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Physicochemical Properties of Seed Extraction Residues and Their Potential Uses in Energy Production

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1. Introduction

Biomonitoring involves observations and evaluations of changes in ecosystems with the use of bioindicators. Biomonitoring programs are implemented to analyze environmental parameters, in particular air and water pollution, accumulation of toxic substances in plants and the physicochemical parameters of plants in view of their potential uses (Coşkun 2006, Gdula-Argasińska et al. 2004, Greinert 2011, Karnosky et al. 2007, Masese et al. 2014, Wójcik et al. 2014). Not long ago, many biological materials did not have practical applications (Nanda et al. 2014). The advance of modern technologies for the production, bioconversion and generation of green energy and the introduction of legally binding targets for reducing CO_2 emissions brought far-reaching changes. The relevant progress has contributed to the significance of biomass as biofuel (Budzianowski 2012a,b; Gendek & Zychowicz 2014; Gołos & Kaliszewski 2015; Sawauchi et al. 2015; Yoshioka & Sakai 2005). Biomass is a highly recommended source of renewable energy because its combustion is associated with low sulfur and nitric oxide emissions. This sustainable resource is part of the carbon cycle (Kratzeisen & Müller 2013, Pindór & Preisner 2011). Biomass is used for generating heat and electricity, and it can be co-combusted with fossil fuels. (Basu et al.

2011, Coronado et al. 2011). Biomass includes forest waste (Aniszewska & Gendek 2016a, b; Gendek & Nurek 2016; Gendek & Zychowicz 2014, 2015; Risovič et al. 2008). Forests in Northern, Central and Eastern Europe, including Poland, are characterized by a predominance of coniferous stands. The most common tree species are the Scots pine (*Pinus Sylvestris* L.), Norway spruce (*Picea abies* H. Karst.), European larch (*Larix decidua* Mill) and Polish larch (*Larix polonica*) (Raciborski & Wóycicki-Domin). Their seeds have wings which promote seed dispersal by wind across considerable distances. Wings are separated from seeds in industrial plants where the husking process lasts 12 to 56 hours, depending on the species (Aniszewska 2012). Wings have to be removed before successive stages of seed production because they hinder sowing, in particular when precision seeders are used. Wings are separated by dry or wet dewinging methods. In the dry method, wings are removed mechanically by rubbing seeds against a hard surface, such as drum or studded rollers. In the increasingly popular wet dewinging method, seeds are moistened with water (Tylek & Walczyk 2009a,b). Seeds imbibe more water than wings, and wings become separated in the process. Wings are attached to seeds differently in the Scots pine and in the Norway spruce. In pines, wings encapsulate the entire seed, whereas in the spruce, the wing is attached to one side of the seed only.

Steven and Carlisle (1959) investigated the morphology of Scots pine seeds and observed that wing shape varies within the same cone and is determined by the size of the seed husk (Białobok et al. 1993).

Seed wings are classified as long, standard or broad based on the ratio of wing length to wing width (Sylven 1916, as cited in Białobok et al. 1993). According to Sylven (1916) & Zajączkowski (1949), the length of standard wings on Scots pine and Norway spruce seeds ranges from 11 to around 16 mm, and their width – from 4.5 to 6.1 mm. Seeds from trees growing in the mountains have smaller and relatively broad wings (Zajączkowski 1949). According to Zajączkowski (1949), the length and width of wings are closely correlated with the length and width of the cone.

Significant variations are observed in the color of seed wings (Białobok et al. 1993). In pines, wing color varies from yellow to red, reddish brown and purple-gray with light and dark streaks, whereas in spruces, wing color is less differentiated and ranges from fawn to light brown. The calorific value of wood, cones, needles and bark has been extensively researched. The calorific value of wood was investigated by Günther et al. (2009), Haufa & Wojciechowska (1986), Komorowicz et al. (2009), Krzysik (1974), Lu et al. (2009), Monkielewicz & Pflaum (1967), Rembowski (2007), Reva et. al. (2012), So & Eberhardt (2013), Stolarski et al. (2013) and Uri et al. (2015). In the cited studies, this parameter was determined in the range of 19.2-21.2 MJ·kg^{-1} for pine wood and 18.8-20.5 MJ·kg^{-1} for spruce wood. In the work of Font et al. (2009), the calorific value of pine needles and cones was determined at 20.14 MJ·kg^{-1} and 18.78 MJ·kg^{-1}, respectively. The calorific value of pine needles was established at 20.6 MJ·kg^{-1} by Zhao et al. (2014). Wanin (1953) determined the calorific value of Norway spruce needles and bark at 20.66 MJ·kg^{-1} and 20.33 MJ·kg^{-1}, respectively, whereas in the work of Zhao et al. (2014), the calorific value of Scots pine bark reached 19.3 MJ·kg^{-1}. The cited authors investigated mostly wood, bark and green parts of trees. The properties of seed extraction residues, including wings and empty seeds, have never been evaluated in view of their potential uses in energy generation. Biomonitoring studies revealed that higher plants are less resistant to high concentrations of heavy metals in soil. The most toxic metals are Cu, Pb, Cd, Co and Ni (Kabata-Pendias & Pendias 1999). Excessive metal levels in plants cause chlorosis, needle yellowing and inhabited growth. High concentrations of Hg, Cd and Pb in plant tissues can slow down photosynthesis, mitosis and water absorption (Kabata-Pendias & Pendias 1999). The ratios of heavy metals in plant tissues are also important for plant growth (Mandre & Ots 2012). The heavy metal content of plants is influenced by various factors, including environmental pollution (soil and air), weather conditions, soil properties, surface structure, age of plant tissues and the species' ability to accumulate and transport metals (Voutsa et al. 1996, Onder & Dursun 2006, Nkongolo et al. 2008, Mandre & Ots 2012). Trees take up heavy metals from soil via the root system. Mycorrhizae can limit the uptake of toxins by trees (Khan et al. 2000). The absorbed heavy metals are distributed to all plant parts, and their concentrations can differ significantly across organs. Needles accumulate less metals than the roots, trunks and branches of coniferous trees (Nkongolo et al. 2008, Sawidis et al. 1995, Fuentes et al. 2007, Onder & Dursun 2006). The highest concentrations of heavy metals are generally noted in bark on account of its porous structure and the ability to absorb metals from atmospheric air. According to Coşkun (2006), bark is a reliable indicator of air pollution. Due to its sorptive properties, coniferous bark (pine, spruce) is used to remove metal ions from aqueous solutions, for example in industrial waste water treatment plants. According to Su et al. (2013), Argun et al. (2009) and Palma et al. (2003), ground cones have similar properties.

The accumulation of metals in different organs of coniferous trees has been extensively researched, but little is known about their impact on seed ecology. In comparison with other plant organs, seeds generally accumulate the smallest amounts of metals. Most heavy metals are microelements that occur naturally in tree seeds. Excessive metal concentrations can have adverse environmental effects, which is why they are controlled as part of biomonitoring programs. Coniferous seeds have a physiological barrier that protects generative reproduction organs against heavy metals (Palowski 2000). The reproductive organs of coniferous trees have a complex structure and a long reproductive cycle, which makes them most sensitive to the harmful effects of anthropogenic pollutants. Seeds harvested from trees growing near heavy-traffic roads were characterized by lower viability (Stvolinskaya 2000). The presence of heavy metals in seeds has a negative effect on the quality of genetic material. Excessive metal accumulation in seeds can inhibit germination and seedling development (Ganatsasa et al. 2011). Prus-Głowacki et al. (2006) subjected seeds to isoenzyme and cytology tests which revealed that heavy metal ions significantly influenced the genetic structure of the examined population of *Pinus sylvestris* L.

