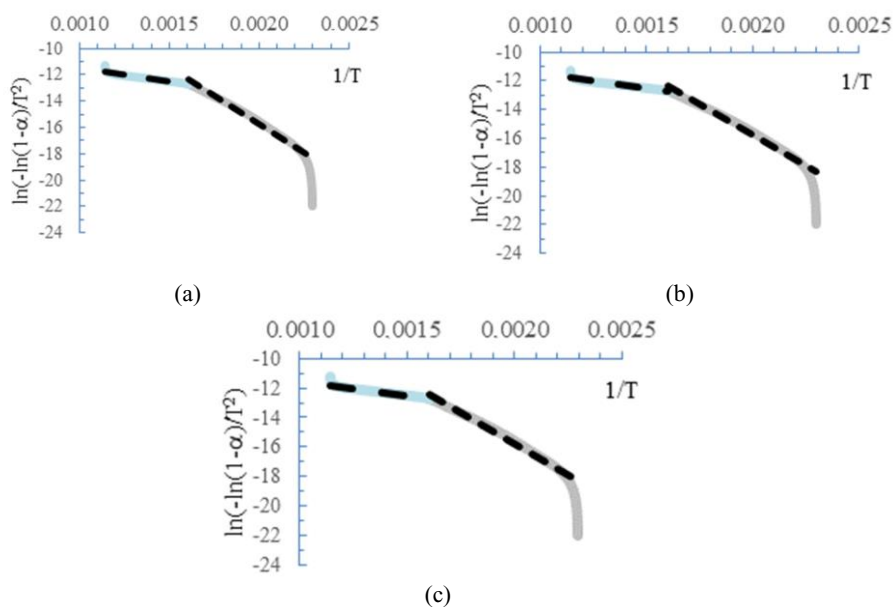


Fig. 2. The dependency $\ln(-\ln(1-\alpha)/T^2)$ from $1/T$: a – straw, b – chips, c – peat.

4 Conclusions

The results of DTA and TGA for biomass samples of several types (straw, chips and peat) are given in this paper. The activation energy of the biomass thermal decomposition is calculated with using of the Coats-Redfern method, developed for evaluation of the thermal analysis results. It has been established that the thermal decomposition of biomass proceeds in two stages: the first stage start at temperature 162-180°C and finish at temperature 340-

366°C; the second stage – from 340-366°C to 565-595°C. Wherein, the most energy-consuming raw material for thermal processing is straw and less energy-consuming is peat.

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