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## Toxic elements, leachability, and the results of thermal analysis of woody biomass from the environment with varying degrees of pollution

### Introduction

Wood fuel (including wood for charcoal) includes coniferous and non-coniferous species. Roundwood is used as fuel for cooking, heating, or energy production. It provides wood obtained from the central trunks, branches, and other parts of trees (if harvested for fuel), whether round or split, and wood that will be used to make charcoal (e.g., in the pit and portable kilns), wood pellets, and other agglomerates. It also includes wood chips intended for use as fuel produced directly (i.e., in the forest) from Roundwood. It does not include charcoal, pellets, or other agglomerates (Eurostat and UNECE 2021). The share of households

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in national wood consumption was 65.1% (GUS – Główny Urząd Statystyczny 2021). The share of households in national energy consumption in 15 European Union countries in 2021 ranged from 11.4% (Luxembourg) to 28.1% (Croatia) (EUROSTAT 2023a).

Most residents in Poland burn coal alternately in the same furnace or separately in furnaces adapted to burn wood. Modern boiler design reduces the emission of harmful substances, meeting the required 5th class and ecodesign (PN-EN 303-5+A1:2023-05). In individual households in Poland and worldwide, hardwoods (hornbeam, birch, oak, and alder) are most commonly used. European Union (EU) countries used 25% of the wood for heating purposes in 2022 (EUROSTAT 2023b). It is expected that wood consumption will further increase in the future due to rapidly rising fossil fuel prices and increased demand by individual households. The agreement of the European Commission (EU), Council, and Parliament on March 30, 2023, regarding the Renewable Energy Directive, known as RED III, maintained the status of firewood as an important renewable fuel. The Renewable Energy Directive, which entered into force in November 2023, increases the 2030 renewable energy target to 42.5% by 2030, with EU countries aiming to achieve 45% (EU Official Journal 2023).

Biomass consumption also varies significantly among EU countries: from one ton per person in Malta to 8 tons per person in Denmark and Ireland, with Poland consuming approximately 3 tons per person. Effective use of wood for energy purposes is not an easy process despite appearances. Quality requirements for wood biofuels are regulated by international regulations that define the quality of solid biomass as fuel, its sources, and the size of biomass particles (Wieruszewski et al. 2022a). The properties of wood vary depending on the tree species, age, and habitat (soil and climatic conditions) (Wieruszewski et al. 2022b). Wood burning can be potentially harmful because wood smoke consists of a complex mixture of gases and fine solid particles, as well as suspended particulate matter (EPA, n.d.). In Poland, annual PM<sub>2.5</sub> emissions from non-industrial combustion sources, including the municipal and residential sectors, constitute 52% of the yearly national emission of this pollutant (Kubica et al. 2022). Wood smoke particles are not just soot, as the most toxic known chemical compounds – dioxins, furans, formaldehyde, toxic metals, and polycyclic aromatic hydrocarbons – can deposit on their surface (Bari et al. 2010; Lhotka et al. 2019; Madruga et al. 2019). Poland is one of the countries where the residential sector is the primary source of dust, benzo(a)pyrene, and other polycyclic aromatic hydrocarbons (PAH) emissions. The leading cause of this situation is the use of commonly available solid fuels, coal, and wood, for space heating, as well as for preparing hot utility water and cooking (Kubica et al. 2022).

Concentrations of some toxic elements, including Cd, Cr, Cu, Ni, and Zn in biomass ash, can be very high (Pastircakova 2004). The diverse properties of woody biomass make wood a complex and challenging fuel to exploit (Zajac et al. 2019). This mainly concerns old stoves, which are not covered by any standards regarding the amount of harmful substances emitted. The minimum requirements for wood-burning households are regulated by European Commission Regulation 2015/1185, which has been in force since 1 January 2022. It contains

requirements for the seasonal energy efficiency of space heating and, in terms of pollutant emissions, introduces new requirements that tighten CO, PM, OGC, and NO<sub>x</sub> emissions (Kubica et al. 2022). The solubility of inorganic components is strongly influenced by pH and redox potential, while the solubility of organic components is influenced by polarity and partitioning effects. Furthermore, the presence of other components may affect the solubility of inorganic components (Makowska et al. 2018). The leaching of various components from biomass ashes can be significant due to the presence of the soluble fraction, which can be up to 61% (Vassilev et al. 2014).

Biomass consists of three main components: cellulose, hemicellulose, and lignin (Chen et al. 2014). Pyrolysis conversion processes are important technological processes in biofuel production and energy recovery from biomass (Allouch et al. 2016). Carbon, hydrogen, oxygen, and nitrogen are primarily responsible for the formation of fuel from biomass, oxidizing during combustion to produce CO, CO<sub>2</sub>, and H<sub>2</sub>O through exothermic reactions (Cruz et al. 2020).

The main goal of this work was to assess the impact of the origin of woody biomass (anthropogenic environment and so-called ecologically clean) on the content of toxic metals (Cd, Pb, As, Cr, Zn, Cu, Hg, Sb, Ni, and Tl) in raw biomass and its ashes. The combustion of alder and birch was conducted under laboratory conditions at temperatures of 450–500 ± 15°C. The leaching of contaminants, which may occur as a result of exposure to natural infiltration or atmospheric precipitation during storage, was discussed. The research allowed for the assessment of the chemical composition of raw biomass (alder and birch). Moreover, its ashes are primarily for use in individual households and from an environmental safety standpoint during disposal. The thermographic analysis allowed us to determine the behavior of wood at wide combustion temperatures, how resistant it is to temperature changes, and at what point chemical and physical changes occur.

A novelty in the research is comparing wood taken from a polluted area and the so-called clean in terms of its use in low-temperature energy processes. The European Union Directive (RED III 2023) on promoting the use of energy from renewable sources recognizes forest biomass as a zero-emission fuel. Therefore, only forest biomass can be used as a renewable raw material.

## 1. Sampling procedures and analytical method

Two wood species were selected for the study – alder and birch, which are most commonly used in individual household hearths. The wood for the study was obtained in Poland, in the Małopolskie Voivodeship (heavily polluted area), and the “Bory Tucholskie” National Park (Pomorskie Voivodeship). Wood samples were taken from the area belonging to the Andrychów Forest District (Targanice and Rzyki forestry), which operates within the structures of the Regional Directorate of State Forests in Katowice. It is located in two voivodeships: Śląskie and Małopolskie.

