# **Combustible in selected biofuels**

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Abstract. The aim of the research was to determine the moisture, combustible and ash content in selected biofuels, in dependence on temperature by the means of gravimetric method. For this purpose, the furnace Nabertherm L9/11/SW/P330 was used. Analyzed samples consisted of crushed biomass which is used in small heat sources (e.g. spruce wood, cherry wood, apple wood, black locust wood) with bark and without additives. Biomass for larger heat sources (woodchips cuttings from coniferous trees), sawdust mix (plum, cherry, walnut, apricot, apple) and pellets (90% spruce and 10% fir) were also analyzed. The results are processed graphically and enable to characterize the tested fuels. The highest content of combustible was found in spruce wood sample without bark (99.889%), the lowest content of combustible indicated cuttings from coniferous trees (88.402%). Gravimetric experiments were supplemented by DSC measurement of selected samples on calorimeter Toledo DSC822e. The graphic courses of reactions are provided up to 500 °C.

Key words: gravimetry, ash, biomass, combustion.

### **INTRODUCTION**

Constantly increasing prices of fossil fuels and efforts to limit the production of gaseous emissions facilitate rapid use of renewable energy sources (Jablonický et al., 2012). An environment protection, fossil fuels depletion in the near future, legislation and development of new technologies are the main reasons for using biofuels (Kosiba et al., 2016). It should be remarked that decrease in fuel consumption is an effective way how to eliminate the negative aspects of the fuel combustion (Szabó et al., 2013a; Szabó et al., 2013b). Renewable energy has become more important globally especially with the current fuel and economic crisis (Branca & Blasi, 2015). Especially solid biofuels will be increasingly used as a source of thermal energy. Biomass means all organic matter that arose through photosynthesis, or material of animal origin. This term often refers to plant biomass usable for energy purposes, as a renewable energy source (Maga et al., 2010). Biofuel is the fuel derived from biomass. According to the chemical composition, the biofuels can be divided into solid, liquid and gaseous. Ouality of solid biofuels as an energy source depends on the moisture and ash content and volatile combustible matter (Mikulová et al., 2014; Holubčík et al., 2016). Research of the amount and course of combustible release in selected biofuels in dependence on temperature is described in the work (Mikulová & Vitázek, 2016). Chemical energy from

biofuels is released mainly from the combustion process. The combustion process is considered as oxidation process, wherein the combustible fuel components are oxidized by atmospheric oxygen, where the energy content of fuel is transformed into heat. The impact of the temperature affects the loss of moisture in the fuel as well. Biofuels as an energy source depend on the quality of combustible and the proportion of ballast moisture and ash. Compared to solid fossil fuels, biomass contains significantly higher proportion of volatile combustible matter, which is essentially due to its origin. Biomass combustion does not pollute the environment by excessive production of CO<sub>2</sub>. Another advantage of the biomass combustion is that the ash as a by-product of combustion may be used as a high quality fertilizer. Biomass offers us a large variety of raw materials and gradually finds its universal use in the energetics. It is a suitable fuel to replace heating with natural gas or electricity. Moreover, it is used for heat and electricity generation in modern combustion plants (Mižáková, 2014). The design and testing of a cost-effective control system for medium-sized biomass boilers based on information regarding not only the oxygen concentration in the flue gases but also the carbon monoxide emission values is discussed in the work (Pitel' et al., 2013). Original composition of solid biofuels (wood, straw, corn) in terms of combustion is as follows (Piszczalka, 2010):

- Volatile combustible matter (wood gas) 60–70%,
- A non-volatile solid combustible (charcoal in the case of wood) to 20%,
- Ballast water (up to <u>cca</u> 14%), and ash from the charcoal combustion 0.5–4%.

This paper presents the method of determining the proportion of the biofuel components by the means of gravimetric method. We focused on the fuels that are used by the heat producer for residential houses in Vráble, and also for the boilers for family houses which use piece wood and pellets. Samples were collected from specific users. An exception is the boiler room in Vráble, which burns wood biomass with different moisture content and composition (waste from wood processing in forests and cuttings from orchards).

Analysis of the course of the release of combustible materials for different fuels is described. Thermal analysis of the samples was carried out using the DSC method (differential scanning calorimetry) by the means of calorimeter Mettler Toledo DSC822e.

