INFLUENCE OF PARTICLE SIZE AND DENSITY OF PELLETED SAMPLES OF FOREST FUEL ON THERMOKINETIC CHARACTERISTICS OF PYROLYSIS AND OXIDATION

by

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This paper presents the results of experimental studies of thermokinetic characteristics of pyrolysis and oxidation of pine needles, taking into account the influence of particle size and density of forest fuel in pelleted samples. The sample densities range within 206-955 kg/m^3 (i.e. from typical sample densities to average ones for pressed pelleted samples), and the component particle sizes amount to 60-140 μm. The range of studied temperatures is 20-1000 °C. The particle size and density of the material are found to be important parameters that significantly affect the kinetics of pyrolysis. According to the results of measurements, the activation energy of needles pyrolysis is within the range of 22.8-113.8 kJ/mol, and that of oxidation corresponds to 134.7-211 kJ/mol. Three intervals with significantly different values of activation energy and pre-exponential factor are distinguished in the studied temperature range. Approximation expressions are formulated for the activation energies of pyrolysis and oxidation as functions of forest fuel particle sizes, sample density and temperature.

Key words*: forest fuel, thermogravimetric analysis, pre-exponential factor inert medium, oxidizing medium, activation energy*

Introduction

Since pyrolysis is an integral part of forest fuel combustion, its study is expedient with the view of development of mathematical models necessary to elaborate the existing and create the new technologies for suppression of flaming combustion and smoldering [1, 2] in effective fire control. To date, the analysis of thermokinetic characteristics of plant materials (mainly, different types of wood) is investigated in numerous papers, among which several of the most significant may be distinguished, in particular [3-8]. Cancellieri *et al*. [3] proposed the model, used in the analysis of conditions of the Mediterranean forest fire development. The experiments were carried out in laboratory and field conditions. The following forest materials were used: rockrose, heather, and pine. Thermokinetic parameters were determined using thermogravimetric (TG) analysis in the temperature range from 77-627 °C. The main achieved result of experimental studies [3] was the creation of a two-stage kinetic model. Similar studies [4, 5] were carried out without sacrificing the material structure, *i.e*. without specialized grinding

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and subsequent pelleting. The used samples were pine needles embedded in skeleton baskets. In [4, 5] it was shown that thermokinetic characteristics significantly depend on the structure of forest fuel in the sample. The results of differential mass spectrometric thermal analysis aimed at studying the thermal decomposition at a high heating rate (150 °C per second) of powders (with particle sizes of 0.17-0.48 mm) based on forest fuel material (tree bark, branches, needles, cones) were given in [6, 7]. The values of thermokinetic constants and decomposition rates were obtained.

In [9] the established regularities of pine needles mass loss for different heating rates (5, 10, 15 and 20 °C per minute) in inert and oxidizing media were considered. It was found that for a detailed description of the mass loss rate it was necessary to take into account three reactions when describing pyrolysis in an inert medium. The TG analysis of needles was undertaken in [10] for inert and oxidizing media. Mass loss rates depending on temperature were recorded. Emission of the following gases was found in the thermal decomposition of pine needles: CH_4, CO, CO_2, NO, and water vapor. Scanning calorimetry of thermal degradation of pine needles in the air was carried out in [11]. In [11] it was shown that the proposed model can be used in predicting conditions for the suppression of combustion of pine needles.

The influence of particle size on the thermal decomposition of olive was studied in [12]. The TG analysis was realized for particles with sizes of 0.5-2.8 mm. It was revealed that the mass loss rate, emissions of CO and CO_2, and the weight of residual ash depend on the material particle size. It was concluded that the samples with a particle size of less than 0.5 mm were the most reactive. The characteristics of the forest fuel components (such as density and particle size) were proved to influence the rate of physical and chemical processes and play an important role in predicting conditions and characteristics of forest fuel burning [3,12,13]. It was concluded that in this regard, the study of thermokinetic characteristics of components close to forest cover is necessary for mathematical modelling of forest fire propagation. In [14] thermophysical and thermokinetic characteristics of pine needles, birch leaves, maple, linden, aspen, birch branches and bark, straw, grass and mixtures of forest fuel materials were determined in a wide temperature range. In particular, for pine needles in inert and oxidizing media, the effective activation energy values were 61 kJ/mol and 154.3 kJ/mol, respectively. On the basis of the results of the mentioned studies, it is possible to formulate a hypothesis that any kinetic models (schemes) developed for forest fuel samples with different bulk density reflect not only the properties of the materials themselves (leaves, needles, and branches), but also the conditions of heat transfer in the fillings. To substantiate this hypothesis, there is a need in experimental studies of the effect of the particle size of the forest fuel components and the backfill density on the thermokinetic characteristics (activation energy and pre-exponential factor) of pyrolysis and oxidation of forest fuel.