There is a general scarcity of published data on the morphology and characteristics of pine and spruce seed wings. The microscopic structure, chemical composition and calorific value of seed extraction residues have never been evaluated. Those parameters could constitute important data for biomonitoring.

2. Research objective

The aim of this study was to describe selected physicochemical properties, including microscopic structure, chemical composition, heat of combustion and calorific value, of seed wings and empty seeds of two coniferous species: Scots pine (*Pinus sylvestris* L.) and Norway spruce

(*Picea abies* H. Karst.). Wings and empty seeds, which constitute seed extraction residues, were evaluated as potential sources of energy. Heavy metal emissions during the combustion of seed discards were measured, and attempts were made to determine whether cell structure influences the calorific value of seeds. The results of this study will fill the existing knowledge gap and will have practical applications for environmental biomonitoring. The study will make a reference to the observations made by Bunse et al. (2011) who postulated the need to bridge the gap between academic research and the research needs of industry, as well as the work of Leturcq (2014) and Uliasz-Bocheńczyk & Mokrzycki (2015) who investigated alternative fuels.

3. Materials and methods

The wings and empty seeds of the Scots pine and Norway spruce were supplied by a seed extraction plant in Grotniki located on the territory managed by the Regional Directorate of State Forests in Łódź, Poland.

The morphology of wings was described based on microscopic observations. The size of cells in the longitudinal section and the cross-section was determined at x40, x100 and x400 magnification under the Nikon Alphaphot -2- TRIN microscope equipped with a camera and connected to a computer with MicroScan software. The surface of pine wings was also viewed at x80 and x1000 magnification under the Quanta 200 scanning electron microscope with a data recording system.

Cell length, cell width, cell wall thickness, cell perimeter and surface area were measured in the longitudinal section. Wing thickness at the widest point and cell lumina were measured in the cross-section. Measurements were performed in MicroScan v. 1.5 software to the nearest 1 μm.

Seed extraction residues were sorted with the use of mesh screens. The fraction that passed through the screen with 0.80 mm mesh size and was captured by the screen with 0.43 mm mesh size was used in chemical composition analysis. The sorted material was extracted with a chloroform-ethanol mixture (93:7) (Antczak et al. 2006) for 10 hours. The content of cellulose (Krutul 2002), lignin (PN-92/P-50092) and holocellulose (Kacik & Solar 1999) was determined in extracted material.

The content of substances soluble in 1% NaOH solution was determined in non-extracted residues. Ash content was analyzed in the powdery fraction which passed through the screen with 0.43 mm mesh size. The material was heated and roasted in a muffle furnace. The final roasting temperature of 600°C was maintained for 6 hours. The moisture content of the examined residues was determined before analysis by the gravimetric method, according to standard PN-EN 13183-1:2004 in three replications.

Heat of combustion and calorific value were determined calorimetrically according to standard PN-ISO 1928:2002. The material was pulverized in a mill, and it was dried to constant weight in the SLW 115 TOP laboratory drier at 104±1°C for 24 hours.

Analytical samples of 1.0 g each were weighed to the nearest 0.001 g on the WSP 210S scale. They were burned in an oxygen bomb calorimeter (KL10). Measurements were performed in 10-11 replications for every type of material. Indoor temperature and humidity were measured to the nearest ±0.1°C and ±0.1%, respectively, with the Rotronik HygroPalm HP23 series humidity meter. Heat of combustion Q_s was determined automatically by the bomb calorimeter.

Calorific value Q_{op} was calculated based on the following formula (PN-ISO 1928:2002):

$$Q_{op} = (Q_s - 206 \cdot H) \cdot (1 - 0.01 \cdot W_w) - 23.0 \cdot W_w \qquad (1)$$

The calculated values of the heat of combustion of various wood components were used to derive empirical formula (2) (Telmo and Lousada, 2011):

$$Q_{ne} = 14.3377 + 0.1228(L) + 0.11353(Ext) \qquad (2)$$

The CHNS (carbon, hydrogen, nitrogen, sulfur) analysis was performed in the Elementar Vario Macro Cube elemental analyzer based on the Alfalfa standard (B2273). Measurement error was: C – 6.7%, H – 18.4%, N – 15.5%, S – 16.4%.

The content of cadmium (Cd), lead (Pb), copper (Cu), zinc (Zn), nickel (Ni), chromium (Cr), molybdenum (Mo), cobalt (Co), iron (Fe), manganese (Mn), calcium (Ca), magnesium (Mg), potassium (K), sodium

(Na) and mercury (Hg) was determined in pine and spruce wings and empty seeds. The analyses were performed by flame absorption atomic spectroscopy (FAAS) with the Thermo Solaar 6M spectrometer. Samples were mineralized in Teflon-lined pressure vessels in a mixture of nitric acid and hydrogen peroxide according to procedure No. DG-EN-19 "Wood chips" for the Milestone Start D microwave mineralizer. Sample weight was 0.5 g, and measurements were performed to the nearest 0.001 g. The reaction mixture was composed of 8 cm^3 of nitric acid (65% HNO_3, ultra pure) and 2 cm^3 of hydrogen peroxide (30% H_2O_2, ultra pure). The temperature profile was as follows: 2 minutes – increase to 85°C, after 5 minutes – increase to 145°C, after 3 minutes – increase to 200°C, last 20 minutes – 200°C. Heating power during mineralization was 1000 W.

Data were processed in the Statistica v. 12 program (Stat Soft Inc. 2014) at a significance level of $\alpha=0.05$. Differences were regarded as statistically significant at $p<0.05$.

4. Results and discussion

4.1. Microscopic structure of wings

Scots pine (Pinus sylvestris L.) wings

Every pine wing has two edges. The inner edge is located near the center of the husk axis, whereas the outer edge is situated near the edge of the husk. The inner edge (Fig. 1a) is composed of similarly sized and regularly overlapping cells with dark brown color. The outer edge consists of variously sized cells with irregular, elongated shape (Fig. 1b). Unlike the inner edge, the outer edge is convex. The tip and the outer edge of a wing comprise irregularly distributed cells with light brown color. Cells contain dark brown, differently sized bodies with an elliptical cross-section. The content of brown bodies in cells increases towards the tip of the wing.

The central part of the wing (Fig. 2a) consists of cells with regular, elongated cells and ribbed cell walls. In this segment, the cells are arranged in a pattern of lighter and darker streaks. Darker streaks are composed of cells with brown bodies (Fig. 2b), similarly to the cells distributed along the outer edge or at the tip of the wing. Light streaks consist of cells without brown bodies.

