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An investigation of the calorific values of biofuel composites based on birch phloem and pine needles

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Abstract. The decomposition features of fuel pellets formed from birch phloem and its composites with the addition of pine needles were studied by methods of thermogravimetric analysis and calorimetry. The characteristic temperature ranges of thermal decomposition of pellets were identified. The rates of mass loss and lower heating values of thermal decomposition under air atmosphere conditions were evaluated. And the combustion indices of composite compositions were determined to identify the possibility of using such composites as alternative fuels.
Keywords: biofuels, pellets, birch phloem, pine needles, lower calorific value, thermogravimetric analysis.

1. Introduction

Modern logging technologies focus on harvesting trunks as the most valuable part of the wood. This leads to the fact that numerous wastes remain at logging sites. According to Rosstat statistics, waste from wood processing and the production of wood and cork products in the period from 2020 to 2022 averaged about 6 million tons [1].

Currently, the least used waste from the woodworking and forestry industries is phloem and needles. The bark consists of phloem (inner layer) and outer bark (outer layer). Phloem is a layer of tree bark with hydrophilic properties. As a percentage, the bark is about 8% of the trunk weight, and the needles are up to 15%. There are several options for recycling such wastes: by composting, using it in the production of biofuels or for landscape design application [2].

In this paper, we will consider a method for recycling birch phloem as the main component for the production of biofuel pellets with the addition of pine needles. In Europe and North America, pellets are increasingly used at thermal power plants as an additive to the main fuel, which is coal, which contributes to the development of the biofuel market [3].

The purpose of this work was to study the thermal transformation of biofuel pellets based on birch bark with the addition of pine needles.

2. Materials and methods

For the research presented in this paper, needles of Scots pine (*Pinus sylvestris L.*) and phloem of silver birch (*Betula pendula*) were used. The initial materials were mechanically ground using a rotational grinder, followed by manual fractionation (sieving) from 0.25 mm to 0.8 mm for wood phloem and from 0.2 mm to 0.25 mm for pine needles (needles). Biofuel pellets were formed using a PGR-10 laboratory hydraulic press at a pressure of 70 bar for all samples.

Thermal decomposition processes of the obtained biofuel pellets were studied using a Netzsch TG 209 F1 Libra thermogravimetric analyzer (Germany). This method of analysis involves continuous recording of the dependence of the change in sample mass on time and temperature. The experiment investigated samples of needles and phloem in an atmosphere of synthetic air (nitrogen EC 5.4 TC 2114-004-37924839-2016 (PTK “Cryogen”, Russia) volume fraction of N_2 not less than 99.9994% and oxygen VC 5.0 TC 2114-006-37924839-2016 (PTK “Cryogen”, Russia) volume fraction of O_2 not less than 99.999%) at an oxygen volume concentration of 20%. All measurements were performed under the following parameters: air flow rate 50 ml/min, heating range 25–900 °C, heating rate 10 °C/min. The mass of each sample was 10 ± 1 mg. The compositions for TGA can be seen in Table 1.

To determine the lower heating value of the mixtures of phloem and pine needles, an IKA C6000 calorimeter (Germany) equipped with an IKA RC2 basic thermostat (Germany) was used. In the experiment samples of pine needles, birch phloem, and their mixtures with mass fractions shown in Table 1 were used. The temperature of the water in the calorimeter before the start of the experiment was kept constant by a thermostat. During the experiment, a known amount of the sample was burned in an oxygen atmosphere (oxygen VC 5.0 TC 2114-006-37924839-2016 (PTK "Cryogen", Russia) volume fraction of O_2 not less than 99.999%) in a calorimetric bomb immersed in a water jacket. The amount of heat released during the combustion of the samples is proportional to the change in the temperature of the water in the calorimeter, the known heat capacity of the entire system, and the mass of the sample. A preliminary calibration of the calorimeter was carried out using a standard substance — benzoic acid from the National Bureau of Standards (NBS-Standard Sample 39 J) with a known and guaranteed heat of combustion. To obtain reliable experimental data, three samples of each sample were investigated. Statistical processing of calorimetry data included determining the average value over three measurements and calculating the standard deviation using the Microsoft Excel data analysis package.

Table 1. Compositions of the obtained pellets (weight ratio).

Calorimetric study **Birch phloem:Pine needles**	**TGA** **Birch phloem:Pine needles**
1:0	1:0
10:1	5:1
7:1	10:1
2:1	15:1
1:1	20:1
1:5	0:1
1:7	
1:15	
0:1	

3. Discussion of the results

3.1. Calorific Studies

To evaluate the specific energy output of the pellets studied, experiments were conducted to determine the lower heating value of samples of birch phloem, pine needles, and their mixtures. Fig. 1 shows the results of the calorimetric study.