The aim of this research is to experimentally determine the ranges of values of the main thermokinetic characteristics of pyrolysis and oxidation of typical forest fuel materials and to analyze their dependences on the sample density and particle sizes. In the first approximation, it is practicable to perform this analysis using needles as an example, since this type of forest fuel is considered to be the most fire-hazardous [15, 16]. Authors in [15, 16] designed risk index maps used as a tool to prevent forest wildfires. According to the data obtained, pine needles represent the greatest fire hazard. This forest fuel is kept alive on tree branches for 2-3 years, and in the case of young pine forests – up to 4 years. The increased fire hazard of needles is connected with the increased content of organic substances, which are characterized by high fire hazard indicators – turpentine, resins and essential oils [15, 16]. Needles have a high calorific value, low ash content and density (compared to branches and leaves) and high values of

the area-to-volume ratio, which promotes the propagation of combustion [15, 16]. In addition, for this type of forest fuel, quite a lot of experimental data on thermokinetic characteristics have been obtained. The main experimental studies are cited previously. A comparative analysis of the established data with the results of these studies is deemed instrumental.

Experimental set-up, methods and materials

To determine the thermokinetic characteristics, different approaches are widely used, *e.g.* TG analysis, differential thermal analysis (DTA) and differential scanning calorimetry (DSC). The analysis is based on the use of thermal balance, continuously measuring the sample mass [17, 18]. The TG-curves serve to determine the mass loss during heating. The DTA is based on the registration of the temperature difference between the test substance and the inert sample of comparison due to their simultaneous heating or cooling [19]. On the DTA curve there are areas that correspond to the release or absorption of heat in the test sample relative to the reference one [20]. The DSC is the method for recording the difference in heat fluxes as a function of temperature and time [19, 21]. To date, synchronous thermal analysis has become widespread; it allows combining TG, DTA or DSC in one unit.

The present research uses the synchronous thermal analyzer Netzsch STA449F3, similar to the experiments of [14], for experimental determination of thermokinetic parameters of forest fuel. This instrument allows for measurements in inert and oxidizing media in the temperature range from 150-2400 °C. The results of such studies of pyrolysis kinetics are given in [6, 22-24]. One of the advantages of the device in comparison with [6, 22-24] is a wider temperature range of measurements.

When conducting thermal analysis, it is important to make a reasonable choice of the sample particle size, sample weight, and experimental conditions (heating rate, measurement medium (inert, oxidative, reducing, static, or dynamic, *etc.*). For example, in [25], the optimal range of particle sizes for forest materials (63-125 μm) and the heating rate of 10 °C per minute (the heating rate corresponds to the real rates of the forest fuel thermal decomposition) are determined. From the data analysis in [3, 26-29], it is possible to distinguish the following ranges: 60-150 μm for the size of components and 200-955 kg/m^3 for the density of the sample material.

In this paper, pine needles were selected as the test material. The preparation of the samples included preliminary grinding of the components in a high speed rotary mill *Pulverisette 14*. The experiments were realized with varying the particle size of needles and density of the pelleted sample of the material. Particle sizes were 60, 100, and 150 μm, and bulk density is 206 kg/m^3. To study the effect of density, forest fuel powder was pressed under different pressures. The height and diameter of the samples were measured by a micrometer. Three measurements were carried out, and their results were averaged. The systematic measurement error of the sample sizes was 0.005 mm. Samples from the compressed material were weighed on laboratory scales, and their density was determined to be 736 kg/m^3 and 955 kg/m^3. The density measurement error did not exceed 1%. For measurements, a sample of the test material (powder) with a density of 206 kg/m^3 or a pellet of compressed material with densities of 736 kg/m^3 and 955 kg/m^3 and mass of 50.5 mg was placed in the crucible of the device. Thermal analysis was carried out under the following conditions [25]: heating temperature from 27-997 °C at a rate of 10 °C per minute in argon and oxygen with a gas-flow rate of 100 ml per minute. The temperature values in the chamber varied by no more than 10 °C. The kinetic parameters of pyrolysis (activation energy and pre-exponential factor) were calculated by the method from [30].