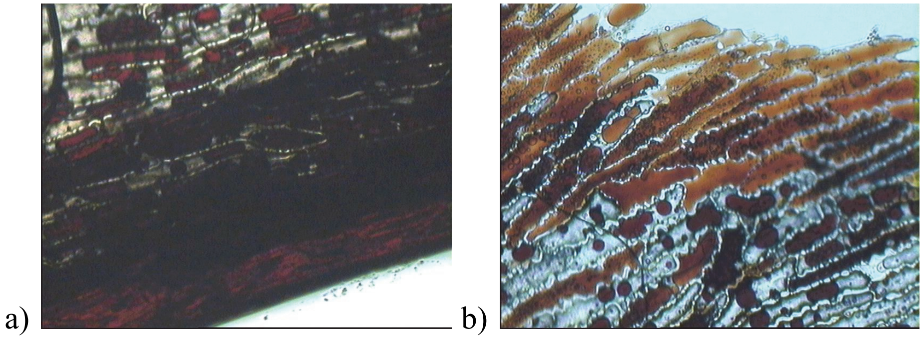

Fig. 1. View of cells along the edge of a Scots pine (*Pinus sylvestris* L.) wing, x100 magnification: a – inner edge, b – outer edge
Rys. 1. Widok krawędzi z komórkami skrzydełka sosny zwyczajnej (*Pinus sylvestris* L.) w powiększeniu x100: a – wewnętrznej, b – zewnętrznej

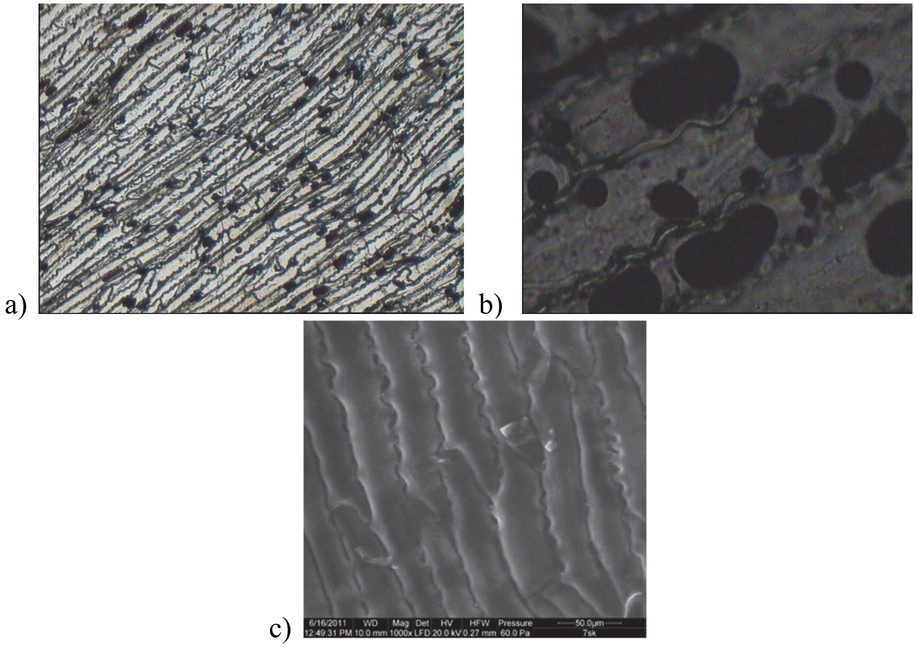

Fig. 2. View of cells in the central part of a Scots pine (*Pinus sylvestris* L.) wing: a – x40 magnification, b – x400 magnification under a light microscope, c – x1000 magnification under SEM
Rys. 2. Widok komórek skrzydełka sosny zwyczajnej (Pinus sylvestris L.) ze środkowej części: a – powiększenie x40, b – powiększenie x400 na mikroskopie świetlnym, c – na mikroskopie skaningowym (powiększenie x1000)

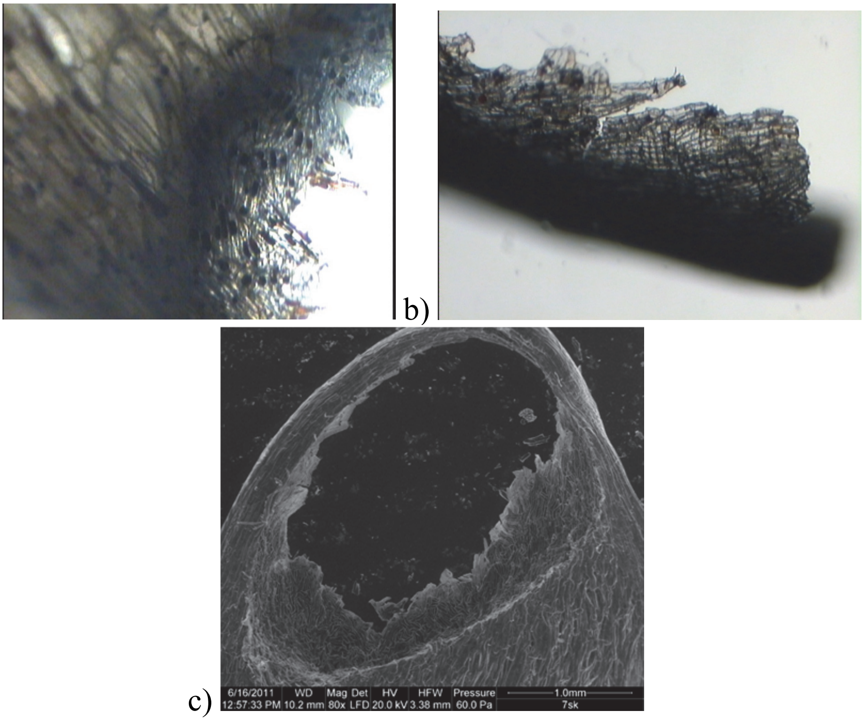

Fig. 3. The point of connection between a Scots pine (*Pinus sylvestris* L.) wing and seed (x40): a – in the central part, b – along the edge, viewed under a light microscope, c – whole, x80, viewed under SEM

Rys. 3. Miejsce połączenia skrzydełka sosny zwyczajnej (*Pinus sylvestris* L.) z nasieniem (powiększenie x40): a – w środkowej części, b – u brzegu kleszczowego zakończenia z mikroskopu świetlnego, c – całe, z mikroskopu skaningowego (powiększenie x80)

Cells with ribbed walls in the central part of the wing change shape at the place of contact with the seed. Several layers of jagged cells with variously shaped cross-sections and thin walls are visible (Fig. 3).

Norway spruce (Picea abies* H. Karst.) *wings

Similarly to a Scots pine wing, a Norway spruce wing also has an inner edge and an outer edge. The inner edge is straight (Fig. 4a), and it comprises regularly shaped cells. The outer edge is convex and jagged (Fig. 4b), and it is composed of irregularly shaped cells.

a) b)

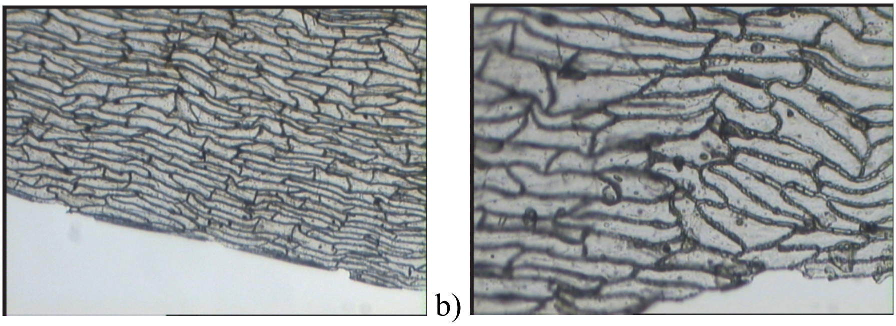

Fig. 4. Edges of a Norway spruce (*Picea abies* H. Karst.) wing: a – inner edge (x40), b – outer edge (x100)
Rys. 4. Krawędzie skrzydełka świerka pospolitego (Picea abies H. Karst.): a – wewnętrzna (x40), b – zewnętrzna (x100)

Cells at the tip and in the central part of the wing are lightly colored in various hues of yellow. Unlike the cells in Scots pine wings, they do not contain brown bodies.