Simultaneous thermal analysis involved the coupling of two research methods: thermogravimetry (TG) and scanning differential calorimetry (DSC) on the same sample. The thermogravimeter (NETZSCH model STA 449 F3 Jupiter) was used for the incineration. Approximately 10 mg of biomass was weighed into a ceramic crucible ( $\text{Al}_2\text{O}_3$ ), and the samples were heated in the temperature range of 35–1,030°C, at a rate of 10°C/min. in a neutral atmosphere (nitrogen) up to 600°C and in synthetic air for temperatures 600–1,030°C. The dynamic gas flow throughout the temperature range was 70 ml/min. Simultaneously, gas emissions were analyzed using the FTIR method. FTIR spectroscopy coupled with thermogravimetric analysis (TG-FTIR) was performed using a Bruker Alfa II FT-IR spectrometer directly coupled to the STA F3 system. Spectra were recorded every 16 s from 400 to 4,000  $\text{cm}^{-1}$ , with a resolution of 4  $\text{cm}^{-1}$ . The gas cell was maintained at a constant temperature of 200°C to prevent gas condensation. The results were analyzed using dedicated OPUS software. FT-IR absorption bands were identified as characteristic of certain gases and functional groups in gas products (Smith 1979; Stuart 2004; Brebu et al. 2013; Chen et al. 2014; Allouch et al. 2016). The analyses were carried out at the Silesian University of Technology in Gliwice.

Weight method in accordance with EN-ISO18122:2023-10 (2023) was used to determine ash content (A). Total moisture content (W) in selected wood species was determined using the oven-drying method in accordance with PN-EN ISO 18134-2:2017-03 (2017). The content of volatile parts ( $V^{\text{daf}}$ ) was determined using the weight method in accordance with PN-EN ISO 18123:2015-01 (2015), and the calorific value (Q) was calculated in accordance with PN-EN ISO 18125:2017-07 (2017). The concentration of potentially toxic elements (As, Cd, Pb, Cu, Zn, Ni, Cr, Tl, and Hg) was determined using the ICP-MS technique (mass spectrometry coupled with inductively coupled plasma – Perkin Elmer Sciex Elan 9000, Bureau Veritas Canada). The quality of analytical results was verified by using standard certified reference materials (STD CDV-1, STD V16, STD OREAS45H, and STD OREAS501D).

The PN-EN 12457-1 (2006) standard prepared samples of water extracts of ash for analysis in deionized water (pH = 7). The method of preparing water extracts of ash from burnt biomass consisted of extracting the sample with water, added in a proportion of 10 parts by weight of water per 1 part by weight of the sample – the extraction was carried out for 24 hours at room temperature, under periodic stirring conditions. After shaking and allowing the liquid to settle with the material, the resulting extract is filtered through filters (membrane filter with a pore diameter of 0.45  $\mu\text{m}$ ). Then the content of the respective component is determined in the resulting solution.

Analyses of anion leachability were performed according to PN-EN ISO 14911 (2002), PN ISO 14911 (1999), and PN-EN ISO 10304-1 (2009) standards. Analyses of toxic element leachability were performed according to PN-ISO 8288:2002 standards.

Nine ions present concentrations,  $\text{NH}_4^+$ ,  $\text{HCO}_3^-$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ , were determined by ion chromatography. An 850 Professional IC (Metrohm) ion chromatograph with a Supp 7–250/4.0 column for anion analysis and Metrosep C-4–150/4.0 for cations was used. An eluent of 3.6 mmol/L  $\text{Na}_2\text{CO}_3$  ( $f = 0.7$  mL/min)

was used for anions and one of 1.7 mmol/L HNO<sub>3</sub> and 0.7 mmol/L of dipicolinic acid ( $f = 0.9$  mL/min) for cations. The limits of detection (mg/L) were 0.01 for Ca<sup>2+</sup> and Mg<sup>2+</sup>, 0.02 for Na<sup>+</sup> and NH<sub>4</sub><sup>+</sup>, 0.03 for K<sup>+</sup>, 0.02 for F, NO<sub>2</sub>, Cl<sup>-</sup>, and Br<sup>-</sup> and 0.01 mg/L for NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>. The analyses were conducted at the Institute of Earth Sciences, University of Silesia.

Toxic metals (Cd, Pb, Cu, Zn, Ni, Cr, and Tl) in the aqueous eluates of ashes were determined using atomic absorption spectroscopy (AAS) with the ICE 3000 spectrometer. The analyses were conducted at the Institute of Earth Sciences, University of Silesia.

Water pH was measured on an Elmetron CP-315 pH-meter with temperature compensation equipped with a glass combined electrode. Water conductivity was measured with a CC-401 conductometer with temperature compensation.

## 2. Results and discussion

### 2.1. Basic biomass components and calorific value

Wood biomass is characterized by very high volatile parts content (67.2% and 82.3%), with a lower value determined for birch (67.2% – Małopolskie Voivodeship and 82.3% – “Bory Tucholskie” National Park) (Table 1). According to Vassilev et al. (2010), the mean volatile part content in biomass does not exceed 78%. Samples of alder from the “Bory Tucholskie” National Park exhibited the highest ash content at 8.6% (Table 1). This is probably because older wood was obtained from the “Bory Tucholskie” National Park than in the Małopolska Voivodeship. An additional factor may be the soil type (poor subsoil, pseudo podzolic, and brown soils). The longer the vegetation period of trees than other plants used for energy, the higher the content of potentially toxic metals in them.

Table 1. Basic parameters of wood biomass ( $n = 3$ )

Tabela 1. Podstawowe parametry biomasy drzewnej ( $n = 3$ )

Parameter	Type of wood biomass			
	A	B	C	D
W (%)	16.8	17.8	14.6	17.7
A (%)	7.7	8.6	2.9	6.3
Q (MJ/kg)	15.0	15.5	16.7	15.7
V <sup>daf</sup> (%)	77.0	79.0	67.2	82.3

W – moisture; A – ash; Q – calorific value; V<sup>daf</sup> – volatile matter.

The calorific value is an important parameter in biomass analysis because it depends on the moisture and composition of the burned wood. The moisture content in wood affects its calorific value. The ash content in firewood residues usually ranges between 0.1 and 18.3% (Vassilev et al. 2010; Jagustyn et al. 2011; Smółka-Danielowska and Jabłońska 2022). Symbols A (raw alder) and C (raw birch) refer to biomass obtained from the Małopolskie Voivodeship – Targanice and Rzyki, while B (raw alder) and D (raw birch) indicate that it originates from the “Bory Tucholskie” National Park.

The high ash content in samples A (alder – Małopolska Province), B, and D (alder and birch – “Bory Tucholskie” National Park) may be related to the higher content of mineral substances in the wood. This may result from biomass contamination, e.g., with soil or sand, and the relatively thick bark of these trees. Among various raw wood materials, the bark contains the most ash (5–10.5%) (Chowdhury et al. 2015). The development of individual tree species is inextricably linked to the inorganic substrate. Various ions (e.g., magnesium, calcium, potassium, iron) and other elements found in groundwater enter individual parts of the wood during vegetation. A characteristic feature is that the mineral substance contained in the contaminated bark of a cut tree consists mainly of silica originating from the substrate. Naik et al. reported that quartz ( $\text{SiO}_2$ ) is the dominant phase in the wood waste ash.