Results and discussion

Figure 1 demonstrates TG curves, obtained in experiments in an inert medium. The influence of this factor on the results of TG analysis is shown. Apparently, the particle size affects the reaction rate, which in turn affects the nature and form of the registered curve. Differences in the values of mass change and mass loss rate are noted. The peak of the mass loss rate corresponds to a temperature of 351 °C. After 550 °C, the rate of mass loss decreases. In fig. 1(a), it is also be seen that the rate of mass loss increases with increasing particle size, the same results were obtained in [12, 14, 31]. At the same time, there are practically no differences in the width and position of the temperature intervals. The residual mass of needles with particle sizes of 140 μm is found to be less by 14.3% than at 60 μm. Figure 1(b) illustrates TG curves in an inert medium for needle samples with varying sample densities. It may be noted that the peak of the mass loss rate shifts to higher temperatures as the sample density increases. The figure also shows that for densities of 736 kg/m^3 and 955 kg/m^3 TG curves are superimposed on each other and the peak rate of mass loss differs little. At the same time, a rather sharp increase in the maximum rate of mass loss for a density of 206 kg/m^3 is noticeable, fig. 1(b).

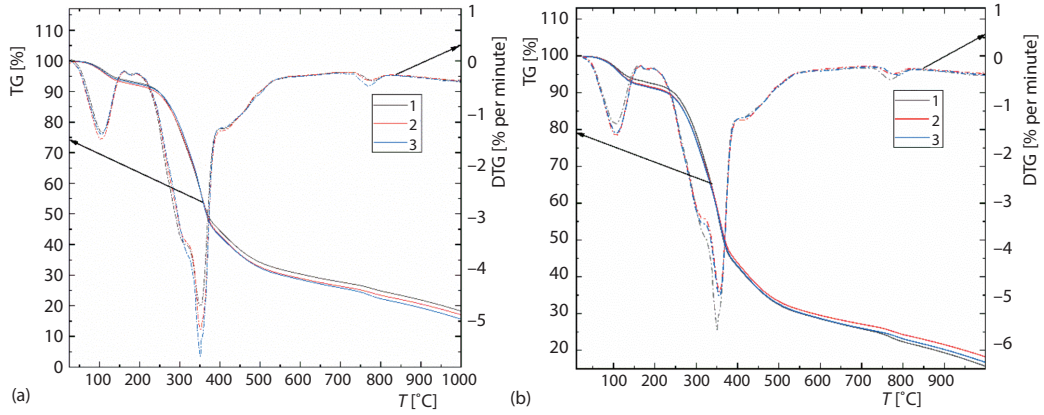

Figure 1. The TG curves of mass loss (TG) and mass loss rate (DTG) in inert medium for needle samples at particle sizes; (a) *1 – 60 μm, 2 – 100 μm, 3 – 140 μm,* **and with particle sizes of about 140 μm and varying density of the pellet sample and (b)** *1 – 206 kg/m^3, 2 – 736 kg/m^3, 3 – 955 kg/m^3*

Pyrolysis reactions can be described by different schemes [9, 29], in particular, by one equation, or several reactions may be presented. However, since pyrolysis may be accompanied by a large number of intermediate reactions that cannot be considered numerously, some of these reactions (or processes) are usually neglected. Mainly, several stages are distinguished (with a characteristic temperature range for each of them). One-stage involves one or more reactions. The first stage is characterized by the release of moisture from the samples (dehydration). The next stage is accompanied by such complex reactions as the formation of gaseous products, temperature 200-550 °C. At the third stage there is decomposition reaction of mineral substance, temperature 550-900 °C, [32].

In [10], the following reactions are distinguished for pine needles: dehydration occurs at the first stage, and it is followed by thermal decomposition reactions. The second reaction is the anaerobic conversion of dry needles into coal and gaseous products. The third reaction runs with oxygen, dry needles are also converted into coal, gaseous products are formed, and oxidized pyrolyzate is obtained. As a result of the fourth reaction, coal turns into ash with

the formation of oxidation products. Each of these reactions has its own kinetic parameters (the activation energy and the pre-exponential factor) which are calculated using the Arrhenius equation [33]. When calculating the activation energy and the pre-exponential factor, the experimental data of TG were linearized. Kinetic constants were determined graphically for each temperature area. To do this, a graph was plotted in the co-ordinates $\ln(k) = f(1/T)$. Here k is the mass loss rate of the sample and T is the temperature. The activation energy was determined from the equation on the inclination angle of the corresponding straight line and on the point of intersection of the latter with a vertical axis, the value of pre-exponential factor was found.