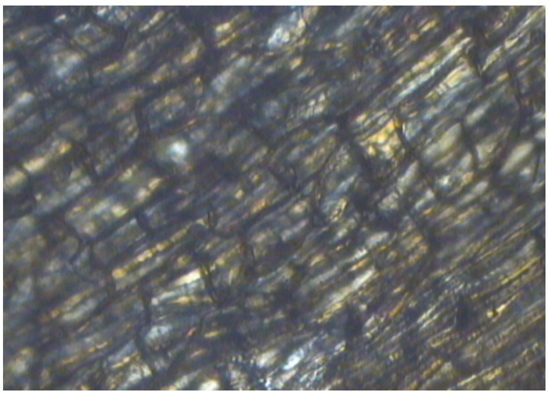

Fig. 5. View of a Norway spruce (*Picea abies* H. Karst.) wing under the seed (x100)
Rys. 5. Widok skrzydełka świerka pospolitego (*Picea abies* H. Karst.) pod nasieniem (x100)

Cells in the part of the wing that supports the seed (in the Norway spruce, the wing encapsulates the seed on one side only) are brown.

4.2. Cell size in Scots pine (*Pinus sylvestris* L.) and Norway spruce (*Picea abies* H. Karst.) wings

Cell parameters (mean, minimum and maximum cell length, cell width, cell wall thickness, cell area and perimeter) measured in the longitudinal section of pine and spruce wings are presented in Tables 1 and 2.

The cells in Scots pine wings had the average length of 305 µm, width of 28 µm, surface area of 8434 µm^2, and perimeter of 704 µm. Brown bodies were differently sized. In the outer (convex) part of the wing, brown bodies filled nearly the entire cell, and their average area was determined at 4759 µm^2. In inner and central segments of the wing, brown bodies were nearly seven-fold smaller (654 µm^2). Some brown bodies adhered to cell walls, and their area was estimated at 65 µm^2.

The analysis of variance confirmed an absence of significant differences in cell width between Scots pine and Norway spruce wings ($F_{(2,52)}$=1.57; p=0.218). Significant differences between Scots pine and Norway spruce were noted with respect to cell length ($F_{(2,46)}$=30.66; p<0.001), cell thickness ($F_{(2,47)}$=20.98; p<0.001), cell area ($F_{(2,69)}$=79.95; p<0.001) and perimeter ($F_{(2.68)}$=86.89; p<0.001)

The cells from outer and inner segments of Norway spruce wings were smaller than the cells from the central part, which is why they were analyzed separately. Their mean length was determined at 127 µm, and width – at 25 µm. Cells from the central part of the wing had the estimated length of 200 µm and width of more than 28 µm. Brown bodies were not observed inside spruce cells. Cell walls were 35% thicker in spruce than in pine wings.

The measured cell parameters were subjected to analysis of variance which did not reveal significant differences in the width of cells distributed in the center and in inner/outer segments of the wing ($F_{(1,15)}$=3.31; p=0.0890). Significant differences were observed in cell length ($F_{(1,15)}$=14.57; p=0.0017), wall thickness ($F_{(1,15)}$=4.91; p=0.0426), cell area ($F_{(1,15)}$=17.60; p=0.0008) and cell perimeter ($F_{(1,15)}$=13.68; p=0.0021), subject to location.

In the cross-section, the average thickness of pine wings (Fig. 6) was determined at 14.23 µm, whereas the thickness of spruce wings was nearly 4 µm smaller (Table 3). Wing cells observed in the cross-section formed a single layer with average lumen of 219 µm in pine and 149 µm in spruce.

Table 1. Cell parameters of Scots pine (*Pinus sylvestris* L.) wings in the longitudinal section (Statistica v. 12)
Tabela 1. Parametry wielkościowe komórek skrzydełek sosny zwyczajnej (*Pinus sylvestris* L.) na przekroju podłużnym (Statistica v. 12)

Parameter	Cell width	Cell length	Cell wall thickness	Cell perimeter	Cell area	Area of brown bodies in cells in wing sections:		
						outer	inner	central
	µm				µm²			
m	27.81	305.08	3.68	703.54	8433.65	4759.24	654.21	64.66
Me	28.12	293.43	3.70	684.32	8617.24	3977.38	680.28	56.46
Min	15.01	129.65	2.27	387.49	3629.29	1355.39	147.68	38.70
Max	36.86	534.08	5.67	1007.12	12733.23	8266.81	1469.83	107.00
SD^2	29.6	8775.2	1.0	24507.0	5579412.0	7532146.0	64289.9	883.8
SD	5.440	93.676	0.992	156.547	2362.078	2744.476	253.555	29.729
V	19.56	30.71	26.96	22.25	28.01	57.67	38.76	45.98
SE	1.047	18.735	0.216	29.585	446.391	1037.314	39.599	14.864
SK E	-0.30	0.30	0.37	0.15	0.00	0.07	0.52	1.42
K	-0.04	0.49	-0.65	-0.38	-0.66	-1.91	1.56	2.29

Table 2. Cell parameters of Norway spruce (*Picea abies* H. Karst) wings in the longitudinal section
Tabela 2. Parametry wielkościowe komórek skrzydełek świerka pospolitego (*Picea abies* H. Karst.) na przekroju podłużnym

Parameter	Wing section									
	Outer and inner					Central				
	Width	Length	Wall thickness	Area	Perimeter	Width	Length	Wall thickness	Area	Perimeter
	µm			$µm^2$	µm	µm			$µm^2$	µm
m	24.91	126.74	5.63	2699.63	313.86	28.12	199.36	4.51	5143.53	439.36
Me	25.49	117.07	5.93	2635.95	303.8	27.97	205.67	4.37	4837.97	442.41
Min	16.60	88.57	3.70	1634.36	236.13	20.94	93.66	3.90	2892.31	278.79
Max	33.00	250.57	7.18	4466.71	408.46	34.4	269.62	5.23	7323.35	609.84
SD^2	26.20	1279.60	1.20	646439.20	2734.50	19.00	4227.00	0.00	1802260.00	6291.00
SD	5.11	35.77	1.08	804.02	52.29	4.40	65.01	0.49	1342.48	79.32
V	20.53	28.23	19.18	29.78	16.66	15.66	32.61	10.84	26.10	18.05
SE	1.542	8.432	0.248	154.733	10.255	1.068	26.542	0.155	325.600	19.237
SK E	-0.13	2.59	-0.50	0.45	0.27	-0.24	-0.73	0.43	0.22	0.14
K	-0.84	8.66	-0.86	-0.80	-1.21	-1.26	0.16	-1.26	-0.76	0.56

Table 3. Cell parameters of Scots pine (*Pinus sylvestris* L.) and Norway spruce (*Picea abies* H. Karst.) wings in the cross-section

Tabela 3. Parametry wielkościowe skrzydełka sosny zwyczajnej (*Pinus sylvestris* L.) i świerka pospolitego (*Picea abies* H. Karst.) w przekroju poprzecznym

Parameter	Species	*m*	*Me*	Min	Max	SD^2	*SD*	*V*	*SE*	*SK E*	*K*
Thickness [μm]	P	14.23	13.98	9.92	19.59	5.44	2.33	16.40	0.344	0.36	-0.44
	S	10.06	10.02	2.32	14.75	7.38	2.72	27.01	0.430	-0.32	0.56
Cell lumen [μm^2]	P	218.94	208.55	145.07	314.97	3208.93	56.65	25.87	20.028	0.70	-0.24
	S	149.34	141.56	49.52	241.05	3752.89	61.26	41.02	20.420	0.30	0.09

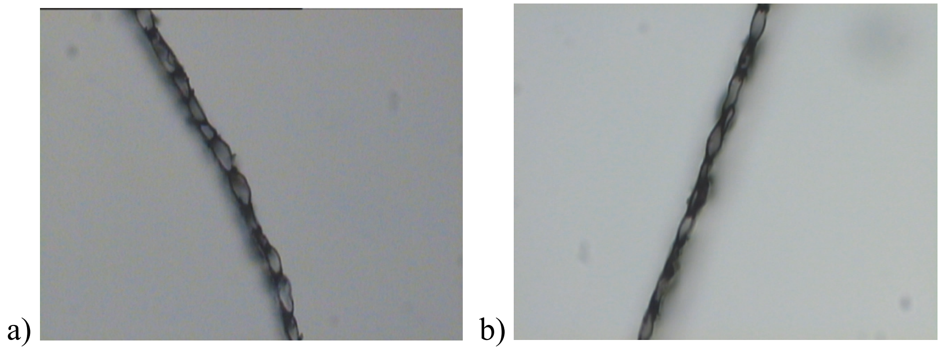

Fig. 6. Wings in the cross-section: a – Scots pine (*Pinus sylvestris* L.), b – Norway spruce (*Picea abies* H. Karst.)
Rys. 6. Skrzydełka w przekroju poprzecznym: a – sosny zwyczajnej (*Pinus sylvestris* L.), b – świerka pospolitego (*Picea abies* H. Karst.)

