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LIGNOCELLULOSIC BIOMASS DERIVED FROM AGRICULTURAL LAND AS INDUSTRIAL AND ENERGY FEEDSTOCK

Lignocellulosic biomass is a natural, renewable and highly versatile resource. In recent years, woody biomass produced in short rotation coppices has become increasingly popular. Hence, this research was undertaken to assess the thermophysical and chemical properties of willow, poplar and black locust stems in relation to a soil fertilization regime. The experiment was set up in the village of Samławki in north-eastern Poland (53°59' N, 21°04' E), on soil considered sub-standard for the traditional agricultural production of food or fodder crops. The black locust biomass was characterised by the lowest moisture content combined with the greatest lower heating value and ash content. The poplar plant had the highest carbon and hydrogen content and the greatest higher heating value, although due to its high moisture content, it had the poorest lower heating value. The willow biomass was characterised by the highest content of cellulose and holocellulose. Mycorrhiza improved the cellulose content as well as the lignin and holocellulose content

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in the wood of the black locust. In the case of the willow wood, the application of lignin to the soil was the only measure that reduced the content of the lignin in the lignocellulosic biomass.

Keywords: willow, poplar, black locust, chemical composition, thermophysical properties, short rotation coppices

Introduction

Wood is a natural, renewable resource that can be used in a variety of ways. Nowadays, it is more widely used in industry, with the actual applications dependent on the economy of a given country. In developed countries, wood processing is comprehensive and rational. In developing countries, however, wood constitutes a major energy source. It is estimated that as much as 90% of the energy is produced from wood, proving itself to be an available and inexpensive resource [Manalula, Meincken 2009]. It is worth noting that lignocellulosic biomass as a source of energy is used in a number of technologies. Processes of energy generation from biomass depend mainly on the type and source of biomass. Lignocellulosic biomass may be transformed into various forms of biofuel including solid, liquid and gaseous ones. Biomass-derived fuel may provide heat energy for residential estates and industrial facilities, generate electric energy and serve as transport fuel [Gross et al. 2003; Keoleian, Volk 2005; Guidi et al. 2009; Somerville 2010; Hanoka et al. 2010; Vaezi et al. 2012].

The rational use of natural resources is crucial for environmental protection. The demand for clean and environmentally-friendly fuels stimulates the search for new energy sources and the development of new production technologies designed to replace conventional fuel with a range of biofuels. Wood as lignocellulosic matter is one of the key resources used for second generation biofuel production. The International Energy Agency (IEA) forecasts that in 2050 biofuel may account for as much as 27% of all transport fuel, substantially reducing the emission of carbon dioxide into the atmosphere. Within the global economy, bioethanol production from lignocellulosic biomass may generate 50 billion dollars by 2022 [IEA 2004].

Nevertheless, it must be underlined that the expected high demand for lignocellulosic biomass by the power engineering industry may result in shortages of this woody resource for other industrial purposes, including cellulose and paper production, as well as furniture and wood-like flooring manufacture [Stolarski et al. 2011]. Therefore, good quality non-forest lignocellulosic resources are urgently being sought. It is most important to evaluate the physicochemical quality of lignocellulosic biomass derived from short rotation coppices cultivated on arable land. This research on the thermophysical and chemical properties of two-year willow, poplar and black locust plants was undertaken for this purpose.

Material and methods

Field experiment

A controlled two level factorial field experiment completed between 20–31 April 2010 at the Research Station in Łężany, affiliated to the University of Warmia and Mazury in Olsztyn, served as the basis for this research. The experiment was located in the village of Samławki in north-eastern Poland (53°59' N, 21°04' E), on soil considered sub-standard for the traditional agricultural production of food or fodder crops.

The first factor of the experiment consisted of three plant species: willow (*Salix viminalis*), poplar (*Populus nigra* x *P. Maximowiczii* Henry cv. Max-5 P) and black locust (*Robinia pseudoacacia*). All the crops were planted at a density of 11.11 thousand plants per hectare. The second factor was soil enrichment, referred to as fertilization. The following substances were applied to amend the soil: lignin (L), mineral fertilization (F), and mycorrhizal vaccination (M). The control treatment (C) added no amending substances to the soil.

Lignin, a paper manufacturing by-product, was introduced to the soil in a quantity of 13.3 Mg ha^{-1}. Liquid mycorrhizal vaccination was applied under each of the crops in a dose of 30–35 cm^3 per plant; the NPK mineral fertilization consisted of 13 N, 50 P and 90 K kg ha^{-1}. The experiment was set up in a split-plot design. In total, 72 plots were established, each divided into three subplots, 18.0 m^2 each.

Collection of lignocellulosic biomass for laboratory analyses

In December 2011, two-year-old plants were manually cut with chain saw type DCS520 (Makita), 5–10 cm above the soil surface. Following this, the whole stems were made into wood chips in a Junkkari HJ 10 G (Junkkari, Finland) chopper coupled with a 96 kW tractor (New Holland, England). During the stem chipping, samples of the biomass corresponding to all the experimental factors were collected from each subfield for laboratory analysis. The collected samples were packed into plastic bags and transported to the Department of Plant Breeding and Seed Production at the University of Warmia and Mazury in Olsztyn.