## 2.2. Content of toxic metals in wood biomass

In Figure 1(a, b), concentrations of potentially toxic elements determined in raw alder and birch biomass, as well as in the ashes from their combustion, are presented. Symbols A (raw alder) and A1 (ash) refer to biomass obtained from the Małopolskie Voivodeship, while B (raw alder) and B1 (ash) indicate that they originate from the “Bory Tucholskie” National Park (Figure 1a). Symbols C (raw birch) and C1 (ash) pertain to biomass obtained from the Małopolskie Voivodeship, while D (raw birch) and D1 (ash) denote that it comes from the “Bory Tucholskie” National Park (Figure 1b).

Higher concentrations of Zn (21.6–38.6 mg/kg) compared to other toxic elements were determined in both raw biomass from anthropogenic regions (Małopolskie Voivodeship) and the area of the “Bory Tucholskie” National Park. The ash from the combustion of alder obtained from the “Bory Tucholskie” National Park is characterized by higher concentrations of Cu (34.3 mg/kg) and Zn (321.1 mg/kg). A high concentration of Ni (121.1 mg/kg) was determined in the ash from alder from the Małopolskie Voivodeship. The susceptibility of Ni to organic substance bonding results in its high mobility in many soils, even under neutral or alkaline conditions (Kabata-Pendias and Szeke 2012). In the case of biomass obtained from polluted areas, the concentration of various elements in biomass ash may be high. Michalik et al. (2013) measured Zn above 1% by weight and Pb ranging from 2,800 mg/kg in ash from biomass from anthropogenic regions. Cruz et al. (2017) found Cd ranging from 3 to 21 mg/kg, Pb 66–130 mg/kg, Ni 12–47 mg/kg, and Zn 700–794 mg/kg in ash from wood biomass. Tarelho et al. (2015) identified

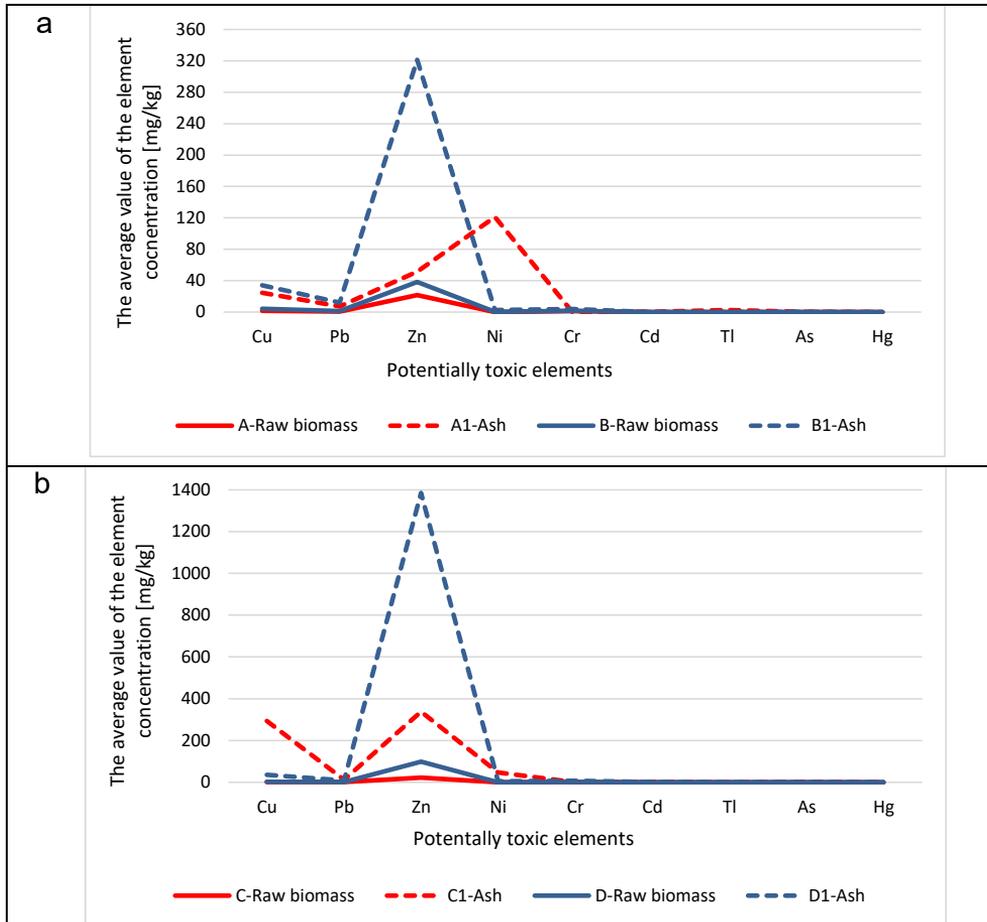


Fig. 1(a, b). The concentration of potentially toxic elements in raw biomass (A, B) and ash from alder A1 and B1 (a), and from birch C – C1 and D – D1 (b), obtained from urbanized areas (Małopolskie Voivodeship – Targanice and Rzyki) and “Bory Tucholskie” National Park in Poland

Rys. 1(a, b). Stężenie pierwiastków potencjalnie toksycznych w surowej biomasie (A, B) i popiele z olchy A1 i B1 (a) oraz z brzozy C – C1 i D – D1 (b), pozyskanych z terenów zurbanizowanych (województwo małopolskie – Targanice and Rzyki) i Parku Narodowego „Bory Tucholskie” w Polsce

Cd at 3.8 mg/kg, Cu 66.4–82 mg/kg, Pb 31–78.6 mg/kg, Ni 36.7–52 mg/kg, and Zn 55–196 mg/kg in ash from wood biomass.

Arsenic was not detected in raw alder biomass. At the same time, ashes are minimally enriched in this element regardless of the origin of alder (0.5–0.6 mg/kg) (Figure 1a). Trace amounts of Tl (0.07–2.7 mg/kg) were found in alder ashes, with higher concentrations in ash from alder from the Małopolskie Voivodeship.

In raw birch samples, the predominant element is also Zn, with values significantly higher than those of alder. Significantly higher concentrations of Zn were measured in raw birch from the “Bory Tucholskie” National Park (98.2 mg/kg) compared to raw birch from the Małopolskie Voivodeship (21.6 mg/kg). Zinc in soils is mobile and occurs in cationic, anionic, and organic complexes in soil solutions. Soil organic matter has high Zn sorption and is concentrated in humus soil horizons and peats. Peat-muck and peat soils occur near lakes. This is probably the reason for the higher Zn content in raw wood. Birch ash from the “Bory Tucholskie” National Park shows a high concentration of Zn (1,384.5 mg/kg) compared to ash from birch from anthropogenic regions (338.1 mg/kg). Fuels of biomass origin also contain specific amounts of mineral substance, which, after combustion, constitute the central part of the ash. Toxic metals found in wood and tree bark escape or remain in the ash during combustion. Therefore, ash particles may be enriched in some elements. High zinc concentration (3,910–43,500 mg/kg) Maj (2024) determined, e.g., ash from birch burning. Birch ash from the Małopolskie Voivodeship also exhibited high levels of Cu at an average of 293.5 mg/kg. Trace amounts of Cd (0.92–2.34 mg/kg) and As (1.8–0.4 mg/kg) were detected in birch ashes. The higher concentration of Zn in alder and birch wood from the “Bory Tucholskie” National Park is primarily attributed to the soil organic matter, which exhibits a high sorption capacity for this element, thereby concentrating it in the humus layers of the soil (Kabata-Pendias and Szteke 2012).