The analysis of variance confirmed significant differences in wing thickness ($F_{(1,84)}=58.67$; $p<0.001$) and cell lumen ($F_{(1,15)}=5.86$; $p=0.0286$) between the analyzed species.

4.3. Chemical composition of Scots pine (*Pinus sylvestris* L.) and Norway spruce (*Picea abies* H. Karst.) wings

The chemical analysis revealed differences in the composition of Scots pine and Norway spruce wings. The equilibrium moisture content of wings ranged from 10% to 11%, and in wood, this parameter is generally determined at 6% to 7% under identical conditions. The above difference can be attributed to the high content of extractive compounds in wings. At the drying temperature of 105°C, water and extractives evaporate from wings, and the same process is observed in pine wood. The resulting loss of mass increases the absolute moisture content of the analyzed material. The content of extractive substances was three times lower in pine wings (4.6%) than in spruce wings (14.5%). The content of structural compounds, i.e. cellulose, lignin and hemicellulose, varied between species. Pine wings contained more cellulose and holocellulose, but less lignin than spruce wings. Lignin concentration was higher in spruce wings. A two-fold difference in the content of substances soluble in 1% NaOH was also noted. The hemicellulose content, which can be theoretically determined from the difference in cellulose and holocellulose content, was similar in both species. The two-fold difference in the content of substances that are soluble in 1% NaOH can be attributed to much higher concentrations of extractive substances (by around 10%) in spruce than in pine. Both species were characterized by relatively low ash content that did not exceed 2% (Figure 7).

The chemical composition analysis revealed that pine and spruce wings contained less cellulose, but significantly more lignin and extractive substances than pine and spruce wood (Sjöström 1993).

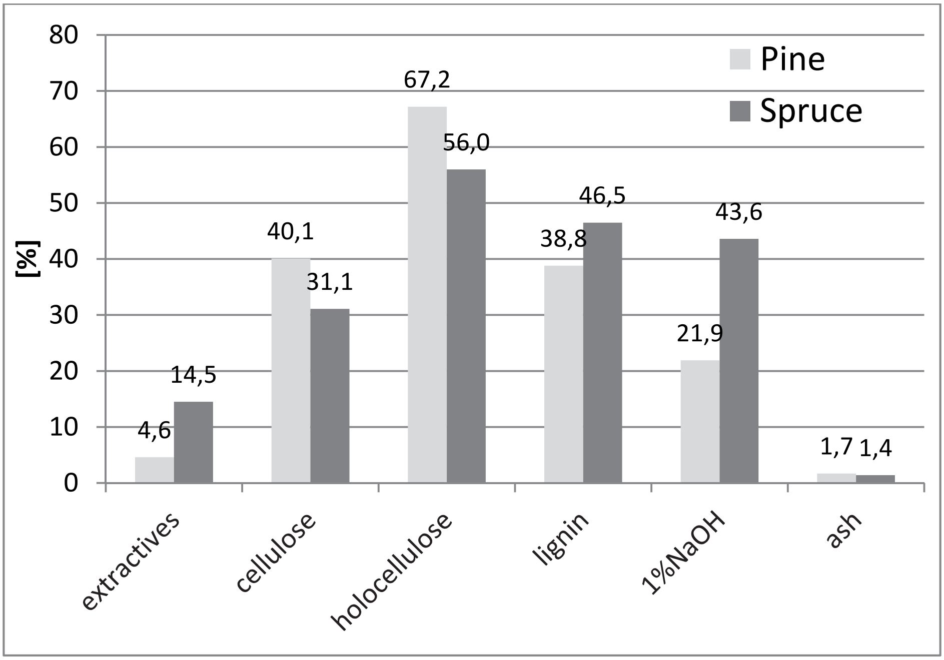

Fig. 7. Chemical composion of Scots pine (*Pinus sylvestris* L.) and Norway spruce (*Picea abies* H. Karst.) wings
Rys. 7. Skład chemiczny skrzydełek sosny zwyczajnej (*Pinus sylvestris* L.) I świerka pospolitego (*Picea abies* H. Karst.)

In wood, heat of combustion is determined by moisture content and composition, including the content of polysaccharides, lignin and extractive substances. The heat of combustion of structural and non-structural wood components was calculated by many authors. This parameter was determined at 17.3 MJ·kg^{-1} in cellulose and 27.7 MJ·kg^{-1} in lignin (Rowell 2012). Coniferous lignin has a different structure, and its heat of combustion is 23.5 MJ·kg^{-1} (Bulk & Jenkins 2000). The highest heat of combustion in the range of 34.89 to 37.22 MJ·kg^{-1} was noted in coniferous extractives (Howard 1973).

Formula (2) was used to calculate the calorific value of wings based on their chemical composition. Calorific value was determined at 19.72 MJ·kg^{-1} for pine wings and at 22.01 MJ·kg^{-1} for spruce wings.

In a study by Font et al. (2009), the calorific value of pine needles and cones was calculated at 20.14 MJ·kg^{-1} and 18.78 MJ·kg^{-1}, respectively.

4.4. Heat of combustion and calorific value of Scots pine (*Pinus sylvestris* L.) and Norway spruce (*Picea abies* H. Karst.) wings and empty seeds

The carbon content of pine and spruce seeds was 45.19% (Table 4), and it was somewhat higher in wings (49.09%-49.15%). Hydrogen concentrations were similar in seeds and wings (5.72%-5.79%), and they were lower than in coniferous wood (6.3%) examined by Munalula & Martin (2009) and Reva et al. (2012). Frank & Cox (2009) determined carbon and hydrogen levels in the seeds of selected species of coniferous trees: Apache pine (*Pinus engelmannii*) – C 58.7%, H 8%, white fir (*Abies concolor*) – C 60.6%, H 8.2%, and the subalpine fir (*Abies lasiocarpa*) – C 63.1%, H 9.2%. According to the cited authors, the carbon and hydrogen content of coniferous seeds decreases during storage.

Seeds were significantly more abundant in nitrogen (2.62%) than wings (0.57%-0.59%). Plant seeds, including the seeds of coniferous trees, are generally rich in protein (Gifford 1988), which explains the higher content of nitrogen. Sulfur content was determined at 0.218%-0.315%. This parameter is generally lower in cones (Brebu et al. 2010, Font et al. 2009). Similarly to nitrogen, sulfur may be derived from seed proteins. In the elemental analysis conducted by Brebu et al. (2010), pine seeds contained 42.62% C, 5.56% H, 0.76% N and 0.05% S.