Laboratory analysis

The average bulk density of the fresh wood chips of each species was determined in a laboratory. It was derived from the weight of the wood chips contained in a pot of 0.08 m^3 capacity. The analysis of the thermophysical and chemical properties was carried out in triplicate for each combination. First, the biomass moisture content was measured using the oven-dry method. For this purpose, the biomass was dried at 105±2°C in a Premed drier (KBC G-65/250; PN 80/G-04511) to obtain dry biomass. Then the dry biomass was ground in an IKA KMF 10 basic analytical mill (IKA Werke Gmbh & CO.KG, Germany) with a 1 mm mesh sieve. During the next stage, the higher heating value for dry biomass was determined with the dynamic method, using an IKA C 2000 calorimeter (IKA Werke Gmbh&CO. KG, Germany) in line with PN-81/G-04513. A sample of approximately 0.5 g was pelleted in an IKA WERKE C-21 press and left to dry. The biomass pellets were dried in a laboratory oven at 105±2°C, weighed with an accuracy of 0.1 mg, placed in a quartz crucible and inserted into a bomb calorimeter for further analysis in a pure oxygen atmosphere under 30 atm pressure. Based on the moisture content and higher heating value, the lower heating value of the biomass was determined, according to Kopetz et al. [2007]. The total content of ash was determined in an ELTRA TGA-Thermostep thermogravimetric analyser (ELTRA Gmbh, Germany) in accordance with the following standards: ASTM D-5142, D-3173, D-3174, D-3175, PN-G-04560:1998 and PN-ISO 562. A sample weighing approximately 1.5 g was prepared for the analysis. The concentrations of carbon, hydrogen and sulphur in the dry biomass were determined in an ELTRA CHS 500 automatic analyser (ELTRA Gmbh, Germany) according to PN/G-04521 and PN/G-ISO 35. A portion of approx. 0.15 g was weighed, as required for the analysis. The content of nitrogen was determined with Kjeldahl's method, using a K-435 mineraliser and a B-324 BUCHI distiller (BÜCHI Labortechnik AG, Schwitzerland). Finally, the content of chlorine was determined in Eschka's mixture.

The material for the chemical analyses was prepared in accordance with PN-92/P-50092. The samples were ground in a laboratory mill (Fritsch type 15) using a sieve with 1.0 mm square screens. The material was passed through brass sieves to separate the 0.5–1.0 mm fraction. The chemical composition was determined with the standard methods applied for chemical analyses of wood. Before determination of the cellulose, lignin and holocellulose content, extraction in 96% ethyl alcohol was performed using a Soxhlet's apparatus. Afterwards, the material was dried under laboratory conditions and the extracted substances (lipids, waxes, resins and others) were dried in a drier at 103±2^{o}C. As a result, the content of the following substances was determined: cellulose (using the Seifert method), lignin (using the Tappi method, using 72% H_2SO_4), pentosans (using the with Tollens method), holocellulose (using sodium chlorite, according to PN-75/50092), base--soluble substances (1% aqueous solution of NaOH) yielding data on the content of hemicelluloses in the tested wood, and finally the content of the substances soluble in cold and hot water. Additionally, the pH was assessed according to PN-Z-15011-1. Firstly, 50 g of the resource material was mixed in a conical flask with 200 cm^3 of distilled water. The flask, tightly closed, was put into a shaker and shaken for 0.5 hours. It was then left for 1 hour and the contents were stirred prior to the pH measurement. The results were read three times with an accuracy of 0.1. All the tests were repeated simultaneously in three replications. The results were calculated in relation to wood dry matter.

Statistical analysis

The research results were submitted to statistical analysis according to a 2×2 factorial ANOVA variance analysis. The SNK multiple test (Student Newman-Keuls) aggregated the means of similar values and generated homogeneous groups at a significance level of $\alpha = 0.01$. Furthermore, the arithmetic means and standard deviation were calculated for the analysed properties. The statistical analyses were conducted with the aid of STATISTICA 9.0 (StatSoft, Inc.).

Results

The bulk density of the fresh wood chips made from two-year stems chipped in a Junkkari HJ 10 G chopper was the highest for the willow (276.5 kg m^{-3}). It was lower for the wood chips made from the poplar (260.87 kg m^3) and the black locust plants (249.74 kg m^{-3}). The average bulk density of the wood chips was 262.36 kg m^{-3}.

In general, the thermophysical properties of the biomass were extremely varied with respect to the analysed factors and their interactions (tables 1 and 2).

Table 1. Significance of major effects and primary interactions for biomass thermo-physical properties
Tabela 1. Istotność efektów głównych i interakcji pierwszego rzędu dla właściwości termo-fizycznych biomasy

Specification *Specyfikacja*	Moisture *Wilgotność*	Ash content *Zawartość popiołu*	Higher heating value *Ciepło spalania*	Lower heating value *Wartość opałowa*	Volatile matter *Części lotne*	Fixed carbon *Części stałe*
Species *Gatunki*	***	***	***	***	***	***
Soil enrichment procedure *Nawożenie*	NS	***	***	NS	***	**
Species × Soil enrichment procedure *Gatunki × nawożenie*	**	***	***	**	***	***

* $p < 0.01 \div 0.001$
** $p < 0.001 \div 0.0001$
*** $p < 0.0001$
NS = not significant; *NS = nieistotne*

Table 2. Thermophysical properties of black locust, poplar, and willow biomass after the second year of vegetation (% d.m.)
Tabela 2. Właściwości termo-fizyczne biomasy robinii, topoli i wierzby po drugim roku wegetacji (% s.m.)