### 2.3. TG/DSC-FTIR analysis of biomass samples

The essence of thermal analysis was to determine the characteristics of raw alder and birch biomass as a function of temperature and time under the assumed temperature program. All types of biomass contain three main components: cellulose, hemicellulose, and lignin, which undergo degradation at different temperature ranges (Vassilev et al. 2012; Szechyńska-Hebda and Hebda 2015) (Table 2). The proportion of individual components in biomass varies, with hardwood containing 42% cellulose by weight, 25% hemicellulose by

Table 2. Temperature ranges at which thermal degradation of biomass components occurs during pyrolysis

Tabela 2. Zakresy temperatur, w których następuje degradacja termiczna składników biomasy podczas pirolizy

Biomass component	Temperature range (°C)		
	Long, Lin and Wang (2015)	Szechyńska-Hebda and Hebda (2015)	Tillman, Rossi and Kitto (1981)
Cellulose	290–400 (360)	320–370	320–370
Hemicellulose	180–370 (300)	250–310	220–320
Lignin	200–580 (320)	220–500	320–500

weight, and 22% lignin by weight (Werle 2021). Each component has a different molecular structure and diverse pyrolysis properties, resulting in the generation of different gas products. These factors lead to varying pyrolysis rates (Corma et al. 2007; Burhenne et al. 2013). The thermal decomposition of wood begins at around 220°C, with its individual components decomposing at subsequent temperatures (Tillman et al. 1981) (Table 2).

The thermograms depict TG and DSC curves (Figures 2 A–B, 3 C–D) from which temperatures corresponding to the maximum gas emission were determined. Analyses revealed differences in the pyrolysis process conducted for the same wood samples but

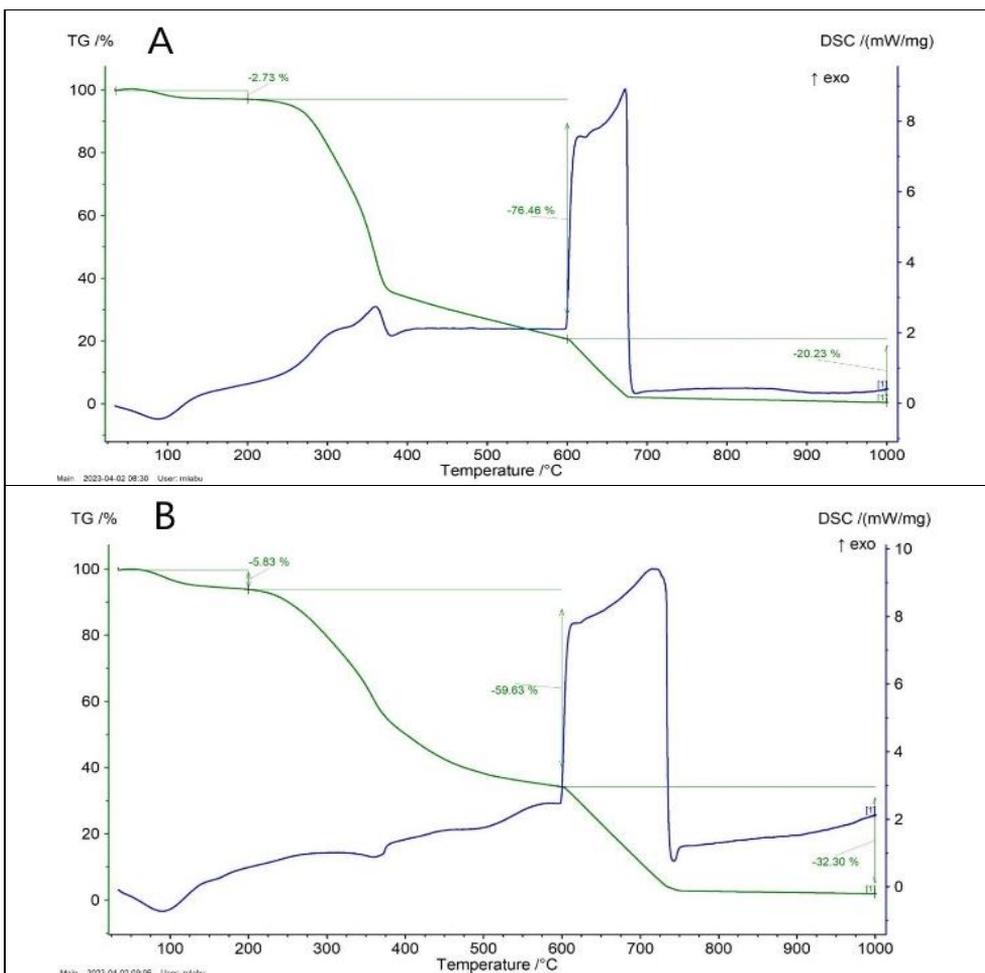


Fig. 2 A–B. Thermograms of alder samples (A – Małopolskie Voivodeship; B – “Bory Tucholskie” National Park) obtained from TG/DSC experiment

Rys. 2 A–B. Termogramy próbek olchy (A – województwo małopolskie; B – Park Narodowy „Bory Tucholskie”) uzyskane z eksperymentu TG/DSC

differing in origin. For these temperatures, as well as consistently for temperatures of 350°C and 650°C, FT-IR spectra were shown. In the temperature range of 35–600°C, samples were heated in a neutral atmosphere (nitrogen). Moisture release from the sample occurs up to a temperature of 200°C, typically resulting in a loss of mass of 3–6%. Pyrolysis of organic matter takes place in the range of 200–600°C, accompanied by gas release.

For samples A and B, gas emission occurs in the temperature range of 300–400°C. In the case of sample A, an endothermic peak is clearly visible on the DSC curve in this range, coupled with a significant mass loss (76.46% on the TG curve). A minor mass loss (59.63%) was determined for sample B. Above 600°C, residual organic matter undergoes further combustion in an oxidizing atmosphere (synthetic air). The mass loss registered in this range indicates the amount of char obtained after pyrolysis. The total mass loss in the entire experiment is close to 100%, and the calculated difference (complementing to 100%) represents the amount of residue left after the ashing process. During pyrolysis, typically charcoal (char), gas with high combustion heat (pyrolytic gas, mainly methane and carbon monoxide), and a water fraction are formed, which includes methanol, acetic acid, and tar (Szechyńska-Hebda and Hebda 2011). Pyrolysis in samples A and B occurs at similar temperatures and often proceeds in two stages. The temperatures read from the peaks of the DTG curves ( $T_{max}$ ) are 305(358)°C for sample A and 306(357)°C for sample B. The decomposition of biomass samples occurs in two stages. Hence, the  $T_{max}$  of the first, smaller peak is also provided in parentheses. The percentage content of char in the sample affects the thermal effect of its combustion reaction in the second stage of the experiment (in an oxidizing atmosphere). The measure of this thermal effect is the enthalpy of combustion, determined based on the DSC curve. The enthalpy of combustion of pyrolytic carbon (char) for sample A is 2,963 J/g, and for sample B, it is 5,487 J/g.