As seen from Fig. 1, there is no linear dependence of the lower heating value on the pine needle content in the sample. The value of the lower heating value of the sample made of pine needles corresponds to the data presented in [4]. Also, from the graph, it can be noted that the calorific value of pine needles is on average ~6.3% higher than that of birch phloem. A significant increase in the calorific value of the pellets is observed when the pine content is 40%. The calorific value of the obtained pellets is higher than that of commonly used firewood [5] and briquettes made from sawdust and shavings [6].

Thus, the use of fuel composites based on pine needles and birch phloem is promising for combustion at industrial power generation facilities without any costs for modernization and re-equipment of furnace equipment.

3.2. Thermogravimetric Studies

The obtained thermogravimetric (TG) curve of birch phloem decomposition, shown in Fig. 2A, reflects the sequence of physical and chemical processes occurring during heating. At the initial stage (up to 250 °C), a dehydration process takes place, during which moisture present in the samples evaporates [4]. At this stage, a gradual decrease in the mass of the sample is observed, with the mass of the pellet made of pure phloem decreasing by 6%, while the masses of the pine pellet and composites based on phloem and pine needles decrease by 9%. This is followed by the main stage (250–550 °C), at which intensive thermal decomposition of the organic components of the pellets begins. This process includes the thermochemical destruction of cellulose, hemicellulose, and other organic compounds present in the phloem and pine needles [4]. With further heating of the sample (from 550 °C), the behavior of the TG curve changes due to a decrease in the rate of thermochemical destruction.

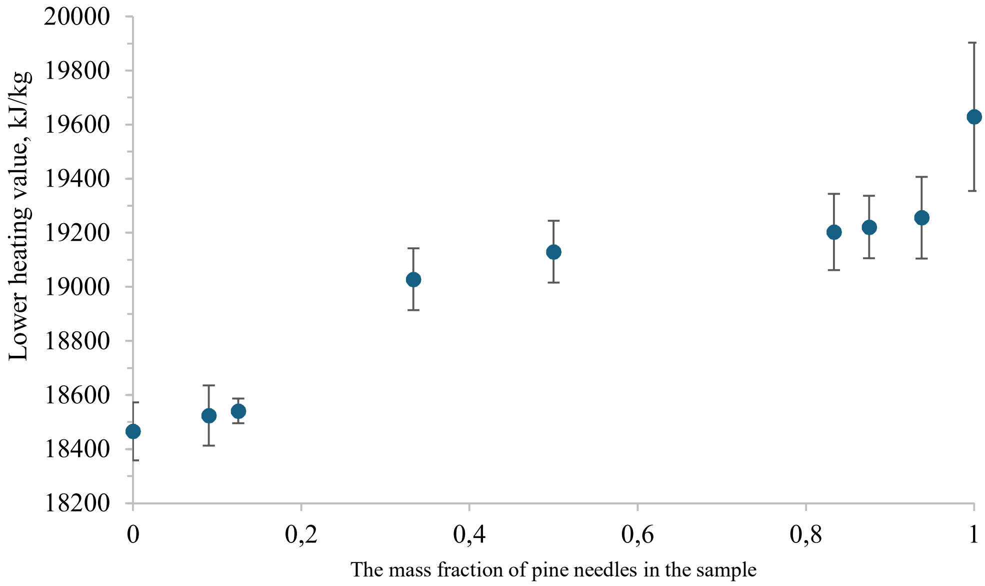

Fig. 1. Dependence of the lower heating value on the pine needle content in the sample.