Due to the fact that the kinetic parameters k and E were calculated from the inclination angle tangent, the error in determining the activation energy and the pre-exponential factor ultimately depended on the accuracy of the approximation curve. The approximation accuracy may be determined by the average error of the approximation, that is, by the deviation of the calculated averages from the actual values corresponding to each experiment. In this paper, the maximum deviation of the approximation value from the experimental value was 21.7-28.3%. As a consequence, the possible range of permissible deviations of activation energies relative to the average was 14.6-21.9 kJ/mol and that of the logarithm of the pre–exponential factor was 1.8-5.1.

The experimental thermokinetic parameters of forest fuel decomposition in inert and oxidizing media at varying particle sizes are given in tabls. 1 and 2. Table 1 shows that the larger is the particle size, the higher the activation energy and the pre-exponential factor are for second and third areas, similar results were obtained in [13]. It is very propable that the intensity of interaction of particles with an oxidizing agent (oxygen) decreases with an increase in their size. Thus, this prevents the early onset of decomposition. It is also seen that in the first area, the activation energy is increased for the smallest particle size. It can thus be suggested that this is connected with the agglomeration of particles of that size in this temperature range that, in turn, increases the activation energy. A similar result was obtained in [32].

In general, the first area is characterized by the smallest change in the activation energy (4.8%), while the second and third areas show much larger changes in this parameter (19.5% and 23.1%). Comparing the results presented in tabs. 1 and 2, it can be seen that the activation energies of thermal decomposition in an oxidizing medium are higher than those for decomposition in an inert medium. Moreover, it is clearly seen from tab. 2 that the activation energy of thermal decomposition is maximum for particles of the smallest size (60 μm), which can also be explained by the effect of agglomeration of small particles described previously.

Table 3 shows that the residual mass of larger particles is smaller than that of smaller particles. A smaller amount of residual ash (2.97%) is formed from the forest fuel with a particle size of 140 μm. These results correlate satisfactorily with previous studies of the effect of particle size on biomass combustion [14].

Table 1. Experimentally determined thermokinetic characteristics of needles pyrolysis in inert medium at varying the particle size and sample density of 206 kg/m^3

Particle size [μm]	E_1 [kJmol^{-1}]	k_1[s^{-1}]	E_2 [kJmol^{-1}]	k_2 [s^{-1}]	E_3 [kJmol^{-1}]	k_3 [s^{-1}]
	Area 1 (450-540 °C)		Area 2 (540-650 °C)		Area 3 (650-900 °C)	
60	113.8	$8.12\cdot10^{10}$	82.93	$4.12\cdot10^{6}$	38.5	1.154·10
100	107.1	$1.15\cdot10^{10}$	85.06	$5.21\cdot10^{6}$	44.22	$2.28\cdot10^{2}$
140	108.3	$1.125\cdot10^{10}$	103	$1.73\cdot10^{8}$	50.08	$6.25\cdot10^{2}$

Table 2. Experimentally determined thermokinetic characteristics of needles oxidation at varying the particle size and sample density of 206 kg/m^3 (450-900 °C)

Particle size [μm]	E [kJmol^{-1}]	k [s^{-1}]
60	197.2	$1.02 \cdot 10^{13}$
100	134.7	$6.26 \cdot 10^{8}$
140	183.8	$2.11 \cdot 10^{8}$

Table 3. Experimentally determined values of residual mass in inert and oxidative media at sample density of 206 kg/m^3

Particle size [μm]	Residual mass [%]	
	Inert	Oxidative
60	18.29	4.04
100	17.09	3.42
140	15.67	2.97