In Figure 3 C–D, thermograms of birch samples are presented. In this case, gas emission also occurs in the temperature range of 300–400°C. Endothermic peaks are visible on the DSC curves, combined with similar mass losses (C – 64.19% on the TG curve, D – 67.67%). Pyrolysis in samples C and D occurs at similar temperatures and often proceeds in two stages. The temperatures read from the peaks of the DTG curves ( $T_{max}$ ) are 305(358)°C for sample C and 290(359)°C for sample D. The decomposition of biomass samples also occurs in two stages. The enthalpy of combustion of pyrolytic carbon (char) for sample C is 5,154 J/g, and for sample D, it is 4,968 J/g).

The lower the temperature at which pyrolysis occurs, the easier it is for side chains in organic compounds to detach, affecting the thermal stability of cell walls (Szechyńska-Hebda and Hebda 2011). These components undergo degradation in different temperature ranges. There is also a mineral substance in wood, the content of which may vary depending on the arid mass of wood. Based on the TG/DSC experiment results, the alder ash content ranges from 2.24% by weight (“Bory Tucholskie” National Park). To 0.58% by weight (Małopolskie Voivodeship), and birches from 3.68% by weight (“Bory Tucholskie” National Park) to 3.38% (Małopolskie Voivodeship). In addition to carbon, hydrogen, oxygen, and nitrogen, there are calcium, potassium, magnesium, sulfur, phosphorus, copper, and other elements,

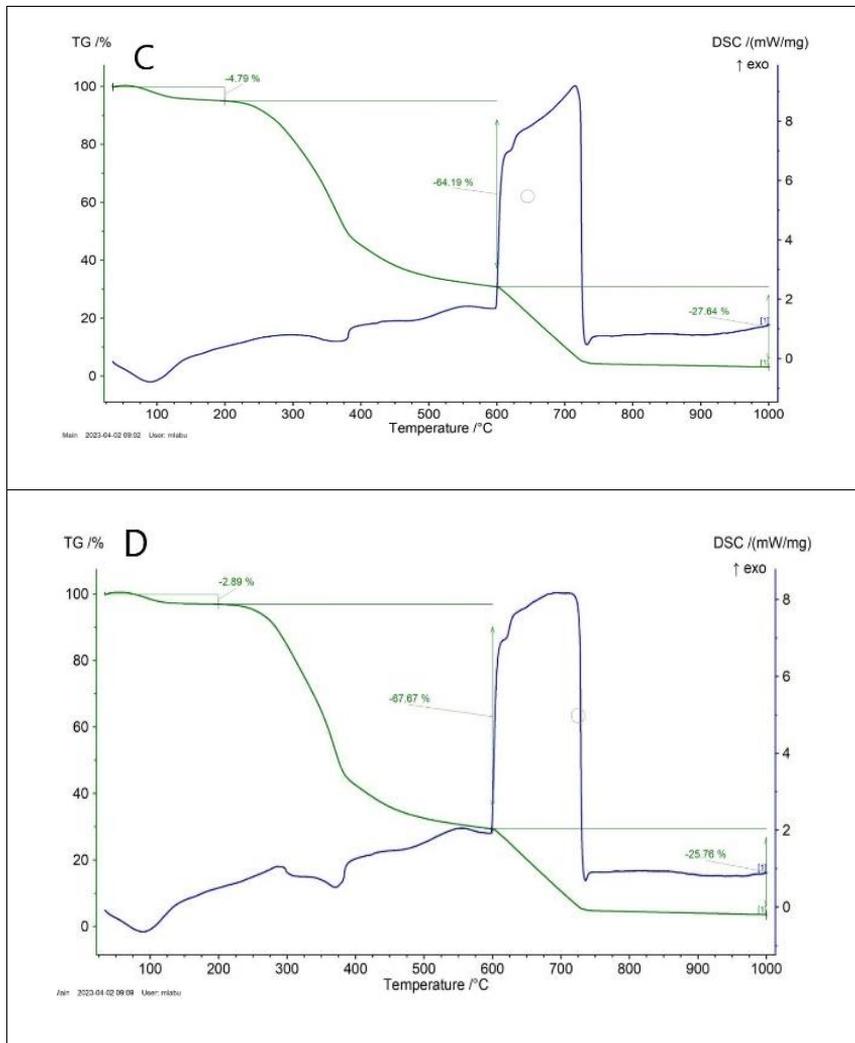


Fig. 3. C–D. Thermograms of birch samples (C – Małopolskie Voivodeship; D – “Bory Tucholskie” National Park) obtained from TG/DSC experiment

Rys. 3. C–D. Termogramy próbek brzozy (C – województwo małopolskie; D – Park Narodowy „Bory Tucholskie”) uzyskane z eksperymentu TG/DSC

as well as silica and oxalates are often found on the surface of the wood cell wall (Demeyer et al. 2001).

For the examined wood samples, the phenomenon of endothermic bending, indicating no change in mass, was observed at temperatures of 700–750°C. This suggests the melting effect of the ash of the tested samples at that point in the process. The obtained thermograms and FT-IR spectra were presented graphically. The results of the analysis of gas products

(FT-IR) are shown in Figure 4 A–B and Figure 5 C–D. FT-IR spectra were presented for temperatures of 350°C (pyrolysis process) and 650°C (combustion of the residual char after pyrolysis).

At 350°C, mainly carbon monoxide (CO) and carbon dioxide (CO<sub>2</sub>) are released. The release of CO<sub>2</sub> is associated with the cracking and restructuring of carbonyl and carboxyl groups, while CO is released due to the breakdown of C–O–C and C=O bonds. Visible vibrations of O–H and H–O–H bonds (in the ranges of 4,000–3,500 and 1,900–1,300 cm<sup>-1</sup>, respectively) indicate the breakdown of bonds in the cellulose chain and the decomposition of other organic compounds, which is associated with the release of water. Thermal dehydration of cellulose into gases usually occurs through two competing reactions: depolymerization and dehydration (Burhenne et al. 2013).

The spectra obtained at 650°C show gases released during the combustion of char. The product of char combustion is CO<sub>2</sub>, and the intensity of its release (expressed in absorbance units) depends on the amount of pyrolytic carbon remaining after the pyrolysis process.

