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CHEMICAL COMPOSITION AND SELECTED ENERGY PROPERTIES OF BLACK LOCUST BARK (*ROBINIA PSEUDOACACIA* L.)

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ABSTRACT

The objective of the paper was to assess the usefulness of bark of black locust trunks as an energy source based on chemical and energy properties. Material for research was collected from five forest stands of black locust (*Robinia pseudoacacia* L.). After determination of the bark mass, its participation in the mass of trees, the content of moisture in bark, density, calorific value, ash, content of C, H, N, S, K and P were established. In comparison to wood, bark has worse chemical properties on account of a high content of sulphur and nitrogen. In the conditions of research, black locust bark had an average density of approx. 400 $kg \cdot m^{-3}$ which is comparable to the willow and poplar wood. Average calorific value of black locust bark was by 10% higher than the average value of this parameter for bark wood.

Introduction

Renewable energy sources pursuant to the policy of saving fossil energy raw materials resources have even a bigger participation in the global energy balance (Komorowicz et al., 2009). Biomass constitutes one of the main renewable energy sources and its participation in obtaining all renewable energy carriers achieved 80.03% in 2013 (Main Statistical Office, 2014). The highest demand for raw materials from biomass is related to the biomass which originates in forest (Bartoszewicz-Burczy, 2012). Among solid biofuels, in the group of wood waste, bark is the most interesting. Bark as an outer layer of a tree has an irregular participation in the mass of trees and a varied physical and chemical properties.

Wood biomass as a fuel has three basic substances (Kubiak and Laurow, 1994; Prosiński, 1984; Rybak, 2006): organic (flammable, mineral and water. The flammable substance consists of such elements as hydrogen, oxygen, nitrogen and sulphur. The remaining elements which occur in wood in small amounts and constitute mineral substance compose ash as a result of the combustion process (Prosiński, 1984; Rybak, 2006). However, the quantity differences in the chemical composition occur not only in wood of various species but also can occur within one species. A habitat type and density of the forest stand as well as age and anatomic structure of wood (early and late wood, alburnum and heartwood, trunk and branches, bark) as pathological changes caused by fungi influenced the above (Kubiak and Laurow, 1994; Rybak, 2006).

Participation of bark in comparison to the total mass of a trunk is varied in relation to the tree species and the most often it is from 5 (pine) to 20% (oak) (Antkowiak, 1997; Prosiński, 1984). However, its participation in the wood mass is important in case of thick wood (large timber) since bark in various wood processing processes is separated from the bark mass and becomes waste. In case of many species e.g. pine and poplar, bark separates itself from wood during its seasoning i.e. drying in natural conditions (Antkowiak, 1997; Prosiński, 1984).

Cultivation of black locust for energy purposes on account of biological properties of the species and very good energy properties of wood becomes more popular. Extensive studies on determination and increase of productivity (Juliszewski et al., 2012; Rédei, et al. 2003), as well as on physico-chemical properties of wood with or without bark in the aspect of energy properties were carried out. It was determined that fresh wood of black locust has relative moisture of approximately 45% (Kraszkiewicz and Szpryngiel, 2008), density in the dry state is approximately 700 $kg \cdot m^{-3}$ (Kraszkiewicz et al., 2011) and in the fresh state less than 1000 $kg \cdot m^{-3}$ (Juliszewski et al., 2012). Other studies refer to the calorific value of trunk wood in bark in dry state, where the value of this parameter is at the average of 17.60 $MJ \cdot kg^{-1}$ (Kraszkiewicz, 2008) and in the fresh state (w=25%) – 13.4 $MJ \cdot kg^{-1}$ (Juliszewski et al., 2012). Within the scope of chemical properties, black locust wood without bark in a dry state includes at the average: carbon – 51.5%; hydrogen – 5.8%; nitrogen – 0.05%; sulphur – 0.006% (Kraszkiewicz, 2009). However, there is no data on physical and chemical properties of black locust bark in the aspect of possibilities of its use for energy purposes. During the black locust wood processing, bark is separated from wood mass and stored on prisms and its management is impeded due to its poisonous properties not only for human but also for many animals (Pacyniak, 1981).

Thus, studies were undertaken the objective of which was to assess the usefulness of bark of black locust trunks as an energy source based on chemical and energy properties.

