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The application of elemental analysis for the determination of the elemental composition of lignocellulosic materials

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Abstract: *The application of elemental analysis for the determination of the elemental composition of lignocellulosic materials.* The presented work includes research on different types of lignocellulosic materials: woody materials, agricultural materials and fruity materials. The aim of the study was the determination of the elemental composition of lignocellulosic materials using elemental analysis by high-temperature combustion, column separation and measuring the gaseous products to determine the carbon, hydrogen, nitrogen and sulfur, and with the use of potentiometric titration to determine the chlorine. In addition, in order to evaluate the relationship between those elements and also the suitability of the tested materials for use, e.g. as a biofuels, their calorific value was also determined.

Keywords: lignocellulosic materials, elemental analysis, elemental composition, solid biofuels

INTRODUCTION

Lignocellulosic material is a conglomeration of macromolecular organic compounds whose chemical structure is mainly carbon's skeleton. In addition to the carbon atoms the main elemental composition are also hydrogen, oxygen, nitrogen and sulfur. Other elements, occurring in minor amounts include chlorine and phosphorus. The composition of these elements is one of the basic information describing the lignocellulosic material, which has an impact on its use, e.g. in solid biofuels. Knowledge of the elemental composition directly, using the formulas of approximation, be directly used to estimate the calorific value [1]. The content of nitrogen, sulfur and chlorine indicate a possible environmental hazards from gas combustion products (NO_x, SO_2, dioxins, difurans, HCl). These compounds are also responsible for high-temperature corrosion of the boiler [2, 3].

To determine the elemental composition of chemical compounds elemental analysis is used. It allows to determine the percentage by mass of the elements included in the tested materials (biomass, food, biofuels).

Elemental analysis can be performed through different techniques. Standard and commonly used technique is a controlled, complete combustion of the sample and then measuring of the separated oxides. This analysis is carried out in a specialized analyzers in which the sample combustion and the determination of carbon, hydrogen, nitrogen and sulfur is performed at the same time. For more advanced techniques of elemental analysis include mass spectrometry, atomic absorption spectrometry and x-ray crystallography.

The direct aim of the study was the determination of the elemental composition of various lignocellulosic materials using elemental analysis by high-temperature combustion, column separation and measuring the gaseous products to determine the carbon, hydrogen, nitrogen and sulfur, and with the use of potentiometric titration to determine the chlorine. In addition, in order to evaluate the relationship between those elements and also the suitability of tested materials for use, e.g. as a biofuels, their calorific value was also determined.

MATERIALS AND METHODS

The samples were chosen from different lignocellulosic materials:
1. Woody materials:
- sawdust - coniferous and deciduous,
- bark - coniferous and deciduous,
- lignocellulosic waste after the hydrolysis process - lignocellulose
2. Non-woody materials:
- herbaceous materials: leaves and empty corn cobs, tobacco stalks, sunflower hulls, hay, lupin (*Lupinus*) straw, cereal straw, Virginia Mallow (*Sida hermaphrodita*), rape (*Brassica napus*) seeds,
- fruit matrials: oil palm (*Elaeis guineensis*) nutshells, oil palm (*Elaeis guineensis*) kernel shells (PKS), argan *(Argania spinosa)* nuts, pomace of olives.

Lignocellulosic materials were prepared for analysis in accordance with appropriate standard [4]. Pre-ground material was disintegrated in a Pulverisette of Fritsh knife-mill into grains of the desired size of 0.2 mm.

The elemental composition of the investigated materials was determined using the procedures according to the standards [5, 6]. Ground to a particle not more than 0.2 mm samples were dried to dry weight at a temperature of (105±2)°C.

Conditions for elemental analysis for the content of carbon (C), hydrogen (H), nitrogen (N) and sulfur (S):

- elemental analyzer FLASH EA 1112 Series of Thermo Electron Corporation,
- reaction tube packed of Copper wires and Tungstic Oxide or Copper Oxide; SS column, 2m long, internal diameter of 6mm,
- temperature of the reaction tube 900°C, temperature of the oven 70°C,
- gases: helium (flow rate - 180 ml/min), oxygen (flow - 250 ml/min),
- sample weight 3-3.5 mg.

In order to determine the content of C, H, N, S elements in the test samples, the multi-stage calibration of the instrument was carried out. The substances used in the calibration were the standard (*Sulfanilamide*) and certified reference materials (CRM) – *BBOT, High Organic Content Sediment Soy Beam Meal* and *Wheat Flour*. Analysis was performed in four independent replications for each CRM and standard. For each element (C, H, N, S) the six-point calibration curves were plotted, which describing the dependence of the peak area on the percentage by mass of the CRM/ standard content. The qualitative analysis of the tested materials was carried out on the basis of the retention times and the quantitative analysis of the elements - by absolute calibration by an external standard. The correctness of the method was verified by elemental analysis of the certified reference material *Birch Leaf*. The acceptable differences between the test results and the certified values are presented in Table 1.

Table 1. The criterion for acceptance of the results for the determination of carbon, hydrogen, nitrogen, and sulfur.