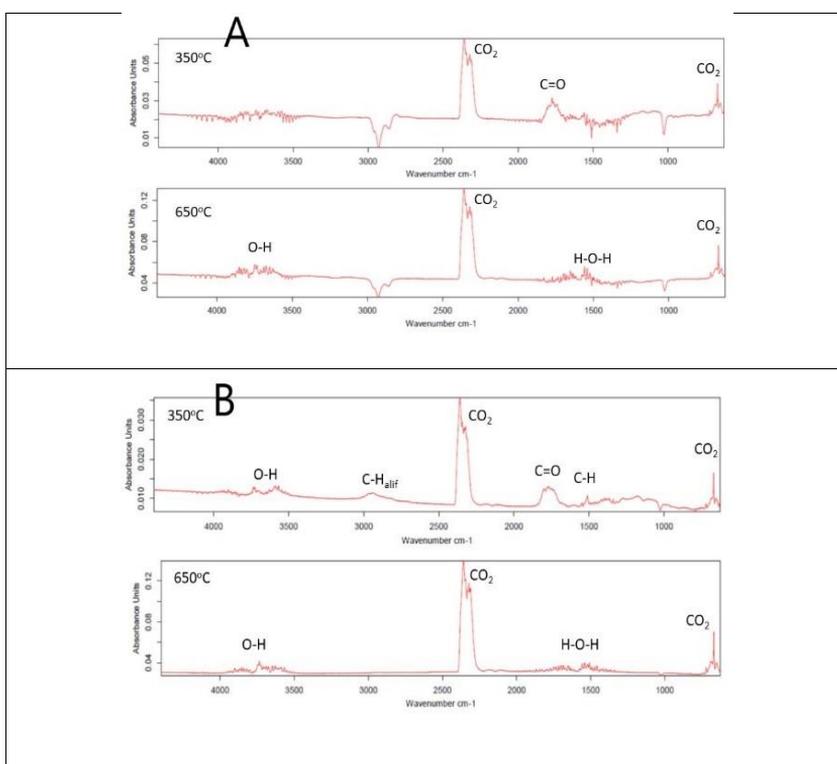


Fig. 4. A–B. FTIR spectra for temperatures of 350°C (pyrolysis process) and 650°C (combustion of the remaining char after pyrolysis) for alder samples (A – Małopolskie Voivodeship; B – “Bory Tucholskie” National Park)

Rys. 4. A–B. Widma FTIR dla temperatur 350°C (proces pirolizy) i 650°C (spalanie pozostałego po pirolizie węgla drzewnego) dla próbek olchy (A – województwo małopolskie; B – Park Narodowy „Bory Tucholskie”)

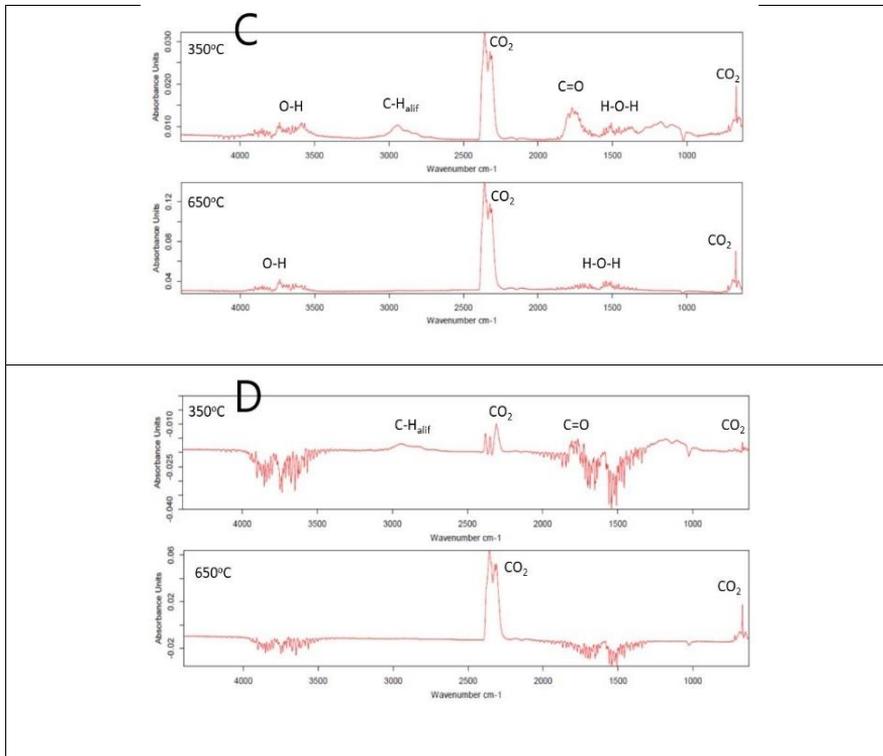


Fig. 5. C–D. FTIR spectra for temperatures of 350°C (pyrolysis process) and 650°C (combustion of the remaining char after pyrolysis) for birch samples (C – Małopolskie Voivodeship; D – “Bory Tucholskie” National Park)

Rys. 5. C–D. Widma FTIR dla temperatur 350°C (proces pirolizy) i 650°C (spalanie pozostałego po pirolizie węgla drzewnego) dla próbek brzozy (C – województwo małopolskie; D – Park Narodowy „Bory Tucholskie”)

The FT-IR data of sample B provide significant information regarding the formation of volatile organic compounds from the pyrolysis of components of wood biomass. The simultaneous evolution of several volatile compounds with similar chemical structures limits the identification of each component through FT-IR spectral analysis.

### 3. Chemical analysis of aqueous suspensions of biomass ashes

According to Vassileva et al. (2014), the content of soluble fractions (sulfates, chlorides, nitrates, poorly soluble phosphates) in biomass ashes can reach up to 61%.

The measured values of conductivity ( $C_{25}$ ) and pH of aqueous suspensions from ashes, as well as selected chemical components, are presented in Table 3. Wilczyńska-Michalik

et al. (2018) obtained a pH of 12 and conductivity of 3.86 mS/cm for the aqueous suspension of wood biomass ash (including birch). A slightly acidic reaction (pH = 6.70) characterizes the aqueous suspension of birch ash obtained in the Małopolskie Voivodeship. In contrast, the remaining samples of aqueous suspensions have alkaline pH values (pH = 9.98–10.52) within a similar range of values (Table 3). These values exceed the permissible pH level in aqueous suspensions A1, B1, and D1 required when introducing wastewater into water or soil, as well as regarding substances particularly harmful to the aquatic environment in Poland.

The results of conductivity of aqueous suspensions of ashes show more significant variability, with higher conductivity values measured in ash samples from alder and birch, which originate from the “Bory Tucholskie” National Park (B1 – 2.190 mS/cm; D1 – 3.170 mS/cm).

During the biomass combustion process, soluble compounds such as K, Na, Ca, and Mg are formed, resulting in a significant increase in the pH of aqueous suspensions of ashes.