The heat of combustion and calorific value of pine and spruce wings and seeds are presented in Table 5. The mean heat of combustion was determined at 20.57 MJ·kg^{-1} in pine wings (19.75 to 22.10 MJ·kg^{-1}), 20.38 MJ·kg^{-1} in spruce wings (20.04 to 20.79 MJ·kg^{-1}) and 20.69 MJ·kg^{-1} in empty seeds (19.94 to 21.08 MJ·kg^{-1}).

Table 4. Elemental composition of samples
Tabela 4. Zawartość pierwiastków w badanych próbkach

Sample	C	H	N	S
	[%]			
Spruce wings	49.09	5.74	0.59	0.273
Pine/spruce seeds	45.19	5.79	2.62	0.315
Pine wings	49.15	5.72	0.57	0.218

In dry material, heat of combustion is higher than its calorific value by the amount of heat required to evaporate water from hydrogen combustion (Krzysik 1974). For this reason, the calorific value of all wings and seeds was lower than their heat of combustion. Calorific value was used in successive analyses as a parameter which has greater practical significance and is generally used to determine the energy efficiency of fuels.

In view of the general scarcity of published information about the calorific value of pine and spruce wings and empty seeds, the obtained values were compared with the calorific value of wood. According to the literature, pine wood has calorific value of 19.2-21.2 $MJ \cdot kg^{-1}$ and spruce wood – 18.8-20.5 $MJ \cdot kg^{-1}$ (Günther et al. 2009, Haufa & Wojciechowska 1986, Komorowicz et al. 2009, Krzysik 1974, Lu et al. 2009, Monkielewicz & Pflaum 1967, Rembowski 2007, Reva et al. 2012, So & Eberhardt 2013, Stolarski et al. 2013, Uri et al. 2015).

The mean calorific value of pine wings was determined at 19.38 $MJ \cdot kg^{-1}$ (18.57 to 20.91 $MJ \cdot kg^{-1}$), and it was 0.18 $MJ \cdot kg^{-1}$ (0.93%) higher than the minimal value and 1.82 $MJ \cdot kg^{-1}$ (8.58%) lower than the maximum value for pine wood.

The mean calorific value of spruce wings was determined at 19.20 $MJ \cdot kg^{-1}$ (18.86-19.62 $MJ \cdot kg^{-1}$), and it was 0.40 $MJ \cdot kg^{-1}$ (2.08%) higher than the minimal value and 1.30 $MJ \cdot kg^{-1}$ (6.34%) lower than the maximum value for spruce wood.

The mean calorific value of empty pine and spruce seeds was 19.49 $MJ \cdot kg^{-1}$ (18.75-19.89 $MJ \cdot kg^{-1}$), and it was 0.69 $MJ \cdot kg^{-1}$ (3.54%) higher than the minimal value for spruce wood and 1.71 $MJ \cdot kg^{-1}$ (8.07%) lower than the maximum value for pine wood.

The mean calorific value of all samples was 19.36 $MJ \cdot kg^{-1}$, and it was 0.56 $MJ \cdot kg^{-1}$ (2.89%) higher than the minimal value for spruce wood and 1.84 $MJ \cdot kg^{-1}$ (8.68%) lower than the maximum value for pine wood. In all cases, the results were closer to the minimum values reported in the literature for a given tree species.

The statistical analyzes presented in Table 5 for calorific value and combustion heat indicate high accuracy of measurement and reproducibility (max. SE = 0.23).

The calorific value of pine wings was 1.72% lower and the calorific value of spruce wings was 12.77% lower in comparison with the empirical values determined based on formula (2).

The analysis of variance ($F_{(2,28)}=1.05$; $p=0.36$) revealed an absence of significant differences in the calorific value of the examined residues, which implies that the analyzed material was homogeneous in this respect (Stat Soft, Inc. 2014; Luszniewicz & Słaby 2008; Rabiej 2012).

According to Aniszewska (2012), extraction residues such as wings and empty seeds account for approximately 0.5% of husked material. In 2009-2012, the total production of cones from four species of forest trees (Scots pine, Norway spruce, European larch and silver fir) reached 1432.3 Mg in Poland (Aniszewska & Kuszpit 2015). Therefore, the mean annual production of cones for seed husking was 35.8 Mg, including around 1.79 Mg of extraction residues that are suitable for energy generation. The total calorific value is estimated 34.46 GJ, and that energy can be used to heat drying cabinets or residential buildings. The energy obtained from the combustion of extraction residues would be sufficient to heat a residential building with a floor area of 100 m^2, standard insulation and energy use intensity of 100 $W \cdot m^{-2}$ for 39-40 days.

Table 5. Heat of combustion and calorific value of Scots pine (*Pinus sylvestris* L.) and Norway spruce (*Picea abies* H. Karst.) wings and empty seeds – descriptive statistics (Stat Soft Inc. 2014)
Tabela 5. Ciepło spalania, wartość opałowa skrzydełek sosny zwyczajnej (*Pinus sylvestris* L.) i świerka pospolitego (*Picea abies* H. Karst.) oraz mieszanki pustych nasion – statystyki opisowe (Stat Soft, Inc. 2014)

Material	***m***	**+95% *m***	**-95% *m***	**Min**	**Max**	SD^2	***SD***	***V***	***SE***	***SK E***	***K***
Heat of combustion [MJ·kg^{-1}]											
Pine wings	20.57	20.05	21.08	19.75	22.10	0.52	0.72	3.50	0.23	1.06	0.98
Empty seeds	20.69	20.48	20.89	19.94	21.08	0.10	0.31	1.49	0.09	-1.33	2.82
Spruce wings	20.38	20.19	20.56	20.04	20.79	0.07	0.26	1.26	0.08	0.23	-1.13
Total	**20.55**	**20.37**	**20.72**	**19.75**	**22.10**	**0.22**	**0.47**	**2.30**	**0.08**	**0.97**	**2.53**
Calorific value [MJ·kg^{-1}]											
Pine wings	19.38	18.87	19.90	18.57	20.91	0.51	0.72	3.69	0.23	1.05	0.97
Empty seeds	19.49	19.29	19.70	18.75	19.89	0.10	0.31	1.58	0.09	-1.29	2.71
Spruce wings	19.20	19.01	19.38	18.86	19.62	0.07	0.26	1.35	0.08	0.24	-1.12
Total	**19.36**	**19.19**	**19.54**	**18.57**	**20.91**	**0.22**	**0.47**	**2.43**	**0.08**	**0.98**	**2.56**

It should be noted that seed wings are very light, which implies high transportation costs. For this reason, the preferred solution would be to burn extraction residues locally in a seed extraction plant.

The macroelement and microelement content of pine and spruce seeds and wings are presented in Table 6. Mercury (Hg) is the most toxic heavy metal. Plants absorb mercury from soil via the root system or directly from air. The analyzed seeds and wings were characterized by low mercury levels which ranged from 0.0015 to 0.0032 $mg \cdot kg^{-1}$. The concentration of cadmium (Cd) in the mixture of pine and spruce seeds was determined at 1.607 (±0.016) $mg \cdot kg^{-1}$. Cadmium content was higher in wings at 1.866 (±0.103) $mg \cdot kg^{-1}$ (pine) and 2.600 (±0.032) $mg \cdot kg^{-1}$ (spruce). Cadmium is not a microelement, and excessive cadmium levels in seeds can lead to genomic changes (Prus-Głowacki et al. 2006, Stvolinskaya 2000). Similarly to cadmium, lead does not demonstrate biological activity. The described metals can disrupt plant metabolism and limit the uptake of other elements (Kabata-Pendias & Pendias 1999). Lead concentrations of 30-300 $mg \cdot kg^{-1}$ exert toxic effects on plants (Mandre & Ots 2012). In this study, the lead content of pine and spruce seeds was below 1 $mg \cdot kg^{-1}$. Similar results were reported by Ganatsasa et al. (<1 $mg \cdot kg^{-1}$) who did not observe excessive Pb levels in the seeds of pine trees growing at various distance from roads. Cadmium and lead concentrations are generally higher in the roots, wood and bark of coniferous trees (Schulz et al. 1999, Coşkun 2006, Nkongolo et al. 2008). In this study, the lead content of wings was determined at 6.75 (±0.179) $mg \cdot kg^{-1}$ (pine) and 1.88 (±0.067) $mg \cdot kg^{-1}$ (spruce), and it was higher than in seeds. Those differences could be attributed to the large area of wings capable of absorbing lead-containing dust.