Element	The maximum acceptable difference between results
C	0.5%
H	0.25%
N	> 0.5% nitrogen content - 10%
	<0.5% nitrogen content - 0.05%
S	>0.05% sulphur content - 10%
	<0.05% sulphur content - 0.005%

Net calorific value was calculated based on gross calorific value which was determined according to instructions in standards [6]. The samples after grinding to a grain

size of not more than 0.2 mm were burned in a calorimeter bomb (KL-12 M of Precyzja Bit) filled with oxygen at a pressure of 3.0±0.2 MPa. In order to determine the chlorine the calorimeter bomb content was quantitatively washed after combustion process. The obtained aqueous solution was potentiometric titrated using ion-selective electrode AgCl by SCHOTT connected to a stationary Orion pH-meter according to instructions in standard [7]. The correctness of the method was verified by standard analysis (Chloride Standard 1000mg/l Cl).

RESULTS AND DISCUSSION

Table 2 shows the results of determinations of woody materials. The analyzed samples have a low sulfur content (<0.01÷0.15%) and chlorine (0.01÷0.03%). Larger differences were found in the range of nitrogen content. The lowest content of this element determined in coniferous and deciduous sawdust (0.1%), as well as in the softwood bark (0.3%). Analysis of the hardwood bark shows a relatively high nitrogen content - 0.9%. However, the determined value is mentioned in the literature and may be related to the specific anatomy of the bark [8, 9] Also, higher than in wood, 0.5% nitrogen content characterized lignocellulosic waste after the hydrolysis process (lignocellulose). The content of the basic elements (carbon and hydrogen) is in the range of 50.3÷52.9% (carbon) and a 5.1÷6.2% (hydrogen).

Table 2. Elemental analysis, chlorine content and net calorific value of woody materials

Material	Elemental analysis				Chlorine	Net calorific value
	C	H	N	S	Cl	Q
	% $_d$	% $_d$	% $_d$	% $_d$	% $_d$	MJ/kg$_{daf}$
sawdust - coniferous	51.8	6.2	0.1	0.02	0.03	19.2
sawdust - deciduous	50.3	6.2	0.1	0.02	0.03	18.0
bark - coniferous	52.2	5.6	0.3	< 0.01	0.01	20.7
bark - deciduous	52.9	5.7	0.9	0.1	0.02	21.0
lignocellulose	51.3	5.1	0.5	0.15	0.02	22.7

Net calorific value designated for coniferous bark (20.7 MJ/kg$_{daf}$) and deciduous bark (21.0 MJ/kg$_{daf}$) is higher than the calorific value determined for sawdust (coniferous - 19.2 MJ/kg$_{daf}$, deciduous - 18.0 MJ/kg$_{daf}$). This is reflected in the chemical structure of both types of materials. According to Janežič et al. [10] lignin has a higher calorific value with respect to the polysaccharides, which is directly involved with a higher ratio of carbon to hydrogen for this compound. On Figure 1. the calculated ratios C/H for tested samples were presented. For wood C/H ratio is lower (1.8) than in the bark (1.9). A similar dependence can be observed in the lignocellulose where high ratio (10.1) of these two elements can indicate a higher content of aromatic hydrocarbons. It is related with a higher calorific value, which confirms the obtained result (22.7 MJ/kg$_{daf}$).

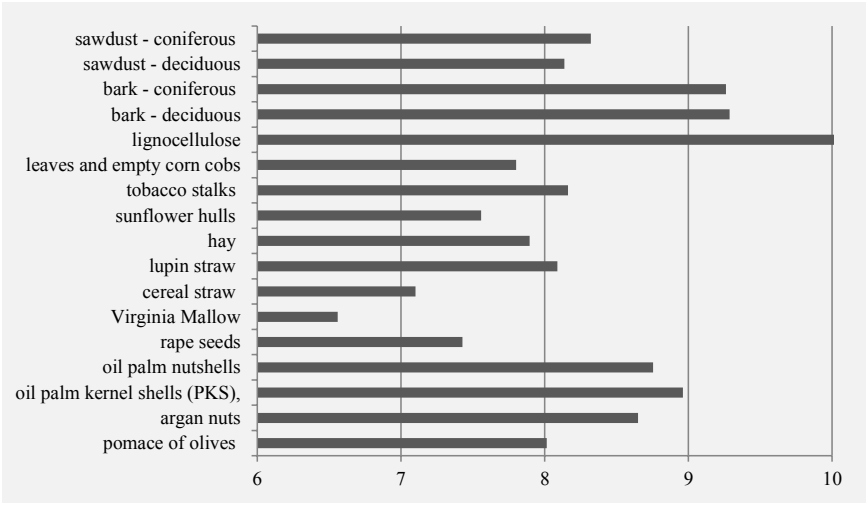

Figure 1. The carbon to hydrogen ratio in the lignocellulosic materials

Table 3 shows the results of analyzes of non-woody materials - herbaceous and fruit. Analyzing the elemental composition of these materials, as in the case of woody materials, low sulfur content (<0.01÷0.2%) was determined. In most of the analyzed samples the content of that element was determined to be below the level of quantification apparatus (<0.01%) or to its limits. It may therefore be concluded that the lignocellulosic materials require more precise analytical methods, for example ion chromatography.