Species *Gatunek*	Soil enrichment procedure *Nawożenie*	Moisture *Wilgotność*	Ash content *Zawartość popiołu*	Higher heating value *Ciepło spalania*	Lower heating value *Wartość opałowa*	Volatile matter *Części lotne*	Fixed carbon *Części stałe*
		%	%	MJ kg^{-1}	MJ kg^{-1}	%	%
1	2	3	4	5	6	7	8
Black locust *Robinia*	C	47.77±0.28 d	1.68±0.04 d	19.40±0.03 e	8.97±0.08 ab	77.65±0.00 c	20.45±0.03 bc
	L	46.38±0.08 e	2.16±0.01 b	19.53±0.04 d	9.34±0.04 a	77.24±0.05 cd	20.07±0.05 cd
	F	48.08±0.02 d	2.67±0.15 a	19.85±0.00 bc	9.14±0.00 a	76.01±0.05 e	21.08±0.07 a
	M	46.65±0.41 e	1.82±0.01 d	19.42±0.03 e	9.22±0.11 a	77.47±0.03 c	20.27±0.03 c
Mean black locust *Średnio robinia akacjowa*		47.22±0.61 c	2.08±0.31 a	19.55±0.15 c	9.17±0.12 a	77.09±0.52 b	20.47±0.31 a
Poplar *Topola*	C	53.33±0.37 a	1.88±0.07 cd	19.93±0.01 b	8.00±0.08 cd	77.14±0.01 cd	20.69±0.07 b
	L	53.64±0.51 a	1.96±0.04 c	19.88±0.01 b	7.91±0.12 d	77.16±0.04 cd	20.56±0.08 bc
	F	54.48±1.27 a	2.22±0.02 b	20.05±0.03 a	7.80±0.30 d	76.86±0.05 d	20.63±0.07 bc
	M	53.09±0.24 a	2.00±0.01 c	20.06±0.00 a	8.11±0.05 cd	77.17±0.03 cd	20.47±0.02 bc
Mean poplar *Średnio topola*		53.64±0.66 a	2.01±0.10 b	19.98±0.06 a	7.95±0.15 c	77.09±0.11 b	20.59±0.08 a
Willow *Wierzba*	C	50.17±1.32 c	1.29±0.04 f	19.89±0.05 b	8.69±0.27 b	78.93±0.02 a	19.53±0.06 d
	L	51.67±0.65 b	1.52±0.03 e	19.82±0.02 c	8.32±0.16 c	77.28±0.46 cd	20.70±0.42 b
	F	50.57±0.01 c	1.33±0.09 f	19.58±0.03 d	8.45±0.01 bc	78.35±0.31 b	20.02±0.22 cd
	M	51.96±0.39 b	1.49±0.05 e	19.92±0.05 b	8.30±0.11 c	78.05±0.16 b	20.16±0.11 cd
Mean willow *Średnio wierzba*		51.09±0.77 b	1.41±0.09 c	19.80±0.11 b	8.44±0.16 b	78.15±0.52 a	20.10±0.38 b

Tabela 2. Ciąg dalszy
Table 2. Continued

1	2	3	4	5	6	7	8
Mean fertilization *Średnio nawożenie*	C	50.43±2.51	1.61±0.26 d	19.74±0.26 c	8.55±0.45	77.91±0.80 a	20.22±0.53 b
	L	50.56±3.28	1.88±0.29 b	19.74±0.16 c	8.52±0.65	77.23±0.24 c	20.44±0.36 a
	F	51.04±2.87	2.08±0.59 a	19.83±0.21 a	8.46±0.60	77.08±1.04 c	20.58±0.48 a
	M	50.57±2.99	1.77±0.22 c	19.80±0.29 b	8.55±0.52	77.57±0.40 b	20.30±0.15 b
Mean for experiment *Średnio z doświadczenia*		50.65±2.81	1.83±0.39	19.78±0.23	8.52±0.54	77.44±0.74	20.39±0.41

± standard error of the mean
± *odchylenie standardowe*
a, b, c… homogenous groups
a, b, c… grupy jednorodne
C control
C kontrola
L lignin
L lignina
F mineral fertilization
F nawożenie mineralne
M mycorrhiza
M mikoryza

Among the examined crops, the poplar produced the biomass with the highest moisture content (53.64%) (table 2). The moisture content in the willow and black locust biomass was significantly lower (2.54 and 6.42% less, respectively). The soil amendment did not greatly influence the biomass moisture. The poplar biomass was characterised by the highest moisture content; the black locust had the lowest moisture content in each variant of soil enrichment. The lowest content of ash was found in the willow biomass (1.41% d.m.). It was much higher in the poplar and black locust (43 and 48% more, respectively). As regards the soil amendment as an experimental factor, the highest ash content was found in the crops from the fertilized plots and the lowest one in the control. The poplar biomass was characterised by the greatest higher heating value. Regarding the moisture content, the greatest lower heating value was achieved by the black locust (9.17 MJ kg^{-1}). This value was 8% lower in the willow and 13% lower in the poplar wood chips. Soil amendment did not significantly affect the lower heating value of the biomass.