The experimentally registered effect of reducing the residual mass of needle samples as a result of pyrolysis with increasing particle size of the material in the pelleted samples is most likely due to the established features of the physical and chemical processes occurring during pyrolysis of needles. After pressing the samples from the particles of ground needles, porous structures with different characteristic pore sizes are formed: the larger is the particle size, the larger the size of each individual pore is. During heating and subsequent thermal decomposition of pelleted samples, several physical and chemical interactions of solid products of pyrolysis of needles (coke) with air oxygen occur. Air oxygen relatively easily penetrates into large pores corresponding to large sizes of needles particles before pelleting. As a result, there is oxidation of coke carbon form gaseous CO. In the heating and pyrolysis of samples made from large particles of needles (for example, 140 μm), large pores (closed at the initial stage of heating) open, and oxygen easily diffuses to the surface of the carbon coke. At small pore sizes, part of them opens, and the described reactions of air oxygen with carbon of solid products of needles pyrolysis do not occur in some part of the pores. So, the output of gaseous pyrolysis products (CO and CO_2) is reduced (compared to large-pore samples).

Tables 4-6 present the values of thermokinetic characteristics, determined in experiments with varying density of the forest fuel sample in inert and oxidizing media for three temperature ranges (areas). It is clear from tab. 4 that as the sample density increases from 206 kg/m^3 to 955 kg/m^3, the activation energy decreases significantly in the first and third areas. In particular, for the first area the change is 24.6%, for the second it is 4.4% and for the third it equals 40.2%. These experimental results give grounds for formulating the conclusion on the relation of the kinetic characteristics of the forest fuel decomposition the conditions of heat transfer in the material. A several times increase in the density of the sample material essentially leads to a decrease in porosity and, consequently, an increase in the effective thermal conductivity of the material. As a result, high density samples warm up much faster than low density samples. Therefore, the pyrolysis of needles in identical heating conditions is faster as well. These regularities are manifested in the processing of experimental results and consist in changing the numerical values of the activation energy of pyrolysis of needles.

Table 4. Experimentally determined thermokinetic characteristics of the needles pyrolysis in an inert medium at particle sizes of about 140 μm and varying density of the pelleted sample

Sample density [kgm^{-3}]	E_1 [kJmol^{-1}]	k_1 [s^{-1}]	E_2 [kJmol^{-1}]	k_2 [s^{-1}]	E_3 [kJmol^{-1}]	k_3 [s^{-1}]
	Area 1 (450-540 °C)		Area 2 (540-650 °C)		Area 3 (650-900 °C)	
206	108.3	$1.125 \cdot 10^{10}$	103	$1.73 \cdot 10^{8}$	50.08	$6.25 \cdot 10^{2}$
736	88.66	$1.18 \cdot 10^{8}$	106.7	$3.25 \cdot 10^{8}$	22.85	5.26
955	81.62	$9.5 \cdot 10^{7}$	98.49	$6.75 \cdot 10^{7}$	29.9	16.05

Table 5. Experimentally determined thermokinetic characteristics of oxidation at particle sizes of about 140 μm and varying density of the pelleted sample (450-900 °C)

Sample density [kgm^{-3}]	E [kJmol^{-1}]	k [s^{-1}]
206	183.8	$2.11 \cdot 10^{8}$
736	211	$2.14 \cdot 10^{14}$
955	185.2	$5.6 \cdot 10^{12}$

Table 6. Experimentally determined values of residual mass in inert and oxidizing media at the size of needles particles of about 140 μm

Sample density [kgm^{-3}]	Residual mass [%]	
	Inert medium	Oxidizing medium
206	15.67	2.97
736	18.24	3.91
955	16.71	3.12

Comparison with data of other researchers is important for assessing the reliability of the results. These experimental data are provided in [6, 22-25, 30, 32]. The thermokinetic characteristics of forest fuel obtained earlier are presented in tab. 7 [6, 22-25, 30, 32]. In [6] the characteristics of thermal decomposition of forest fuel were compared at different heating rates (0.17 °C per second and 150 °C per second) using the method of differential mass spectrometric thermal analysis. The powder of forest material was prepared in a mortar and sieved. The particle size of the investigated powder was 0.17-0.4 mm. Before the study, the powders were not dried. Thermal decomposition was carried out on the analyzer TG/DSC STA409PC. The experiments were realized in inert (helium) and oxidizing (helium/21% oxygen) media. The weight of the sample (powder) was 4 mg. The heating rates were 10, 20, 30, 40, and 50 °C per minute. It was found that with increasing heating rate, the pyrolysis decomposition rate constants increase. The pyrolysis kinetics for live and pre-dried fragments was studied in [22]. Experimental studies were performed in a TG analyzer under inert conditions for five heating rates (10-30 °C per minute). The average activation energy for pine needles was 183.4 kJ/mol. An increase in the activation energy for live samples in comparison with forest litter was found. This increase was associated by the authors with physiological reasons: living plants try to retain moisture, so, evaporation requires more energy. In [23] kinetic characteristics were obtained for pyrolysis of plant samples using the GSCRM global one-component reaction model. The activation energy for pyrolysis of leaf samples was found to be within 43-80 kJ/mol, and for stems it was in the range of 84-110 kJ/mol. The research [24] presents the results of experi-