Table 3. The leachability of contaminants from the aqueous suspensions of biomass ash

Tabela 3. Wymywalność zanieczyszczeń z wodnych zawiesin popiołu z biomasy

Leachability	A1	B1	C1	D1	Limit values (Regulation of the Ministry of Maritime Economy and Inland Navigation 2019; Regulation of the Ministry of the Environment 2014)
pH	9.98	10.27	6.70	10.52	6.5–9.0
C <sub>25</sub> (mS/cm)	0.678	2.19	0.451	3.17	–
Ions (mg/L)					
Ca <sup>2+</sup>	6.86	20.39	13.69	18.73	–
Mg <sup>2+</sup>	6.59	60.68	8.74	80.30	–
Na <sup>+</sup>	6.71	23.51	2.68	40.56	800.0
K <sup>+</sup>	208.85	620.85	112.25	943.36	80.0
Cl <sup>-</sup>	2.66	32.79	9.63	47.32	1,000.0
SO <sub>4</sub> <sup>2-</sup>	26.48	1,775.77	25.10	305.33	500.0
NO <sub>3</sub> <sup>-</sup>	3.36	29.15	1.48	31.64	30.0
PO <sub>4</sub> <sup>3-</sup>	5.67	20.61	40.24	19.62	–
Toxic elements (µg/L)					
Zn	1.6	1.8	3.3	2.5	2,000.0
Cu	1.0	0.8	2.7	2.2	500.0
Ni	1.0	1.0	1.4	1.1	500.0

Conductivity measurements confirm that conductivity is a measure of the amount of salts dissolved in water. Salt emissions at landfills are associated with the leaching process. Therefore, their quantity will depend on water supply.

The aqueous eluates of ashes A1 and C1 are characterized by low leachability of  $\text{SO}_4^{2-}$  – ions (Table 3) compared to the aqueous suspension of ash B1, for which the permissible value of sulfate ions has been exceeded more than 3 times. The conducted research showed very high leachability of potassium ions (620.854–943.369 mg/L) in samples B1 and D1. According to Dahlin et al. (2016), the leaching of potassium from biomass ashes can lead to an increase in conductivity due to its increased concentration in the ash. Higher concentrations of leached potassium and sulfate ions likely result from the relatively high solubility of the potassium cation (Alves et al. 2019). The high leachability of these ions is confirmed by research results obtained by various authors (Jaworek et al. 2013; Vassilev et al. 2013; Wilczyńska-Michalik et al. 2018). Phosphates (V),  $\text{NO}_3^-$   $\text{Na}^+$ , and  $\text{Ca}^{2+}$  are leached to the least extent in all examined aqueous suspensions of ashes. The low concentration of chloride ions in aqueous suspensions of biomass ashes may be related to the organic occurrence of chlorine in woody biofuel (Vassilev et al. 2013). In aqueous suspensions of biomass ashes,  $\text{NH}_4^+$ ,  $\text{F}^-$ , and  $\text{Br}^-$  ions are present below the detectability limit of the method.

The differences in the occurrence of ions in ash samples determine the following sequence from the highest to the lowest value:

- ◆ sample B1:  $\text{SO}_4^{2-} > \text{K}^+ > \text{Mg}^{2+} > \text{Cl}^- > \text{NO}_3^- > \text{Na}^+ > \text{PO}_4^{3-} > \text{Ca}^{2+}$ ,
- ◆ sample D1:  $\text{K}^+ > \text{SO}_4^{2-} > \text{Mg}^{2+} > \text{Cl}^- > \text{Na}^+ > \text{NO}_3^- > \text{Ca}^{2+} > \text{PO}_4^{3-}$ .

Among the toxic metals leached from the aqueous suspensions of ashes, only Zn, Cu, and Ni were determined. The studies showed that Zn, Cu, and Ni are leached to a lesser extent from samples A1, B1, and D1. This is the result of leaching of pollutants under alkaline conditions. From the slightly acidic aqueous suspension of ash (sample C1), the amounts of leached Zn and Cu are slightly higher, at 3.3  $\mu\text{g/L}$  and 2.7  $\mu\text{g/L}$ , respectively (Table 3). In none of the aqueous suspensions of biomass ash were the permissible values of Zn, Cu, and Ni exceeded.

Laboratory studies of aqueous suspensions of biomass ashes only partially reflect the simulation that would take place under environmental conditions. Therefore, according to Li et al. (2012), they should not be considered entirely safe for the environment.

#### 4. The Biomass Ash Toxicity Indicator (BATI)

The Biomass Ash Toxicity Indicator (BATI) is used to assess the toxicity of individual potentially toxic elements, which are crucial in evaluating the suitability of biomass ash when used as fertilizer for agricultural purposes (Nahlik et al. 2019; Mohan and Reddy 1996 – modified). Values below 0 indicate exceeding the permissible limit when using specific ash for agricultural purposes, and a negative value represents the magnitude of this

exceedance (Figure 6). The threshold values for ash were established based on the threshold levels obtained for compost from household waste:

$$BATI = \frac{BATI_{\max} - PTE}{BATI_{\max}}$$

- ↪  $BATI_{\max}$  – limit value for potentially toxic elements: Cd (0.7 mg/kg), Cr and Cu (70 mg/kg), Pb (45 mg/kg), Ni (25 mg/kg), Zn (200 mg/kg) (Rakshit et al.2018; Yang et al. 2022),
- $PTE$  – amount of the potentially toxic element in the sample.

In the samples of biomass ashes, negative values were obtained for samples B1, C1, and D1 for zinc, and for samples C1 and D1, the limit for cadmium was exceeded.

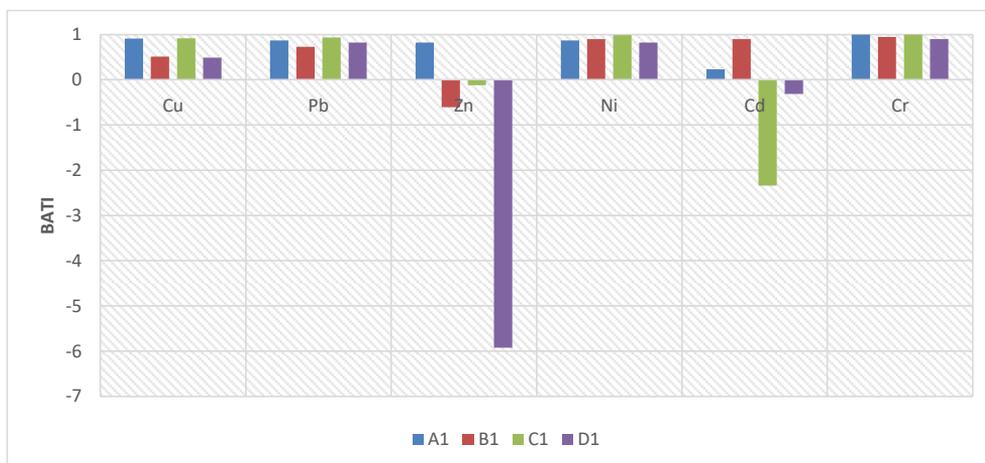


Fig. 6. Biomass ash toxicity indicator ( $BATI$ ) for biomass ash samples

Rys. 6. Wskaźnik toksyczności popiołu z biomasy ( $BATI$ ) dla próbek popiołu z biomasy

## Conclusions

In samples of raw alder and birch biomass, similar concentrations of Zn and Cu were determined regardless of origin, with higher concentrations found in birch samples from the “Bory Tucholskie” National Park. All wood biomass ashes are enriched in Zn and Cu. Higher concentrations of these elements were detected in ashes from burning birch from the “Bory

Tucholskie” National Park. The higher concentration of these elements may be associated with organic matter in forest soils and their concentration in humus soil layers. A higher content of Ni was determined in the ash from alder from the Małopolskie Voivodeship, which may be related to anthropogenic processes in the soil due to various sources of this element. Both biomass ash samples for birch exceeded the acceptable threshold limit for Zn and Cd, beyond which it may be problematic to use this ash for agricultural purposes. Based on the obtained research results, it is not possible to definitively determine which biomass and from which area are suitable for combustion in low-temperature energy combustion processes.