Research methods

Material for research was collected from five forest stands of black locust (*Robinia pseudoacacia* L.) in various age. Research objects were located in: Lublin (4-year stand – no. 1), Snopków, Jastków municipality, LubelskieVoivodeship (8-year stand – no. 2), Piaseczno, Łoniów municipality, Świętokrzyskie Voivodeship (35-year forest stand – no. 3), Zawidzy, Łoniów municipality, ŚwiętokrzyskieVoivodeship (41-year forest stand – no. 4), Skrzypaczowice, Łoniów municipality, ŚwiętokrzyskieVoivodeship (64-year forest stand – no. 5).

A forest stand location and characteristic of habitat conditions was presented in table 1.

In all forest stands in the last decade of December on the surface area of 500 m^2 (20×25 m) and with the use of test trees method (Bruchwald, 1999) from the main forest stand, one tree with an average height, breast height diameter and cut cross section was cut down. The height of the trees, which were cut down, was respectively 2.0; 7.5; 19.0; 24.5; 24.0 m, breast height diameter 4.5; 12.0; 21;0 26.5; 38.5 cm.

From each cut tree, a trunk was separated in bark and divided into pieces whose thickness was 1.1-5.0 cm, 5.0-10.0 cm, 10.1-15.0 cm and further every 5 cm. In the determined classes of thickness, mass of bark was measured, participation in relation to wood and samples were collected for laboratory research. Material thus obtained was dried to the dry state in driers with air circulation in the temperature of 105ºC, determining the total moisture of raw material and analytical moisture. Then, density of bark was measured with the xylometric method and the calorific value of samples was measured with the calorimetric method with the use of a static calorimeter KL-12 Mn.

Table 1.
Location of forest stands and characteristic of habitat conditions

No. of a forest stand (age in years)	Location in the landscape, protrusion, declination in percentages, height of a scarp (slope); forest stand location	Soil formation	Content of nutritious components ($g \cdot kg^{-1}$) and resourcefulness of soils				C:N
			$N_{og.}$	P	K	$C_{org.}$	
1 (4)	plain surface	dust	0.43 insufficient	0.059 average	0.063 average	3.62	8.42
2 (8)	plain surface	dust	1.95 good	0.176 good	0.260 good	10.37	5.32
3 (35)	scarp; N; 70%; 40 m; upper part of a scarp	clay	0.77 average	0.054 average	0.142 good	6.60	8.57
4 (41)	plain surface	clay	0.78 average	0.007 insufficient	0.025 insufficient	6.05	7.76
5 (64)	scarp of a valley cut with shallow gullies; SE; 15%; 20 m; central part of the scarp	dust	1.23 average	0.015 average	0.028 insufficient	6.79	5.52

Some part of the research material was defragmented in laboratory mills to the fraction of ≤ 0.4 mm and in the so-determined samples of the trunk bark sample of particular forest stands - the content of the following was established:

- of carbon, hydrogen, sulphur – with IT absorption method;
- nitrogen – with catalometric method;
- phosphorus – with calorimetric method;
- potassium – with flame photometry;
- ash – with weight method in the temperature of 550ºC.

Research results were subjected to statistical analysis in STATISTICA 10.0 program with the use of one-factor analysis of variance and Tukey's test. The age of forest stands was a grouping factor and the level of significance of $\alpha = 0.05$ was assumed in analyses. For the collected data coefficients of Pearson's linear correlation was determined.

Research results and discussion

Average values of physical properties of the black locust bark were presented in table 2. An average content of the total moisture in the biomass of black locust bark in particular forest stands decreased along with the increase of their age. In the forest stand no. 1 (4-years old) the content of the total moisture was 60% and in the forest stand no. 5

(64-years old) – 40%. As a rule, the participation of bark in dry mass was within 6.0-16.5% and increased proportionally to the age of forest stands; only in the 41-years old forest stand it was 9.80% and was lower than in the 8-years old forest stand. In the considered forest stands the mass of bark (by weight) was within 0.19 to 34.59 $Mg \cdot ha^{-1}$. On the other hand, the average density of black locust density in a dry state was within 361 $kg \cdot m^{-3}$ (64-years old forest stand) to 460 $kg \cdot m^{-3}$ (4-years old forest stand) (table 2).