### MATERIAL AND METHODS

Currently, biomass is widely used for heating of the drying medium as a substitute for natural gas. The use of solid biofuels in combustion process enhances the competitiveness of the modern agriculture. Biomass is used to heat family houses and is also used in boilers for central heat supply. An important factor in the combustion of biofuels is the release of combustible. The residue is substantially ash. Ash content is determined after the combustion of fuel. Analyzed samples consisted of crushed biomass which is used in small heat sources (e.g. spruce wood, cherry wood, apple wood, black locust wood) with bark and without additives. Biomass for larger heat sources (woodchips cuttings from coniferous trees), sawdust mix (plum, cherry, walnut, apricot, apple) and pellets (90% spruce and 10% fir) were also analyzed. To measure the proportions of components in solid biofuels, gravimetric method was used. It was performed by the means of a furnace Nabertherm L9/11/SW/P330. Input of the heating element is 3.0 kW. The controller P330 enables to program the selected courses of heating and endurance by the computer. Heating of the tested samples is possible up to the temperature of 1,100 °C. To measure weight during the course of the experiment, digital scales were used. The device is connected to a computer and enables to record the temperature and weight curves for the selected time intervals. This device enables to determine the proportion of moisture, combustible and ash in the tested solid biofuels.

# Proportions of particular components are calculated according to the following relations

Moisture content w:

$$w = \frac{m_1 - m_2}{m_1} 100 \tag{1}$$

Ash content in original sample A':

$$A' = \frac{m_3}{m_1} 100$$
 (2)

Ash content in dry matter  $p_{ps}$ :

$$p_{ps} = \frac{m_3}{m_2} 100 \tag{3}$$

*Combustible content in original sample h':* 

$$h' = \frac{m_4}{m_1} 100 \tag{4}$$

*Combustible content in dry matter p<sub>hs</sub>:* 

$$p_{hs} = \frac{m_4}{m_2} 100 \tag{5}$$

where  $m_1$  – original weight of sample, g;  $m_2$  – weight of dry matter, g;  $m_3$  – weight of ash, g;  $m_4$  – weight of combustible, g.

For the determination of the volatile matter, the standard STN EN 15148 is applied. For the determination of ash content in solid biofuels, the standard STN EN 14775 applies together with STN ISO 1171. The experiments were carried out in accordance with standard STN ISO 1171. The required temperatures and operating times were programmed by the means of PC. Table 1 shows the parameters during gravimetric measurements. The given intervals allow determination of the moisture, combustible and ash content. In the last interval, the sample was annealed at 815 °C for 60 minutes. The same method is used by the Agricultural Technical and Testing Institute in Slovak Republic (Rusňák & Šmidová, 2010).

	Time interval							
	1	2	3	4	5	6		
Impact period, minute	60	120	60	60	6	60		
Temperature, °C	20-105	105	105-500	500	500-815	815		

Table 1. Parameters for gravimetric measurement procedure

Source: EN 14775:2010, and ash content determination - STN ISO 1171:2003.

The analysed sample is first heated to  $105 \text{ }^{\circ}\text{C} \pm 2 \text{ }^{\circ}\text{C}$  and dried for 120 minutes. Weight loss in this interval is considered as the removed moisture. Weight loss in the fourth interval (500 °C) is considered as volatile combustible matter, whereas mass residue at the end of the experiment consists of ashes.

For the thermal analysis of the samples by differential scanning calorimetry (DSC method), Mettler Toledo DSC822e device was used. Two instances of the reaction up to 500 °C are presented – for samples of spruce wood and black locust wood.

### **RESULTS AND DISCUSSION**

Processed results of gravimetric measurements are shown in Table 2. Proportions of moisture, ash and combustible are calculated according to the relations (1) to (5). Heating with biomass is increasingly used as an alternative to natural gas. The boiler manufacturers have begun to react to this trend. Even with the gradual arrival of new innovations of biomass boilers, high ash content and inadequate temperature can cause sintering of ash. This can cause temporary interruption of combustion and lead to partial or permanent damage to the boiler. Therefore it is necessary to take into account the information about release of the combustible substances in solid biofuels.