Table 7. Famous kinetic parameters of thermal decomposition of forest fuel in inert and oxidizing media

Forest fuel	E [kJmol^{-1}]				k [s^{-1}]	
	Inert medium					
Pine branches (0.17-0.4 mm) [6], heating rate 150 K/s	68.1				6.1	
Pine branches (0.17-0.4 mm) [6], heating rate 0.17 K/s	167.6				10.6	
Pine bark (0.17-0.4 mm) [6], heating rate 150 K/s	55.6				5.2	
Pine bark (0.17-0.4 mm) [6], heating rate 0.17 K/s	184.3				12	
Needles (0.17-0.4 mm) [6], heating rate 0.17 K/s	164.3				10.2	
Grass [22]	145.4				$3.5\cdot10^{8}$	
Long-needle pine [22]	167.4				$4.4\cdot10^{11}$	
Pine [23]	86.31				$8.07\cdot10^{4}$	
Needles [34]	291.5				–	
	Oxidative medium					
Pine branches (0.17-0.4 mm) [6], heating rate 150 K/s	93.2				7.2	
Pine branches (0.17-0.4 mm) [6], heating rate 0.17 K/s	133.7				5.8	
Pine bark (0.17-0.4 mm) [6], heating rate 150 K/s	73.1				5.6	
Pine bark (0.17-0.4 mm) [6], heating rate 0.17 K/s	–				–	
Forest fuel	Area 1		Area 2		Area 3	
	E_1 [kJmol^{-1}]	k_1 [s^{-1}]	E_2 [kJmol^{-1}]	k_2 [s^{-1}]	E_3 [kJmol^{-1}]	k_3 [s^{-1}]
Lignite (38 μm) [32]	53.11	$4\cdot10^{8}$	200.74	$2.9\cdot10^{9}$	422.49	$3.4\cdot10^{19}$
Lignite (150 μm) [32]	48.24	$1.7\cdot10^{3}$	197.66	$2.2\cdot10^{9}$	517.2	$2.7\cdot10^{24}$
Lignite (2360 μm) [32]	41.03	5.4	151.2	$5.2\cdot10^{6}$	–	–
Pine brunches (<75 μm) [14]	207.43	$3.1\cdot10^{7}$	45.67	$1.7\cdot10$	33.82	2.71
Pine brunches (75–150 μm) [14]	232.21	$2.02\cdot10^{8}$	55.27	$4.2\cdot10$	32.78	2.71
Pine brnches (150–300 μm) [14]	246.68	$7.2\cdot10^{8}$	67.25	$1.26\cdot10^{2}$	33.52	2.71
Pine needles (<75 μm) [14]	178.74	$3.01\cdot10^{6}$	43.14	$2.2\cdot10$	34.64	3.89
Pine needles (75–150 μm) [14]	188.51	$8.1\cdot10^{6}$	49.19	$3.9\cdot10$	34.34	4.26
Pine needles (150–300 μm) [14]	184.43	$4.9\cdot10^{6}$	52.46	$5.9\cdot10$	34.57	3.706

mental studies of pyrolysis of wood wool and granules of eucalyptus wood. The influence of the heating rate and particle size on the thermal decomposition characteristics and parameters was studied in a TG analyzer in nitrogen. The average size of the granules was 8 mm in diameter and 25 mm in length. The wood wool was 20 mm wide and 25 mm long. The heating rates were 5, 10, and 15 °C per minute. It was revealed that the particle size was a key factor, significantly determining the pyrolysis rate. It was noted that the sample with larger particles reacted more slowly than the material with smaller particles. It was concluded that the particle size may be

the cause of displacement of the characteristic temperatures on the TG and DTG curves due to a decrease in the rate of heat and mass transfer within a larger particle. Similar regularities were registered in the present research in the analysis of the influence of forest fuel particle sizes on the kinetics of pyrolysis.