Table 6. Elemental composition of Scots pine (*Pinus sylvestris* L.) and Norway spruce (*Picea abies* H. Karst.) wings and empty seeds [$mg \cdot kg^{-1}$ DM]

Tabela 6. Zawartość pierwiastków w skrzydełkach sosny zwyczajnej (*Pinus sylvestris* L.) i świerka pospolitego (*Picea abies* H. Karst.) oraz w pustych nasionach [$mg \cdot kg^{-1}$ s.m.]

	Pine wings				**Empty seeds**				**Spruce wings**				**GO*)**	**u*)**
	m	***SD***	***V***	***SE***	***m***	***SD***	***V***	***SE***	***m***	***SD***	***V***	***SE***		
Cd	1.87	0.10	5.51	0.06	1.61	0.02	0.97	0.01	2.60	0.03	1.24	0.02	0.5	10
Pb	6.75	0.18	2.66	0.10	0.56	0.27	48.57	0.16	1.88	0.07	3.56	0.04	1	10
Cu	3.84	0.25	6.55	0.15	9.93	0.06	0.59	0.03	3.75	0.15	3.92	0.08	1	20
Zn	42.23	0.88	2.09	0.51	83.43	1.23	1.48	0.71	33.59	1.55	4.61	0.89	1	20
Ni	3.27	0.13	3.93	0.07	13.16	0.31	2.36	0.18	3.66	0.12	3.26	0.07	1	20
Cr	0.50	0.08	15.52	0.04	8.27	0.15	1.79	0.09	0.58	0.15	25.22	0.09	1	10
Mo	1.12	0.48	42.98	0.28	33.03	2.24	6.77	1.29	0.82	0.23	28.23	0.13	2	15
Co	1.07	0.08	7.41	0.05	1.34	0.08	6.31	0.05	0.50	0.36	73.43	0.21	1	10
Fe	124.13	3.10	2.50	1.79	1130.33	30.92	2.74	17.85	22.00	1.71	7.78	0.99	2	15
Mn	39.20	1.07	2.73	0.62	65.40	2.76	4.22	1.59	12.49	0.81	6.46	0.47	1	10
Ca	992.33	7.02	0.71	4.06	1603.33	60.28	3.76	34.80	1059.67	60.87	5.74	35.14	2.5	13
Mg	1523.33	75.06	4.93	43.33	1226.67	60.28	4.91	34.80	950.47	23.09	2.43	13.33	2.5	10
K	2029.00	101.43	5.00	58.56	2062.00	52.12	2.53	30.09	3416.00	114.94	3.36	66.36	0.2	8
Na	132.33	10.69	8.08	6.17	91.03	1.38	1.52	0.80	127.01	2.16	1.70	1.25	0.2	10
Hg	0.0032	0.0003	8.27	0.0002	0.0028	0.0002	6.19	0.0001	0.0015	0.0002	13.33	0.0001	0.0007	15

*) limit of detection (*LOD*) and uncertainty (*u*) at k = 2 and α=0.95.

Copper is a microelement that influences enzymatic processes in plants, including photosynthesis. Copper and iron deficiencies lead to yellowing of needles, death of side shoots and inhibited seedling growth. However, coniferous trees are resistant to high environmental levels of Cu. Pine is a hyperaccumulator of Cu in strongly polluted environments (Kirchner et al. 2008). In this study, the copper content of pine and spruce seeds was determined at 9.93 (±0.059) $mg \cdot kg^{-1}$. In the work of Ganatsasa et al. (2011), copper levels in pine seeds reached 8.36-11.21 mg/kg, whereas Cheikh-Rouhou et al. (2006) determined the copper content of Aleppo pine (*Pinus halepensis*) seeds at 22.5 $mg \cdot kg^{-1}$. In this study, copper concentrations were much lower in wings at 3.84 (±0.25) $mg \cdot kg^{-1}$ (pine) and 3.75 (±0.147) $mg \cdot kg^{-1}$ (spruce). Zinc is a ubiquitous element with low toxicity, and excessive zinc levels in soil do not inhibit plant growth. This microelement is a component of plant growth regulators, mostly auxins and indoleacetic acid (IAA), and it participates in enzymatic reactions (Kabata-Pendias & Pendias 1999). The analyzed pine and spruce seeds contained 83.4 (±1.2) $mg \cdot kg^{-1}$ of zinc, whereas the zinc content of wings was significantly lower (33.6-42.2 $mg \cdot kg^{-1}$). Cheikh-Rouhou et al. (2006) determined the Zn content of pine seeds at 134.9 $mg \cdot kg^{-1}$. Nickel is used as a cofactor by numerous enzymes, and it affects nitrogen metabolism in plants (Kabata-Pendias & Pendias 1999). Plants have a low demand for this element. Similarly to Cd and Pb, excessive levels of Ni can inhibit growth and induce genomic changes in seeds (Kabata-Pendias 1999, Prus-Głowacki et al. 2006, Stvilinskaya 2000). Pines can act as hyperaccumulators of Ni in strongly polluted environments (Kirchner et al. 2008). In this study, the nickel content of pine and spruce seeds was determined at 13.16 (±0.31) $mg \cdot kg^{-1}$, and wings were significantly less abundant in this metal (3.27-3.66 $mg \cdot kg^{-1}$). Chromium is also an important plant microelement. Chromium levels reached 8.27 (±0.15) $mg \cdot kg^{-1}$ in pine and spruce seeds, but did not exceed LOD in wings (<1 $mg \cdot kg^{-1}$). Molybdenum is a component of nitrogen metabolizing enzymes (Kabata-Pendias & Pendias 1999), and its deficiency can compromise the quality of seeds. The Mo content of pine and spruce seeds was determined at 33.0 (±2.2) $mg \cdot kg^{-1}$ in pine and spruce seeds, and it was below LOD in wings (<2 $mg \cdot kg^{-1}$). Cobalt is not an essential microelement for most plants (Greinert 2011), and its concentrations were determined at 1.337 (±0.084) mg·kg^{-1} in pine and spruce seeds, 1.072 (±0.079) mg·kg^{-1} in pine wings, and below 1 mg/kg in spruce wings. Iron plays a host of important roles in plants. It is involved in enzymatic reactions, it controls nitrogen metabolism and influences photosynthetic processes (Kabata-Pendias & Pendias 1999). Pine and spruce seeds contained 1130 (±31) mg·kg^{-1} of iron, whereas wings were significantly less abundant in this element at 124 (±3) mg·kg^{-1} (pine) and 22 (±2) mg·kg^{-1} (spruce). The iron content of pine seeds was determined at 271 mg·kg^{-1} by Cheikh-Rouhou et al. (2006) and at 94.38-135.05 mg·kg^{-1} by Ganatsasa et al. (2011). Manganese and calcium are iron antagonists in plant tissues (Kabata-Pendias & Pendias 1999, Mandre & Ots 2012). Similarly to iron, manganese participates in photosynthesis and is a component of many enzymes (Kabata-Pendias & Pendias 1999). Manganese concentrations were determined at 65.4 (±2.8) mg·kg^{-1} in seeds and 12.5-39.2 mg·kg^{-1} in wings. The manganese content of pine seeds was determined at 22.68-37.78 mg·kg^{-1} by Ganatsasa et al. (2011) and at 51.3 mg·kg^{-1} by Cheikh-Rouhou et al. (2006).