The elemental composition of the black locust, poplar and willow biomass after the second year of growth was extremely varied with respect to the analysed factors and their mutual interactions (tables 3 and 4). The poplar biomass was characterised by the highest content of carbon (on average 52.65% d.m.) and hydrogen (6.19% d.m.) but the lowest content of sulphur (0.032% d.m.) and chlorine (0.005% d.m.). The sulphur content in the willow biomass was at the same level but the chlorine content was slightly higher than in the poplar. The hydrogen content in the black locust biomass was at the same level as in the poplar. The black locust was characterised by the lowest carbon content and highest sulphur, chlorine, and nitrogen content. The content of the latter was 2.3-fold higher than in the poplar biomass and 2.7-fold higher than in the willow biomass. Mineral fertilization significantly increased the content of sulphur, nitrogen and chlorine in the black locust biomass versus the two other species and in comparison to the soil enrichment.

Table 3. Significance of major effects and primary interactions for elementary composition of biomass
Tabela 3. Istotność efektów głównych i interakcji pierwszego rzędu dla składu elementarnego biomasy

Specification *Specyfikacja*	C	H	S	N	Cl
Species *Gatunki*	***	***	***	***	***
Soil enrichment procedure *Nawożenie*	***	NS	***	***	***
Species × soil enrichment procedure *Gatunki × nawożenie*	***	***	***	***	***

* $p < 0.01 \div 0.001$
** $p < 0.001 \div 0.0001$
*** $p < 0.0001$
NS = not significant; *NS = nieistotne*

Table 4. Elementary composition of black locust, poplar, willow biomass after the second year of vegetation (% of d.m.)
Tabela 4. Skład elementarny biomasy robinii, topoli i wierzby po drugim roku wegetacji (% s.m.)

Species *Gatunek*	Soil enrichment procedure *Nawożenie*	C	H	S	N	Cl
Black locust *Robinia*	C	51.66±0.13 c	6.28±0.02 a	0.059±0.000 b	1.16±0.01 c	0.019±0.001 b
	L	49.80±0.00 e	6.14±0.03 b	0.058±0.002 b	1.21±0.01 b	0.016±0.001 d
	F	50.76±0.14 d	6.13±0.03 b	0.073±0.002 a	1.70±0.05 a	0.024±0.001 a
	M	51.03±0.27 d	6.24±0.00 b	0.057±0.001 b	1.14±0.00 c	0.017±0.001 c
Mean black locust *Średnio robinia akacjowa*		50.81±0.55 c	6.20±0.05 a	0.061±0.005 a	1.30±0.18 a	0.019±0.003 a
Poplar *Topola*	C	53.14±0.09 a	6.30±0.09 a	0.028±0.001 c	0.55±0.01 e	0.005±0.001 f
	L	52.52±0.07 b	6.15±0.06 b	0.032±0.001 b	0.57±0.00 e	0.003±0.000 g
	F	52.56±0.31 b	6.15±0.01 b	0.035±0.001 ab	0.65±0.01 d	0.005±0.001 f
	M	52.39±0.07 b	6.17±0.01 a	0.032±0.002 b	0.51±0.01 f	0.008±0.001 e
Mean poplar *Średnio topola*		52.65±0.26 a	6.19±0.06 a	0.032±0.002 b	0.57±0.04 b	0.005±0.001 c
Willow *Wierzba*	C	50.73±0.19 d	6.02±0.10 c	0.031±0.004 bc	0.45±0.02 g	0.008±0.001 e
	L	50.77±0.06 d	6.15±0.01 b	0.029±0.001 c	0.56±0.01 e	0.004±0.001 g
	F	51.58±0.22 c	6.17±0.04 b	0.037±0.003 ab	0.42±0.00 g	0.008±0.001 e
	M	51.04±0.14 d	6.08±0.02 bc	0.034±0.001 b	0.48±0.01 f	0.005±0.001 f
Mean willow *Średnio wierzba*		51.03±0.29 b	6.11±0.06 b	0.032±0.003 b	0.48±0.04 c	0.006±0.001 b
Mean fertilization *Średnio nawożenie*	C	51.85±1.06 a	6.20±0.15	0.039±0.015 b	0.72±0.34 c	0.010±0.006 b
	L	51.03±1.20 c	6.15±0.04	0.039±0.014 b	0.78±0.32 b	0.007±0.006 c
	F	51.63±0.81 b	6.15±0.03	0.048±0.018 a	0.92±0.59 a	0.012±0.009 a
	M	51.49±0.70 b	6.16±0.07	0.041±0.012 b	0.71±0.32 c	0.010±0.006 b
Mean for experiment *Średnio z doświadczenia*		51.50±0.97	6.17±0.09	0.042±0.015	0.78±0.40	0.010±0.007