The obtained values of pine needles activation energies are comparable with the results presented in [6, 13]. Deviations of the results do not exceed 30-45%. They are due to different conditions of measurements. For example, in [13] before the tests, the samples were stored in the furnace for 48 hours at a constant temperature of 85 °C. In this study, pre-drying of the samples was not carried out in order to comply with the conditions of the forest fuel location in the forest. In [13] the activation energies were presented for a group of particles (for example, for a wide range of particle sizes: 75-150 μm and 150-300 μm).

The differences may also be related to different heating rates, which significantly affect the kinetics of pyrolysis [6, 13]. In particular, in [13], measurements were carried out for a rate of 2 K/s, in [6] – for a rate of 0.17 K/s, and in this paper the heating rate was 10 K/s (it corresponds to the real conditions of thermal decomposition of the forest fuel when combustion propagation). In [5], when comparing the results for inert and oxidizing media, the decomposition rate constant was found to be higher in an oxidizing medium than that in an inert medium at a low heating rate (0.17 K/s) but lower at a high heating rate (150 K/s). These conclusions correlate with the results obtained in this work – an increase in the values of the activation energy and pre-exponential factor in an oxidizing medium.

The difference in the results and a rather wide range of thermokinetic constants (activation energy and pre-exponential factor) may also be due to the characteristics of the sample: size, weight, shape, variety of forest material [22-24], as well as differences in the initial data, in particular, material moisture and density. The aforementioned factors could influence the type of TG curves, and, as a consequence, the reproducibility of the results.

Conclusions

Summing up the experimental studies and comparative analysis performed, we can draw several conclusions.

- Firstly, the particle sizes of the ground forest fuel, the kinetic characteristics of which are determined in experiments using compressed pelleted samples, significantly affect the calculated values of k and E.
- Secondly, such a relationship between the particle sizes in the samples and the kinetic characteristics in inert and oxidizing media cannot be a consequence of changes in the properties of the materials. Materials and their states at any size of the ground particles are identical.
- Thirdly, the main reason for the change in the values of k and E with varying particle sizes is the porous structure of the latter.
- Fourthly, this is connected with the fact that the thermal conductivity of heterogeneous media essentially depends on the proportion of components (in this case, these are forest material and air in the pores) even at low concentrations of the second component (typically, a mixture of air and products of pyrolysis and combustion). Therefore, the changes in the particle size do not lead to a change of thermokinetic characteristics of the materials, but change thermal conductivity of these materials. Consequently, the temperature in each layer of samples in each moment of time also changes. The latter entails changes in the kinetic parameters established in numerous experiments.
- Fifth, the most reliable results (from any experimental techniques) on the kinetic characteristics of pyrolysis and oxidation of forest fuel can be provided at the maximum possible

pressures of compacting the pelleted samples and the minimum sizes of particles that fill these samples.

- Analyzing the obtained results of thermal analysis of pine needles, it can be concluded that one of the main factors affecting the activation energy and the pre-exponential factor are the particle size and density of the material under study. According to the measurements, the activation energy of needles corresponds to the range of 22.8-113.8 kJ/mol for inert medium and 134.7-211 kJmol for oxidative one. The highest values of the activation energy have been registered in experiments with a sample density of 206 kg/m^3 and particle sizes of 60 μm, *i.e.* at the minimum considered density and the minimum dispersion of the forest fuel powder.
- Particle sizes have a significant impact on the mass loss rate in the range of 250-550 °C. Differences in particle size and density of needles cause unequal kinetics of thermal decomposition, which can be determined by the type of TG curves and by the difference in kinetic parameters (activation energy and pre-exponential factor). From the results of experimental studies it has been found that the density of the sample has a more significant effect on the thermokinetic characteristics than the particle size of the material in a limited range. A change in the activation energy by 4.8-33.3% with an increase in particle sizes from 60 μm to 140 μm, and a change in the activation energy by 4.4-40.3% with an increase in the density of the pelleted sample of forest fuel from 206 kg/m^3 to 955 kg/m^3 have been registered.
- The important results of the study are experimental values of the activation energy and pre-exponential factor affecting the thermal destruction of needles at different particle sizes and packing density. These results can be used to model the thermal decomposition of needles when forest fire spreading.

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Nomenclature

E – activation energy, [Jmol]
k – pre-exponential factor, [s^{-1}]
T – temperature, [K]

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