Table 2.
Physical properties of black locust bark

Parameter (average values)	Unit	Forest stand				
		no. 1	no. 2	no. 3	no. 4	no. 5
Total moisture of raw material in the working state	(%)	60 a	59	42 a	43 a	40 a
Analytical moisture	(%)	7	8	7	7	8
Participation of bark	(%)	6.00 a	11.50 a, b	15.75 a, b, c	9.80 a, c, d	16.0 a, b, d
Fresh mass	($Mg \cdot ha^{-1}$)	0.19 a	5.11 a	15.64 a	12.47 a	34.59 a
Density in the dry state	($kg \cdot m^{-3}$)	460 a	435 b	397 a, c	406 a	361 a, b, c

a-a, b-b, etc., mark non-uniform groups

From the point of view of the amount of energy obtained from biofuels combustion, except for the content of moisture and their density, element composition of fuel, level of ash from combustion and its possibilities of management and content of energy expressed with calorific value are also significant. Thus, the mentioned energy properties of the considered research material were presented in table 3.

Elemental analysis proved that the average content of carbon in the black locust bark was within 49.59% in the bark of the 35 years old forest stand (no. 3) and 50.81% in the bark of the 4 years old forest stand (no. 1). Content of hydrogen in the considered raw material from forest stand in the age of 8 was approx. 5.70% and in the samples from old trees it was within 5.91-5.97%. The content of nitrogen in the bark, as a rule, did not exceed 3% and was within 2.28% (35 years old forest stand) and 2.91% (8 years old forest stand). Only in the 4-year forest stand, bark included 3.42% of nitrogen (table 3). The content of sulphur in the bark of trunks was within 0.15-0.18 % only in the bark of a forest stand no. 5 the content of sulphur was lower and it was 0.09%. The content of potassium and phosphorus in the trunk bark in the considered forest stands was varied and was respectively within 0.078-0.298% and 0.033-0.112%. An average ash content in the black locust bark biomass, as a rule, was oscillating around 4% (forest stands no. 1, 4 and 5), only in the forest stands no. 2 and 3 was higher and it was respectively 5.14 and 4.70% (table 3).

Table 3.
Energy properties of black locust bark in the analytical state

Parameter (average values)		Unit	Forest stand				
			no. 1	no. 2	no. 3	no. 4	no. 5
Basic composition	C	(%)	50.81	50.63	49.59	49.80	50.77
	H	(%)	5.71	5.70	5.97	5.93	5.91
	N	(%)	3.42	2.91	2.28	2.78	2.64
	S	(%)	0.16	0.18	0.16	0.15	0.09
K		(%)	0.078	0.298	0.096	0.166	0.198
P		(%)	0.112 a	0.092 b	0.033 a, b	0.034 a, b	0.042 a, b
Calorific value		($MJ \cdot kg^{-1}$)	19.84 a	19.15 a, b	20.29 b	19.95 b	19.90 b
Ash		(%)	3.90 a	5.14 a, b	4.70	4.00 b	3.90 b

a-a, b-b, etc. mark non-uniform groups

The calorific value of the tested samples of black locust bark in the dry state usually was within 19.84-19.95 $MJ \cdot kg^{-1}$, only for the trunk bark of the 8-years old forest stand this value was lower and it was 19.15 $MJ \cdot kg^{-1}$ and for 35-years old forest stand it was higher and amounted to – 20.29 $MJ \cdot kg^{-1}$ (table 3).

Statistical analysis ($\alpha = 0.05$) of the research results concerning bark of tree trunks from particular forest stands proved significant differences between average values of the following parameters: total moisture of raw material in the working state ($p = 0.00000$), participation of bark ($p = 0.00000$), fresh mass of bark ($p = 0.00000$), bark density ($p = 0.00016$), calorific value ($p = 0.00070$), potassium ($p = 0.00108$), phosphorus ($p = 0.00062$) and ash ($p = 0.00453$). The Tukey's test which was carried out proved respectively 2, 4, 5, 3, 2, 2, 2 and 2 non-uniform groups. For the remaining parameters: analytical moisture ($p = 0.49941$), content of carbon ($p = 0.20292$), nitrogen content ($p = 0.07907$), sulphur content ($p = 0.07363$), hydrogen content ($p = 0.06144$), at the level of significance α=0.05, no statistically significant differences were determined (tab. 3). Statistical analysis of the research results also proved negative linear tendencies between the age of forest stands and moisture and density of the trunk bark as well as between the age and content of carbon, nitrogen, sulphur, phosphorus and ash in bark. Coefficients of correlation were respectively -0.86; -0.91; -0.15; -0.48; -0.63; -0.77; -0.35. On the other hand, between the age of forest stands and the content of hydrogen, potassium, bark participation, bark mass and calorific value there was a positive relation for which the coefficient of correlation were respectively 0.62; 0.95; 0.01; 0.42.