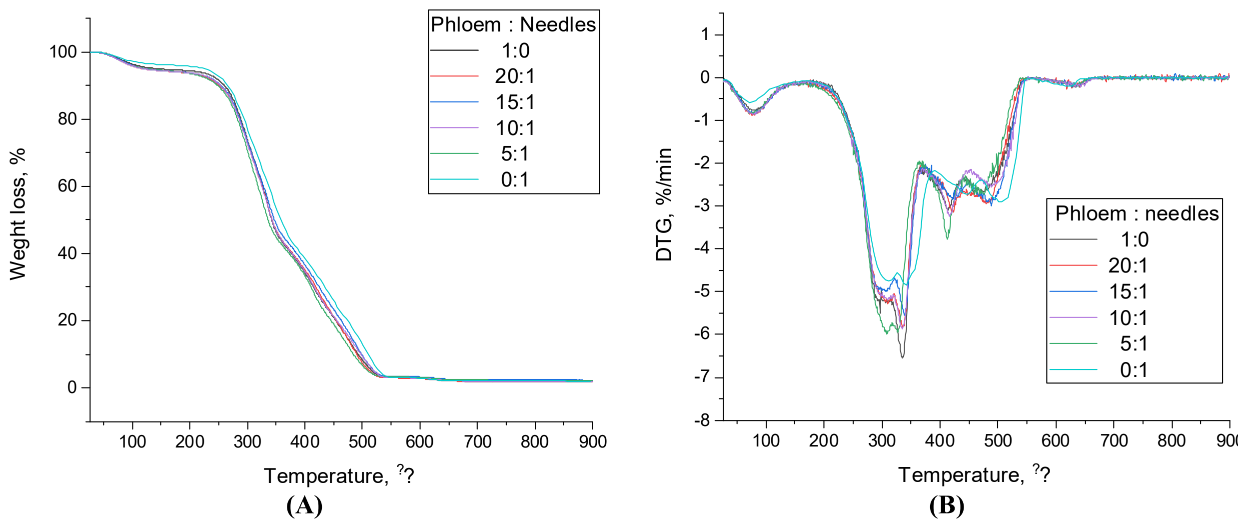

Fig. 2. Thermal decomposition of pellets from birch bark and pine needles in various ratios
(A) – TGA; (B) – DTG.

The obtained differential thermogravimetric (DTG) curve, shown in Fig. 2B, indicates that the decomposition process of the investigated pellets is divided into several stages. This process can be divided into six stages: (1) removal of moisture and easily volatile components at a temperature <150 °C, (2) decomposition of extractives at a temperature of 150–330 °C, (3) decomposition of hemicellulose occurs in the temperature range of 330–375 °C, (4) 375–460 °C, mainly decomposition of cellulose and lignin, (5) at a temperature of 460–560 °C, lignin decomposes, which has a relatively high carbon content compared to cellulose and hemicellulose and contributes to the formation of charring, (6) decomposition of the coke residue occurs at a temperature of 560–660 °C [4]. Table 2 shows the maximum temperatures for each of the six stages.

Table 2. Maximum temperatures of decomposition stages.

Composition of pellets Birch phloem: Pine needles	T_{max1}, °C	T_{max2}, °C	T_{max3}, °C	T_{max4}, °C	T_{max5}, °C	T_{max6}, °C
1:0	84.1	296.0	332.9	411.9	468.6	641.7
20:1	76.8	312.1	334.6	422.4	477.6	619.3
15:1	76.8	307.0	337.9	427.2	488.1	628.1
10:1	77.6	311.3	337.1	417.4	487.4	641.6
5:1	77.6	308.8	327.9	412.6	469.3	638.1
0:1	72.8	311.3	341.9	444.7	501.2	622.8

It can be seen from Table 2 that when pine needles are added to the pellet composition, the maximum shifts to a higher temperature region in the first stage of decomposition. The remaining decomposition process maxima did not show a clear correlation from the composition. The ash residue values for each sample are presented in Table 3. Table 3 shows that the ash content for all samples is approximately 2.5%.

Table 3. Ash residue values.

Pellet composition.Birch phloem: Pine needles	Ash residue, mass. %
1:0	2.30
20:1	2.47
15:1	2.58
10:1	2.56
5:1	2.18
0:1	1.97

3.3. Determination of Characteristic Combustion Indices

During thermogravimetric analysis, mass loss, time, and temperature were simultaneously recorded, which were used to compile the thermal decomposition profile. From the obtained data, thermal parameters were determined, including the ignition temperature T_i, burnout temperature $T_{b/o}$, and peak temperature T_{max}, to describe the characteristics of the combustion process. These parameters reflect the thermal behavior of organic matter during thermal decomposition and determine the end of combustion or burnout. These parameters were determined using the method described in [7].

The ignition temperature T_i is the lowest temperature of a substance at which the vapors above the surface of the combustible substance are released at such a rate that ignition is observed when exposed to an ignition source. The burnout temperature $T_{b/o}$ was defined as the temperature at which the DTG profile reaches the inflection point of the curve after the main decomposition stage [7], while the peak temperature T_{max} corresponds to the temperature at the maximum rate of weight loss. Based on the identified parameters, characteristic indices of the thermal decomposition process were determined according to the formulas presented in [8].

The ignition index D_i was determined from the following equation (1):

$$D_i = \frac{(dw/dt)_{max}}{T_i \times T_{b/o}}, \quad (1)$$

where $(dw/dt)_{max}$ is the maximum rate of mass loss. T_i is the ignition temperature, and $T_{b/o}$ is the corresponding burnout temperature.

The ignition index D_i reflects the ability of the fuel to ignite. The higher it is, the easier the fuel ignites.

Analyzing the obtained values of the ignition index of the obtained samples, it can be observed that the ability of the fuel to ignite is higher for pine needles than for birch phloem (see Table 4).