Legend as in table 2
Legenda tak jak w tabeli 2

In general, the chemical composition of the lignocellulosic biomass was very varied in respect of the major experimental factors and their mutual interactions (tables 5–8). The levels of soluble substances in cold and hot water as well as in the organic dissolvent are presented in table 6. Lignin-based fertilization for the black locust increased the quantity of the soluble compounds in both cold and hot water and in ethanol, as compared to the control. The levels of the substances soluble in cold water increased by 0.5%; in the case of the substances soluble in hot water, it increased by over 3%. In the black locust wood growing in the combination, to which lignin was applied, the quantity of ethanol-extracted substances also increased by approx. 3%, as compared to the control. Moreover, the pH reaction also changed slightly, reaching a level of 6.19. In the case of the poplar wood, as compared to the control, mycorrhiza caused the level of the substances soluble in hot water to rise by over 4.5%; for those soluble in cold water, the recorded rise exceeded 1%. These changes did not significantly influence the overall quantity of compounds soluble in ethanol, and the pH reaction for the poplar wood did not noticeably change either. Analysing the willow wood growing in the combination, to which lignin and mineral fertilization were applied, in comparison to the control, the quantity of the compounds soluble in cold water was reduced by 1.51–1.63%. The combinations with mineral fertilization and lignin did not significantly influence the quantity of the substances soluble in hot water in the willow wood, as compared to the control. The variations ranged from 0.68 to 0.95%. The same change in the growing conditions for the willow caused the quantity of the soluble substances dissolving in the organic dissolvent to decrease, ranging from 1.14% to 1.49%, as compared to the control of the willow wood. Fertilization caused a noticeable acidification of the wood. The wood pH reaction for the willow decreased by 1.14, as compared to the control, and reached 5.58.

Table 5. Significance of major effects and primary interactions for properties under consideration
Tabela 5. Istotność efektów głównych i interakcji pierwszego rzędu dla badanych cech

Specification *Specyfikacja*	Content of substances soluble in cold water *Zawartość substancji rozpuszczalnych w zimnej wodzie*	Content of substances soluble in hot water *Zawartość substancji rozpuszczalnych w gorącej wodzie*	Content of substances soluble in 96% alcohol *Zawartość substancji rozpuszczalnych w alkoholu 96%*	pH of wood *pH drewna*
Species *Gatunki*	***	***	***	***
Soil enrichment procedure *Nawożenie*	***	***	*	NS
Species × soil enrichment procedure *Gatunki × nawożenie*	***	***	***	NS

* $p < 0.01 \div 0.001$
** $p < 0.001 \div 0.0001$
*** $p < 0.0001$
NS = not significant; *NS = nieistotne*

Table 6. Content of substances soluble in water, and in ethanol, and pH of black locust, poplar and willow biomass after the second year of vegetation (% of d.m.)
Tabela 6. Zawartość substancji rozpuszczalnych w wodzie, etanolu oraz pH biomasy robinii, topoli i wierzby po drugim roku wegetacji (% s.m.)

Species *Gatunek*	Soil enrichment procedure *Nawożenie*	Content of substances soluble in cold water *Zawartość substancji rozpuszczalnych w zimnej wodzie*	Content of substances soluble in hot water *Zawartość substancji rozpuszczalnych w gorącej wodzie*	Content of substances soluble in 96% alcohol *Zawartość substancji rozpuszczalnych w alkoholu 96%*	pH of wood *pH drewna*
Black locust *Robinia*	C	13.88±0.20 b	14.28±0.15 b	9.76±0.43 e	5.83±0.02
	L	14.39±0.18 a	17.58±0.66 a	12.74±0.20 b	6.19±0.09
	F	12.92±0.31 c	13.05±0.18 d	10.37±0.26 e	5.86±0.01
	M	12.62±0.19 d	14.33±0.44 b	10.43±0.42 e	6.20±0.03
Mean black locust *Średnio robinia akacjowa*		13.46±960 a	14.81±1.40 a	10.82±0.94 b	6.02±0.14 a
Poplar *Topola*	C	10.85±0.15 f	9.06±0.37 g	14.03±0.56 a	5.40±0.05
	L	10.81±0.16 f	9.16±0.20 g	13.06±0.64 b	5.36±0.01
	F	9.64±0.24 g	9.11±0.34 g	14.82±0.03 a	5.46±0.05
	M	11.62±0.11 e	13.62±0.06 c	14.16±0.37 a	5.29±0.07
Mean poplar *Średnio topola*		10.73±0.59 b	10.24±1.58 b	14.02±0.60 a	5.38±0.06 b
Willow *Wierzba*	C	8.37±0.04 h	10.22±0.05 f	10.62±0.45 d	6.72±1.19
	L	6.86±0.08 i	10.90±0.54 e	9.13±0.62 g	6.31±0.52
	F	6.74±0.08 i	11.17±0.15 e	9.48±0.26 f	5.58±0.01
	M	8.22±0.18 h	8.72±0.15 g	11.9±0.62 c	6.22±0.08
Mean willow *Średnio wierzba*		7.55±0.60 c	10.25±0.80 b	10.28±0.96 c	6.21±0.52 a
Mean fertilization *Średnio nawożenie*	C	11.03±2.39 a	11.19±2.38 c	11.47±2.00 b	5.98±0.83
	L	10.69±3.26 b	12.55±3.87 a	11.64±1.95 b	5.95±0.52
	F	9.77±2.69 c	11.11±1.72 c	11.56±2.49 b	5.63±0.18
	M	10.82±2.00 b	12.22±2.66 b	12.16±1.68 a	5.90±0.46
Mean for experiment *Średnio z doświadczenia*		10.58±2.56	11.77±2.72	11.71±1.98	5.87±0.54