The research on chemical composition and energy properties of black locust bark were carried out based on the black locust forest stand in various age, which were growing in various habitat conditions (table 1). Calorific value of black locust bark was by approximately 10% higher than the calorific value of black locust bark (Kraszkiewicz, 2008), and referred to the bark of other species of trees it was comparable.

The literature (Antkowiak, 1997; Demirbas, 2004; Grzybek, 2004; Prosiński, 1984; Rybak, 2006) provides that barkless wood includes: carbon – 48-52%; hydrogen – 6.2-6.4%; nitrogen– 0.1-0.5%; sulphur– < 0.05%, and bark includes per average: carbon – 48-

52%; hydrogen– 4.6-6.8%; nitrogen– 0.3-0.8%; sulphur – < 0.05%. As a rule, the content of carbon and hydrogen determined during research in the black locust bark were comparable with the content of these elements provided for bark of other tree species as well as black locust wood. Only, the amount of nitrogen and sulphur in the bark of these species was approximately three times higher than the upper values of the ranges of content of these elements in the bark of other tree species. Black locust bark includes also considerably more sulphur and nitrogen than the black locust wood (Kraszkiewicz, 2009). These elements in the combustion process are responsible for fumes hazardous for environment (NO_x, N_2O, SO_2 and SO_3) (Dzurenda, 2004; Rybak, 2006), which, inter alia, cause depreciation of this raw material in the aspect of its energy use. When comparing the content of nitrogen and sulphur in the black locust bark to the requirements included in the PN-EN 14961-2:2011 standard concerning the quality requirements for the pellet we find out that they are respectively 2 and 4 times higher than the requirements for pellet in the lowest B class.

In comparison to the density of black locust wood, density in the dry state of the trunk bark is also radically lower by approximately 58%. But, this parameter is comparable to the willow and poplar wood density (Kubiak and Laurow, 1994).

In the aspect of energy use of black locust bark, the amount of ash in the process of its combustion is also important. The content of ash from black locust bark biomass in comparison to other types of biomass was higher due to possible contamination with sand or soil of this outside layer of trees. In comparison to the requirements of PN-EN 14961-2:2011 standard, the content of ash from trunk bark was maximally by less than 50% higher than the value of this parameter in the wood biomass pellet. However, the ash may be used for the purpose of fertilization. Kalembasa (2006) found out that ash from biomass combustion includes macro and micro-nutrients taken with the yield from soil and may be used for fertilization of agricultural crops. In the author's own research it was stated that the potassium and phosphorus content in the analysed research material was comparable to the data in the literature (Grzybek, 2004).

Conclusion

The paper evaluated the usefulness of bark of black locust trunks as an energy source based on chemical and energy properties.

Based on the analysis of the obtained results one may state that:

1. The composition of elements of black locust bark is comparable with the chemical composition of bark of other tree species.
2. In comparison to wood, bark has worse chemical properties mainly because of a considerable content of sulphur and nitrogen.
3. In the conditions of research, black locust bark had an average density of approx. 400 $kg \cdot m^{-3}$ which is comparable to the willow and poplar wood.
4. Average calorific value of black locust was by 10% higher than the average value of this parameter which occurs in the literature for the black locust wood.

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SKŁAD CHEMICZNY I WYBRANE WŁAŚCIWOŚCI ENERGETYCZNE KORY ROBINII AKACJOWEJ (*ROBINIA PSEUDOACACIA* L.)

Streszczenie. Celem pracy była ocena, na podstawie cech chemicznych i energetycznych, przydatności kory z pni robinii akacjowej do wykorzystania jako źródła energii. Materiał do badań pobrano w pięciu drzewostanach robinii akacjowej (*Robinia pseudoacacia* L.). Po określeniu masy kory, jej udziału w masie drzew, określono zawartość wilgoci w korze, gęstość, wartość opałową, popiół, zawartość C, H, N, S, K i P. W porównaniu z drewnem kora posiada gorsze właściwości chemiczne ze względu na znaczną zawartość siarki i azotu. W warunkach badań kora pni robinii akacjowej średnio posiadała gęstość około 400 $kg \cdot m^{-3}$, która jest porównywalna z drewnem wierzbowym i topolowym. Średnia wartość opałowa kory robinii akacjowej była o 10% większa niż wartość średnia tego parametru dla drewna pni.

Słowa kluczowe: biopaliwo stałe, kora, robinia akacjowa