Also, to evaluate the combustion processes of pine needles and phloem in an atmosphere of synthetic air, the flammability index C was calculated. The flammability index C was determined from the equation (2):

$$C = \frac{(dw/dt)_{max}}{T_i^2}. \quad (2)$$

The flammability index indicates the trend of change in the TG curve from the ignition point to the maximum rate of mass loss and characterizes the reactivity of the sample under investigation at the moment of ignition, its combustibility. The higher the flammability index, the higher the combustibility of the fuel under these conditions.

According to the calculation results presented in Table 3, the combustibility of pellets from pine needles is higher than that of the studied composites and pellets from birch phloem. It can be noted that the flammability index C is approximately the same for all composites.

The burnout index $C_{b/o}$, the values of which are presented in Table 4, is a characteristic of the degree of burnout of the studied samples of birch phloem and pine needles and was determined according to the equation (3):

$$C_{b/o} = \frac{f_1 \times f_2}{\tau_0}, \quad (3)$$

where $f_1 = (m_0 – m_1)/\Delta m$ is the ratio of the change in the masses of the sample before and after ignition, depending on the composition and quality of the fuel; $f_2 = (m_0 – m_2)/\Delta m$ is the rate of change in mass after burnout; τ_0 is the burnout time; m_0 is the initial mass of the sample, m_1 is the mass of the sample at the moment of ignition, m_2 is the mass of the sample at the moment of burnout, $\Delta m = m_2 – m_1$.

$C_{b/o}$ combines the factors influencing the stability of fuel combustion and burnout in the flame: the higher its value, the better the combustion characteristics of the fuel.

For pellets made of pure components, there is a relatively large difference in the values of the burnout index: the combustion characteristics for pellets made of pine needles are better than for those made of birch phloem. However, evaluating burnout indices for their composites is more difficult.

The comprehensive combustion index S is a generalized characteristic of the combustion process. Its value can be used to assess the activity of the combustion process of the sample under investigation. A higher value of S indicates better combustion characteristics of the samples. The comprehensive combustion index S was determined according to the equation (4):

$$S = \frac{(dw/dt)_{max} \times (dw/dt)_{mean}}{T_i^2 \times T_{b/o}}, \quad (4)$$

where $(dw/dt)_{mean}$ is the average combustion rate.

Based on the calculated comprehensive combustion indices of phloem and coal presented in Table 4, it can be concluded that the combustion process of pine needles and all studied composites based on phloem and needles is more active than the combustion process of birch phloem.

The calculated indices of the combustion process of pellets from pure phloem, pure pine, and their composites are presented in Table 4.

From Table 4, looking at the column with the values of Δt, it can also be noted that pellets containing only birch phloem in their composition burn more slowly than pine pellets.

Table 4. Results of the calculation of characteristic combustion indices of pellets from pure phloem, pure pine, and their composites in atmospheric air.

Composition of pellets Birch phloem: Pine needles	T_i, °C	T_{max}, °C	$T_{b/o}$, °C	Δt, min	$(dw/dt)_{max}$, %/min	$D_i \cdot 10^{-5}$	$C \cdot 10^{-5}$	$C_{b/o} \cdot 10^{-3}$	$S \cdot 10^{-8}$
1:0	252.8	335.8	436.8	18.4	6.6	1.8	2.4	4.6	3.8
20:1	249.7	335.7	436.7	18.7	5.9	1.6	2.2	5.2	3.4
15:1	246.9	339.9	445.9	19.9	5.6	1.8	2.1	2.9	3.8
10:1	248.2	336.2	438.2	19.0	5.9	1.6	2.2	4.7	3.4
5:1	243.8	309.8	431.8	18.8	6.0	2.0	2.2	3.7	3.6
0:1	251.9	341.9	466.9	21.5	4.9	1.3	1.8	2.2	2.7

4. Conclusion

In this work thermogravimetric and calorimetric analysis were performed that allowed us to establish the main characteristics of the combustion processes of pellets based on birch phloem and pine needles. As a result of the calorimetric study, it was found that the lower heating value depends non-linearly on the content of pine needle particles in the mixture with birch phloem. It was also determined that the values of the lower heating value of pellets of all studied compositions are not lower than 18.4 kJ/kg, which is comparable to the woody combustibles used as fuel, therefore, it is possible to use the obtained pellets as a fuel. Although pure pine needles exhibit superior combustion characteristics, the primary objective of this study is the utilization of birch phloem. Therefore, for this purpose, biofuel compositions with 40–50% pine needle content are considered optimal, as the calorific value of pellets with pine needle content ranging from 40% to 90% remains relatively consistent.

Based on the thermal decomposition data of the obtained pellets, the ranges of the main combustion stages of the samples and their ash content were established as well as the temperatures of the decomposition rate maximums of the considered stages. Additionally, of the main combustion indices of the samples were estimated using the thermogravimetric data.

The studies carried out will allow for a more efficient and environmentally sustainable use of birch phloem and pine needles in the fuel industry.

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