The conductivity values of water suspensions of biomass ashes vary greatly depending on the origin of the biomass. Potassium and sulfate ions are the dominant components in the water suspensions of alder and birch ashes from the “Bory Tucholskie” National Park. The leaching of potassium and sulfate ions does not meet the criteria for neutral waste, and their leaching should be considered a potentially harmful factor in the environment. Due to the alkaline pH of the water suspensions of biomass ashes, the efficiency of leaching toxic elements is lower. The chemical composition of water suspensions of wood biomass ashes indicates the need for further research in this area to determine the leaching of pollutants from them under natural conditions.

Thermal analysis made it possible to analyze the reactivity of wood and examine the processes that wood undergoes during temperature changes. DSC/TG analysis showed lower thermal stability of alder obtained from the Małopolskie Voivodeship than alder from the “Bory Tucholskie” National Park. Based on the thermograms, hemicelluloses are probably the least durable component of wood. Further research in this area should be conducted at this stage. Thermal analysis of alder and birch biomass showed the influence of its composition and origin on behavior under high-temperature conditions. It proved effective in observing biomass mass changes and their reactivity in the energy process, releasing fuel components, and analyzing the composition of gases emitted during the process.

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**TOXIC ELEMENTS, LEACHABILITY, AND THE RESULTS OF THERMAL ANALYSIS  
OF WOODY BIOMASS FROM THE ENVIRONMENT WITH VARYING DEGREES OF POLLUTION**

**Keywords**

biomass, ash, leachability, toxic elements, thermal analysis

**Abstract**

Experimental studies were conducted in laboratory conditions to assess the suitability of alder and birch for use in individual home furnaces and the potential storage of ashes in the environment. Raw biomass samples were combusted at  $450\text{--}500 \pm 15^\circ\text{C}$ . The tree species (alder and birch) originated from Poland (Małopolskie Voivodeship) and the “Bory Tucholskie” National Park (Pomorskie Voivodeship). This study aimed to determine the content of toxic metals (As, Cd, Cr, Cu, Hg, Ni, Pb, Tl) in raw biomass and its ashes, ions eluted from water eluates of ash, and to analyze the thermal degradation process of wood. In addition to the analysis, the study used inductively coupled plasma optical emission spectroscopy (ICP-OES) and ion chromatography (IC), thermogravimetric analysis analyses (TG/DSC), and powder X-ray diffraction. The content of volatile parts in wood biomass ranges between 67.2–82.5%, ash content 2.9–19.1%, and calorific value 14.8–17.1 MJ/kg. Moisture content in the wood biomass ranges from 14.6–18.7% (birch) and 17–19.2% (alder). The content of toxic metals was generally low in raw biomass, except for Co, Zn, and Ni, and higher in ashes, varying depending on the origin of the biomass. TG/DSC curves allowed for the identification of the main stages of wood biomass degradation, corresponding to moisture content in the range of

2.73–5.83% (wt.%), ash (0.58–3.68% wt.%), volatile matter (59.63–76.46% wt.%), and fixed carbon (20.23–32.3% wt.%). Higher sulfate and potassium ion concentrations were detected in water eluates of ashes from the “Bory Tucholskie” National Park. The research results do not indicate that alder and birch may be used for low-temperature combustion. However, it is advisable to conduct comprehensive studies research in this area.

#### PIERWIĄSTKI TOKSYCZNE, WYMYWALNOŚĆ I WYNIKI ANALIZY TERMICZNEJ BIOMASY DRZEWNEJ ZE ŚRODOWISKA O RÓŻNYM STOPNIU JEGO ZANIECZYSZCZENIA

##### Słowa kluczowe

biomasa, popiół, wymywalność, pierwiastki toksyczne, analiza termiczna

##### Streszczenie

Przeprowadzono badania eksperymentalne w warunkach laboratoryjnych w celu oceny przydatności olchy i brzozy do wykorzystania w indywidualnych piecach domowych oraz potencjalnego wykorzystania i składowania popiołów w środowisku. Próbkę biomasy surowej spalano w temperaturze  $450\text{--}500 \pm 15^\circ\text{C}$ . Gatunki drzew pochodzą z Polski (województwo małopolskie) oraz z Parku Narodowego „Bory Tucholskie” (województwo pomorskie). Celem niniejszego badania było określenie zawartości metali toksycznych (As, Cd, Cr, Cu, Hg, Ni, Pb, Tl) w biomacie surowej i jej popiołach, wymywanych jonów z eluatów wodnych popiołów i analiza procesu termicznej degradacji drewna. W badaniach wykorzystano metodę spektroskopii emisyjnej ze wzbudzeniem w plazmie indukcyjnie sprzężonej (ICP-OES) i chromatografię jonową (IC), wykonano analizy termograwimetryczne (TG/DSC) oraz dyfrakcję rentgenowską metodą proszkową (XRD). Zawartość części lotnych w biomacie drzewnej waha się między 67,2–82,5%, zawartość popiołu 2,9–19,1%, a wartość kaloryczna wynosi 14,8–17,1 MJ/kg. Zawartość wilgoci w biomacie drzewnej waha się między 14,6–18,7% (brzoza) i 17–19,2% (olcha). Skład mineralny badanych próbek jest mało zróżnicowany. Zawartość metali toksycznych jest na ogół niska w biomacie surowej, z wyjątkiem miedzi, cynku i niklu, oraz wyższa w popiołach, zróżnicowana w zależności od pochodzenia biomasy. Krzywe TG/DSC pozwoliły zidentyfikować główne etapy degradacji biomasy drzewnej, które odpowiadają zawartości wilgoci w zakresie 2,73–5,83% (wag.), popiołu 0,58–3,68% (wag.), materiałów lotnych 59,63–76,46% (wag.) oraz węgla stałego 20,23–32,3% (wag.). Wyższe stężenia jonów siarczanowych i potasowych oznaczono w eluatach wodnych popiołów z Parku Narodowego „Bory Tucholskie”. Wyniki badań niejednoznacznie wskazują, że olcha i brzoza mogą być wykorzystane w spalaniu niskotemperaturowym; jednak wskazane jest prowadzenie kompleksowych badań w tym zakresie.