Legend as in table 2
Legenda tak jak w tabeli 2

Table 7. Significance of major effects and primary interactions for properties under consideration
Tabela 7. Istotność efektów głównych i interakcji pierwszego rzędu dla badanych cech

Specification *Specyfikacja*	Substances soluble in 1% NaOH *Substancje rozpuszczalne w 1% NaOH*	Cellulose *Celuloza*	Holocellulose *Holoceluloza*	Lignin *Lignina*	Pentosans *Pentozany*
Species *Gatunki*	***	***	*	***	**
Soil enrichment procedure *Nawożenie*	***	*	***	***	*
Species × soil enrichment procedure *Gatunki × nawożenie*	***	*	**	***	NS

* $p < 0.01 \div 0.001$
** $p < 0.001 \div 0.0001$
*** $p < 0.0001$
NS = not significant; *NS = nieistotne*

Analysing the change in the quantity of the soluble substances in 1% NaOH in the black locust wood, it was noticeable that the lignin applied to the soil substantially increased the quantity of these compounds, by almost 5%, in comparison to the control (table 8). Mycorrhiza did not influence the quantity of the substances soluble in alkalis in the black locust wood. Mineral fertilization caused the content of such substances to increase by 2.57% in comparison to the black locust growing in the control treatment. Mycorrhizal vaccination caused the cellulose content to rise slightly, by 1.79%, in the black locust wood, as compared to the control. Neither the lignin nor mineral fertilization induced significant changes in the values of the major wood components, as compared to the quantity of cellulose in the control black locust wood. The mycorrhiza caused slight changes in the content of holocellulose (an increase of 3.58%), lignin (a decrease of 0.6%) and pentosans (an increase of 0.82%) in comparison to the control.

In the case of the poplar wood, versus the control, lignin and mycorrhiza, as well as mineral fertilization, did not have any stronger impact on the modifications in the content of the base soluble substances (table 8). The quantity of these compounds ranged from 35.58% to 36.49%. There were no substantial changes in the content of the remaining key components i.e., cellulose, lignin, holocellulose and pentosans, in comparison to the poplar wood growing in the control treatment. The cellulose content ranged from 36.72% to 37.67%; the content of lignin varied from 25.10% to 26.66%; holocellulose content was from 67.91% to 69.83%, and the content of pentosans ranged from 20.46% to 20.80%.

Table 8. Content of substances soluble in alkalines, and cellulose, holocellulose, lignin and pentosans in black locust, poplar, willow biomass after the second year of vegetation (% d.m.)
Tabela 8. Zawartość substancji rozpuszczalnych w alkaliach, celulozy, holocelulozy, ligniny i pentozanów w biomasie robinii, topoli i wierzby po drugim roku wegetacji (% s.m.)

Species *Gatunek*	Soil enrichment procedure *Nawożenie*	Substances soluble in 1% NaOH *Substancje rozpuszczalne w 1% NaOH*	Cellulose *Celuloza*	Holocellulose *Holoceluloza*	Lignin *Lignina*	Pentosans *Pentozany*
Black locust *Robinia*	C	33.88±0.31 c	36.54±0.43 c	66.67±1.07 c	22.43±0.31 c	20.69±0.48
	L	38.75±0.44 a	35.91±0.64 d	65.86±0.56 c	22.07±0.18 c	20.60±0.28
	F	36.45±0.10 b	36.10±0.23 c	67.59±0.24 b	24.67±0.19 c	21.07±0.22
	M	33.79±0.34 c	38.33±0.79 b	70.25±0.62 a	21.83±0.82 b	21.51±0.41
Mean black locust *Średnio robinia akacjowa*		35.72±1.66 a	36.72±0.88 b	67.59±1.40 b	22.75±0.97 c	20.97±0.40 a
Poplar *Topola*	C	36.27±0.43 b	36.89±0.72 bc	66.96±0.47 c	26.45±0.32 a	20.53±0.45
	L	35.95±0.16 b	37.42±0.29 bc	67.91±0.60 b	25.10±0.52 b	20.61±0.17
	F	36.49±0.46 b	36.72±0.84 c	68.02±0.74 b	26.66±0.12 a	20.46±0.23
	M	35.58±1.17 b	37.67±0.57 b	69.83±0.64 ab	25.14±0.21 b	20.80±0.10
Mean poplar *Średnio topola*		36.08±0.58 a	37.17±0.55 b	68.18±0.95 b	25.84±0.63 a	20.60±0.21 b
Willow *Wierzba*	C	33.23±0.63 c	41.69±0.93 a	71.06±1.16 a	24.37±0.58 b	20.10±0.33
	L	33.13±0.37 c	41.74±0.59 a	68.09±0.65 b	21.78±0.72 c	20.51±0.51
	F	33.58±0.56 c	40.77±0.73 a	67.30±1.93 bc	24.31±0.20 b	19.76±0.21
	M	33.29±0.90 c	40.75±0.82 a	69.36±1.05 ab	24.57±0.33 b	20.48±0.55
Mean willow *Średnio wierzba*		33.31±0.46 b	41.24±0.66 a	68.95±1.42 a	23.76±0.98 b	20.21±0.40 c
Mean fertilization *Średnio nawożenie*	C	34.46±1.45 b	38.38±2.57 ab	68.23±2.28 b	24.41±1.78 b	20.44±0.45 b
	L	35.94±2.45 a	38.36±2.66 ab	67.29±1.19 b	22.98±1.65 d	20.57±0.31 b
	F	35.51±1.49 a	37.86±2.27 b	67.64±1.09 b	25.21±1.11 a	20.43±0.60 b
	M	34.22±1.29 b	38.92±1.54 a	69.81±0.79 a	23.85±1.60 c	20.93±0.57 a
Mean for experiment *Średnio z doświadczenia*		35.03±1.81	38.38±2.23	68.24±1.70	24.11±1.70	20.59±0.52