The chlorine content in fruit materials is between (0.0002÷0.2%), while the content in herbaceous materials is higher and amounts from 0.03% in the rape seeds to 0.6% in the tobacco stalks. The determined nitrogen content in herbaceous is in most of the analyzed samples in the range of 0.5% (Virginia Mallow) to 1.9% (hay), while in the fruit material from 0.3 to 1.8% for argan nuts and oil palm nutshells, respectively. Only in case of rape seeds it was determined in significantly higher levels of nitrogen (6.2%), which may be related to the applied fertilizers. Percentage of basic elements - carbon and hydrogen - ranges from 46.3 to 55.0% (carbon) and a 5.5÷6.9% (hydrogen).

Table 3. Ultimate analysis, chlorine content and net calorific value of non-woody materials

Material	Ultimate analysis				Chlorine	Net calorific value
	C	H	N	S	Cl	Q
	% $_d$	% $_d$	% $_d$	% $_d$	% $_d$	MJ/kg$_{daf}$
Herbaceous materials						
leaves and empty corn cobs	48.8	6.3	1.1	<0.01	0.1	18.6
tobacco stalks	46.7	5.7	1.4	<0.01	0.6	18.3
sunflower hulls	49.4	6.5	1.2	0.06	0.1	19.6
hay	48.8	6.2	1.9	<0.01	0.3	19.0
lupin straw	48.5	6.0	0.8	<0.01	0.1	18.4
cereal straw	47.7	6.7	1.0	<0.01	0.3	18.1
Virginia Mallow	46.3	7.1	0.5	<0.01	0.1	17.0
rape seeds	47.6	6.4	6.2	0.2	0.03	20.2
Fruit materials						

oil palm nutshells	48.2	5.5	1.8	0.18	0.02	21.1
oil palm kernel shells (PKS),	51.1	5.7	0.7	0.16	0.0002	20.0
argan nuts	51.6	6.0	0.3	<0.01	0.01	19.3
pomace of olives	55.0	6.9	1.1	<0.01	0.02	22.6

Net calorific value of non-woody materials is in the range of 17.0÷22.6 MJ/kg$_{daf}$ and the herbaceous materials are characterized by a significantly lower calorific value (from 17.0 MJ/kg$_{daf}$ for Virginia Mallow to 20.2 MJ/kg$_{daf}$ for rape seeds). For fruit materials calculated value ranges from 19.3 MJ/kg$_{daf}$ for argan nuts to 22.6 MJ/kg$_{daf}$ for pomace of olives. The above relation is confirmed in most of the calculated ratio of carbon to hydrogen in these samples. In herbaceous materials this parameter is between 6.6÷8.2 (Figure 1), while in fruits 8.0÷9.0. The exception is the high calorific value determined in the pomace of olives (22.6 MJ/kg$_{daf}$), which calculated ratio C/H is 8.0. This can be explained by the presence of extractives in the material [11, 12].

CONCLUSIONS

Based on the study and analyzing the results presented above the following can be concluded:
- elemental analysis allows the assessment of the quality of lignocellulosic materials for use as a solid biofuel,
- for the analysis of sulfur content in lignocellulosic materials, there is a need for more accurate and precisely analytical techniques.

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Streszczenie**:** *Zastosowanie analizy elementarnej w określaniu składu pierwiastkowego materiałów lignocelulozowych***.** Celem pracy było określenie składu pierwiastkowego różnych materiałów lignocelulozowych z wykorzystaniem analizy elementarnej poprzez technikę wysokotemperaturowego spalania z rozdziałem na kolumnie chromatograficznej i pomiarem ulatniających się gazów do oznaczenia zawartości węgla, wodoru azotu i siarki oraz z zastosowaniem miareczkowania potencjometrycznego do oznaczenia chloru. Dodatkowo, w celu oceny zależności między oznaczonymi pierwiastkami oraz oceny przydatności badanych materiałów do zastosowania, na przykład w charakterze biopaliw, wyznaczono również ich wartość opałową. Badania przeprowadzono na drzewnych (trociny iglaste i liściaste, kora iglasta i liściasta, ligninoceluloza pohydrolityczna) i niedrzewnych (zielnych i owocowych) materiałach lignocelulozowych. Oznaczono zawartość węgla, wodoru, azotu, siarki i chloru oraz wyznaczono wartość opałową badanych prób. Zawartość węgla i wodoru, a szczególnie stosunek tych pierwiastków daje pośrednie informacje na temat wielkości wartości opałowej. Z kolei zawartość azotu, siarki i chloru wskazuje na możliwość wystąpienia zagrożeń dla środowiska ze strony gazowych produktów ich spalania, a także korozji wysokotemperaturowej kotła. Stwierdzono, że analiza elementarna pozwala na ocenę jakości materiałów lignocelulozowych do zastosowania na przykład w charakterze biopaliw.

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