Light metals such as Ca, Mg, K and Na are macroelements essential for plant growth and development. According to Zhan et al. (2014), their concentrations in wood, bark and green parts of plants are influenced by seeding rate, which can also affect the content of those macroelements in seeds and wings. The examined seeds were most abundant in potassium, followed by calcium, magnesium and sodium. Cheikh-Rouhou et al. (2006) also reported high levels of essential macronutrients in the seeds of the Aleppo pine (*Pinus halepensis*). In their study, the predominant element was K (6171 mg·kg^{-1}), followed by Mg (3303 mg·kg^{-1}), Ca (1167 mg·kg^{-1}) and Na (69.6 mg·kg^{-1}). Sukhdolgor et al. (2003) also noted the highest levels of magnesium and calcium in Scots pine seeds. The predominant heavy metal was manganese, followed by copper, zinc and iron. The content of Ni, Cr, Mo and Pb was 10- to 100-fold lower in comparison with the above metals.

5. Conclusions

Biomonitoring is an essential part of environmental protection and resource management programs. The threats and potential outcomes of resource management projects have to be continuously monitored in protected areas. Biomonitoring schemes are obligatory under the provisions of Polish and EU laws. Changes in ecosystems can be evaluated with the use of bioindicators, including seed extraction residues. This paper describes selected physicochemical parameters of extraction residues based on the results of microscopic and chemical analyses. Morphological differences were noted between the wings of Scots pine (*Pinus sylvestris* L.) and Norway spruce (*Picea abies* H. Karst.) seeds. Microscopic observations revealed that pine and spruce wings were composed of variously sized cells with different wall thickness. The cells in pine wings were longer and larger than the cells in spruce wings. Spruce cells had thicker walls, which contributed to greater rigidity and overall strength of spruce wings. The results of chemical analyses demonstrated that spruce wings contained 8% more lignin and 9% less cellulose than pine wings. The observed differences in the chemical composition of pine and spruce wings did not affect their calorific value. The cellulose content of pine wings is generally similar to the amount of cellulose found in pine cones, and it was determined at 39.3% by Font et al. (2009) and at 40.1% in this study. The lignin content of pine wings was 8% lower in comparison with the published data.

The heat of combustion and the calorific value of pine and spruce wings and empty seeds did not differ significantly and were determined at 19.25 $MJ \cdot kg^{-1}$ on average. The mean results noted in this study were within the range determined by various authors for pine and spruce wood, but they were only 0.36-3.14% higher than the minimum values.

Pine and spruce wings differed in color. Pine wings were darker along the edges, but they contained 10% less extractive substances and 21% less compounds soluble in NaOH than spruce wings. Spruce wings were lighter along the edges and in the center, but they were visibly darker under the seed (due to morphological differences, this part is not present in pine wings). The above segment of spruce wings probably has a high content of the analyzed chemical compounds.

Heavy metal concentrations were higher in seeds than in wings of the analyzed tree species. The only exception was lead. Contamination with lead could be attributed to the deposition of lead-containing dust on the surface of wings. The content of heavy metals in the examined seeds should not have adverse environmental effects, and it was similar to that reported by other authors. The evaluated seeds were abundant in potassium, calcium and magnesium.

Wings and empty seeds separated from fully developed seeds in the cleaning process can be used for energy generation. In Poland, the annual production of seed extraction residues is estimated at 1790 kg, which would be sufficient to heat a medium-sized home for 40 days. However, seed wings are very light, which considerably increases transportation costs. For this reason, wings should be burned locally in a husking plant or added to pellets containing other types of biomass.

Abbreviations

Ext – content of extractive substances,
F – Fisher's F-test,
LOD – limit of detection,
H – hydrogen content, %,
K – coefficient of kurtosis,
L – content of Klason lignin relative to dry matter content of wood after extraction,
Me – median,
Q_{ne} – calorific value of wood before extraction, $MJ \cdot kg^{-1}$,
Q_{op} – calorific value, $MJ \cdot kg^{-1}$,
Q_s – heat of combustion, $MJ \cdot kg^{-1}$,
SD – standard deviation,
SD^2 – sample variance,
SE – standard error,
SK E – coefficient of skewness,
V – coefficient of variation,
W_w – relative moisture content, %,
m – mean,
p – probability at α=0.05,
u – uncertainty.

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Właściwości fizykochemiczne i możliwości energetycznego wykorzystania pozostałości wyłuszczarskich

Streszczenie

W przedstawionych badaniach określono ciepło spalania i wartość opałową pustych nasion i ich skrzydełek, które mogą być wykorzystane na cele energetyczne. Opisana została ich budowa komórkowa oraz zawartość toksycznych metali i innych pierwiastków (Cd, Pb, Hg, Cu, Zn, Ni, Cr, Mo, Co, Fe, Mn, Ca, Mg, K, Na), które mogą być emitowane do środowiska. Ciepło spalania wyznaczono metodą kalorymetryczną, budowę komórkową określano na podstawie zdjęć z mikroskopu z kamerą Nikon Alphaphot -2- TRIN i mikroskopu skaningowego Quanta 200. Analizę elementarną i pierwiastkową wykonano analizatorem Elementar Vario Macro Cube oraz mineralizatorem mikrofalowym Milestone Start D. Uzyskano średnią wartość opałową badanych materiałów w zakresie 19,20-19,49 $MJ \cdot kg^{-1}$. Zawartość metali ciężkich w nasionach sosny i świerka jest wyższa niż w skrzydełkach, jednak ich ilość nie powinna powodować negatywnych skutków ekologicznych. Zawartość metali była zbliżona do wartości podawanych przez innych autorów. Nasiona były zasobne w potas, wapń i magnez. Skrzydełka i puste nasiona po procesie wyłuszczenia szyszek można spalać i wykorzystywać jako paliwo pochodzące z OZE.

Abstract

The heat of combustion and calorific value of empty seeds and seed wings were determined. The structure of seed and wing cells and the content of toxic metals and other elements (Cd, Pb, Hg, Cu, Zn, Ni, Cr, Mo, Co, Fe, Mn, Ca, Mg, K, Na) were described. Heat of combustion was measured in a bomb calorimeter. Cell structure was described based on microscopic images acquired with the Nikon Alphaphot -2- TRIN microscope and camera and the Quanta 200 scanning electron microscope. The elemental analysis was performed in the Elementar Vario Macro Cube analyzer and the Milestone Start D microwave digestion system. The mean calorific value of the tested materials ranged from 19.20 to 19.49 $MJ \cdot kg^{-1}$. Heavy metal content was higher in pine and spruce seeds than in wings, but the noted concentrations should not have adverse environmental effects. Metal concentrations were similar to those reported by other authors. The tested seeds were abundant in potassium, calcium and magnesium. Wings and empty seeds from extraction residues can be burned and used as sources of renewable energy.

Słowa kluczowe:
bioenergia, biomasa, biomonitoring, odpady leśne, metale, pozostałości wyłuszczarskie

Keywords:
bioenergy, biomass, biomonitoring, forest waste, metals, seed extraction residues