Legend as in table 2
Legenda tak jak w tabeli 2

Analysis of the content of the key components in the willow wood growing in the treatments amended with lignin, mycorrhizal vaccination and mineral fertilization, as compared to the content of these components in the willow wood growing in the control treatment, showed similar levels of the determined values (table 8). The content of the substances soluble in 1% NaOH in the willow wood growing in the amended soil ranged from 33.13% to 33.58%; the cellulose content ranged from 40.75% to 41.74% and the holocellulose content varied from 67.30% to 69.36%. In comparison to the control, the lignin content decreased by 2.59% in the willow wood growing in the lignin-amended treatment. The content of pentosans in the willow lignocellulosic biomass ranged from 19.76% to 20.51%. The results indicated that the best properties, in the context of further use of the resource for industrial purposes, were found in the willow wood chips, which contained the most cellulose (41.24% on average), and was characterised by a fairly high level of pentosans (20.97%) and a low level of lignin (23.76%).

Discussion

The research indicated that out of the three species, the black locust produced the biomass which was the most valuable solid fuel owing to the lowest moisture content and the greatest lower calorific value. Other research has also shown that the moisture content in black locust biomass at harvest may be lower than in other species of woody crops and maybe approximate 40% [Gasol et al. 2010]. The moisture content of willow biomass is *ca* 50% [Tharakan et al. 2003; Keoleian, Volk 2005; Stolarski 2009]. On the other hand, the biggest problem concerning the quality of poplar biomass grown in short rotations is the high moisture at harvest, which can be as high as 60% [Kauter et al. 2003; Tharakan et al. 2003]. The average ash content in poplar biomass estimated during the cited studies was 1.85–2.13% d.m., which is congruent with the results achieved in this research. The quality of poplar fuel is expected to improve with an extension of rotations, since one of the factors determining the quality of poplar biomass is the content of bark in the biomass, which depends on the age of the crops and diameter of the stems. A higher content of bark directly raises the content of ash and other elements undesirable in fuel [Klasnja et al. 2002; Guidi et al. 2008]. A similar relationship between the ash content and the quantity of the bark in stems of different age and stem diameter exists in the case of willow plants [Stolarski 2009]. The bark and wood ratio in willow and poplar biomass directly influences the quality of fuel. Adler et al. [2005] state that bark is characterised by a much higher content of elements, including N, P, K, Mg, Ca, Cd, Pb, Co and Zn, than wood. This characteristic affects the combustion process and may accelerate the corrosion of boilers. The ash content in willow biomass directly depends on the content of alkaline elements; the lower their content in the fuel, the less ash generated during the combustion process [Tharakan et al. 2003]. In the research presented here, the greatest lower calorific value was recorded for the black locust biomass, which also contained higher levels of sulphur, nitrogen and chlorine than the willow and poplar biomass. Other research shows that poplar and willow biomass is characterised by low levels of nitrogen and sulphur, as well as chlorine [Gasol et al. 2009; Tharakan et al. 2003; Stolarski 2009].

The chemical composition of wood depends not only on the tree species but also on a number of other factors including age, tree organ, harvest time and growing conditions [Prosiński 1984; Baeza, Freer 2000; Rowell et al. 1997; Waliszewska, Prądzyński 2002]. For example, the cellulose content in 1-, 2- and 3-year-old willow stems increases with crop age [Prosiński 1984; Stolarski et al. 2011]. In the experiment presented, the analysed black locust, poplar and willow wood had grown for two years. The willow wood was characterised by the highest content of cellulose: from 40.75% to 41.75% (41.24% on average). The wood of the 2-year-old poplar and 2-year-old black locust contained on average approx. 37% of cellulose. Willow wood, owing to its fairly high cellulose content, may be used as a substitute raw material for the production of chipboards, fibre-boards, paper and cardboard [Mc Adam 1987; Surmiński 1990; Warboys, Houghton 1993]. The two-year-old black locust, poplar, and willow wood examined in this study with respect to their content of cellulose, holocellulose and lignin, may be used as a substitute raw material for the production of cardboard or chipboards. The chemical composition of lignocellulosic biomass is extremely important when crops are grown for cellulose production and, possibly, for ethanol production. Young wood of both coniferous and deciduous trees generally contain less cellulose and lignin than mature wood [Rowell et al. 1997; Wróblewska et al. 2009; Komorowicz et al. 2009]. This tendency was proven in the research conducted by Guidi et al. [2009], who stated that poplar wood originating from two-year rotations contained less cellulose (42.5%) and more lignin (22%) than wood from four-year rotations, where the respective percentages were 51.6% and 19%. González-Garćia et al. [2010] found a cellulose content of 43.2% d.m., hemicellulose equal to 26.6% d.m. and lignin reaching 21.3% d.m. in biomass from five-year rotations of poplar. In bamboo shoots, the content of substances soluble in water and alkali decreased, while that of cellulose, lignin and pentosans increased in older plants [Rowell et al. 1997].

In this study, the tested soil enrichment with lignin, mineral fertilization and mycorrhiza did not result in significant changes in the content of the primary components in the lignocellulosic biomass from the three plant species. The content of the analysed types of biomass corresponds to a fairly good quality of lignocellulosic matter earmarked for power generation purposes. According to Waliszewska [2002], the growing conditions of willows, especially the level of environmental pollution, influence the content of hydrocarbons. Pentosans as well as hexosans are hydrolysed into monosaccharides. Consequently, aqueous solutions are formed, which contain 2–4% of monosaccharides, and which are a valuable resource for ethanol and yeast production [Kin 1980]. The growing conditions altered in the discussed experiment by adding lignin, fertilizers or mycorrhiza to the soil, did not significantly influence the content of pentosans in the 2-year-old wood of the black locust, poplar and willow. A fairly high content of pentosans and the content of substances soluble in 1% NaOH in young wood indicates the presence of low-polymerised hydrocarbons, which means that this material may be used for bioethanol production. The wood of all the three species contained large quantities of substances soluble in cold water (from 9.77% to 11.03% on average) and hot water (from 11.11% to 12.55% on average). A high percentage of 96%-ethanol extracted substances (from 11.47% to 12.16%) was also reported. This confirms low levels of lignified tissue on young crops. On the other hand, this implies its particular suitability for biofuel production.

The black locust biomass was characterised by the lowest moisture content and the greatest lower heating value and ash content. The poplar, on the other hand, was characterised by the highest carbon and hydrogen content as well as the greatest higher heating value. However, due to its highest moisture content it had the poorest lower heating value. The willow biomass was characterised by the highest cellulose and holocellulose content. Sound knowledge of the composition of the lignocellulosic biomass helps us to define objectives for further research and specify its best industrial use. The soil enrichment technologies for lignocellulosic biomass plantations may influence the content of key biomass components and their properties. In the experiment presented, the most substantial positive changes in the content of the cellulose, lignin and holocellulose in the black locust wood were induced by mycorrhiza. In respect of the willow wood, only lignin application to the soil slightly decreased (approximately by 2.6%) the content of lignin in the lignocellulosic biomass. Owing to the high content of cellulose, pentosans and substances soluble in 1% NaOH, this biomass may be used for biofuel production. Research on the physicochemical composition of lignocellulosic biomass proves that the climatic and soil conditions and agricultural techniques under which the experiment was conducted are beneficial. Furthermore, the results indicate the need to continue research on SRWC in order to evaluate the quality of biomass derived from respective treatments in longer rotations, as they seem to be some of the key factors influencing the physicochemical composition of lignocellulosic biomass. This is immensely important as this may allow us to improve the efficiency and capacity of biofuel production and the manufacture of industrial products.

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DENDROMASA POZYSKANA Z GRUNTÓW ROLNICZYCH JAKO SUROWIEC PRZEMYSŁOWY I ENERGETYCZNY

Streszczenie

Dendromasa to naturalny, odnawialny surowiec o szerokim i wszechstronnym zastosowaniu. W ostatnich latach wzrasta zainteresowanie biomasą drzewną pozyskiwaną w krótkich rotacjach zbioru z upraw polowych. Dlatego też podjęto badania oceny termofizycznych i chemicznych właściwości dwuletnich pędów wierzby, topoli oraz robinii akacjowej w zależności od sposobu nawożenia gleby. Doświadczenie zlokalizowane było w północno-wschodniej Polsce w miejscowości Samławki (53°59’ N, 21°04’ E) na glebie mało przydatnej do tradycyjnej produkcji rolniczej pod uprawy konsumpcyjne czy paszowe. Biomasa robinii charakteryzowała się najniższą wilgotnością oraz najwyższą wartością opałową i zawartością popiołu, natomiast topola – najwyższą zawartością węgla i wodoru i najwyższym ciepłem spalania; jednakże ze względu na maksymalną wilgotność posiadała najniższą wartość opałową. Najwięcej celulozy oraz holocelulozy miała biomasa wierzby. Najkorzystniejsze zmiany w zawartości celulozy, ligniny i holocelulozy w drewnie robinii miało zastosowanie mikoryzy. W przypadku drewna wierzbowego, jedynie zastosowanie ligniny do nawożenia obniżyło w niewielkim stopniu zawartość ligniny w pozyskanej dendromasie.

Słowa kluczowe: wierzba, topola, robinia akacjowa, skład chemiczny, właściwości fizykochemiczne, uprawy w krótkich rotacjach