BIOFUELS	PARAMETER						
	W	$A^{'}$	h	$p_{ps}$	$p_{hs}$		
Spruce wood without bark	8.742	0.101	91.157	0.111	99.889		
Pellets	10.329	0.549	89.123	0.616	99.388		
Black locust wood	6.204	0.239	93.557	0.255	99.745		
Cherry wood without bark	13.551	0.425	86.024	0.492	99.508		
Cherry wood with bark	17.197	1.198	81.605	1.447	98.553		
Apple wood with bark	11.211	0.834	87.956	0.939	99.061		
Woodchips from Vráble	58.782	0.657	40.562	1.593	98.407		
Apricot wood with bark	7.320	1.628	91.052	1.757	98.243		
Sawdust mix	9.206	2.399	88.394	2.643	97.357		
Walnut wood with bark	24.869	2.352	72.779	3.131	96.869		
Cuttings from coniferous trees	44.277	6.463	49.261	11.598	88.402		

Table 2. Processed results of gravimetric measurements of analyzed samples



Figs 1 and 2 show weight loss rate of analysed samples of solid biofuels.

Figure 1. Weight loss rate of analyzed samples of solid biofuels.



Figure 2. Weight loss rate of analyzed samples of solid biofuels.

Figures show samples of biofuels before the processing for the purpose of the experiment. Fig. 3 shows Apple wood, Fig. 4 shows sawdust mix, Fig. 5 shows cuttings from coniferous trees, Fig. 6 shows woodchips from Vráble.



Figure 3. Apple wood.



Figure 4. Sawdust mix.



Figure 5. Cuttings from coniferous trees.



Figure 6. Woodchips from Vráble.

The amount of volatile matter in biomass depends on the type of fuel and is inversely proportional to water and ash content of the fuel. In terms of long-term storage, the water content of 14–15% is considered as the most suitable. According to (Maga et al, 2010), biomass combustion as a process does not always provide the maximum amount of energy contained in it. More preferably, the biomass may be converted to the kind of fuel that allows extracting the most out of its energy. As regards methods of biomass conversion, thermal conversion is of significant importance. This method enables to produce liquid, gaseous or solid fuel of higher quality from biomass, which allows achieving a high energy yield and increase of combustible content in solid biofuel. The results show a significant difference in the proportion of the combustible of solid biofuels. The highest content of combustible was found in spruce wood without bark (99.889%), the lowest content was present in cuttings from coniferous trees (88.402%). The results show content of the substances in dry matter. When comparing the content in original samples (moist), the highest content of combustible was present in black locust wood (93.557%), the lowest content in woodchips from Vráble (40.562%).

Figs 1 and 2 show weight loss rates of analysed biomaterial samples at a time interval from 180 minute (after evaporation of moisture) to 420 minute, when volatile combustible is being released and weight loss is apparent to the greatest extent. In addition, Fig. 7 depicts weight loss rate at an interval from 200 to 230 minute. Fig. 8

shows the course of the experiment for the fuels with the highest moisture content – woodchips from Vráble and apricot wood with bark, when rapid weight loss occurs after moisture removal. This weight loss is accounted for the release of volatile combustible.



Figure 7. The fastest weight loss rate of analysed samples of solid biofuels at a selected time interval.



Figure 8. The fastest and slowest weight loss rates of analysed samples of solid biofuels.

Figs 9 and 10 show results of thermal analysis measurements of samples by differential scanning method using the calorimetric device Mettler Toledo DSC822e. Weight of the examined samples was 1.5 mg. The released energy is measured only in a certain time interval and at the temperature up to 500 °C. For the sample from black

locust wood, the amount of released energy equals  $11,790 \text{ J g}^{-1}$  and for spruce wood it is 8,098 J g<sup>-1</sup>. In the case of spruce wood, the beginning of the reaction was significantly affected by the initial moisture, but the end of the reaction can be observed clearly. The initial moisture content of the sample affects beginning of the reaction – an exothermic reaction takes place continuously from endothermic.



**Figure 9.** Graphic representation of the results of measurements for the black locust wood sample – DSC method.



**Figure 10.** Graphic representation of the results of measurements for the spruce wood sample – DSC method.

In both cases, two peaks can be observed. The sample of woodchips from Vráble shows even three peaks (not shown). The results for the different materials will be processed after a special software is obtained. Selected samples will be examined by the means of the method of thermogravimetry (TG). The results of the non-isothermal

thermogravimetric analysis in the dynamic air atmosphere, which can be used for the optimization of combustion process, are presented in the article (Ondro et al., 2017).

Experiments were carried out with fuels, which are used in family houses with lowpower heat sources as well as in the heat source for residential district heating in Vráble. Samples were collected from specific users. An exception is the boiler room in Vráble, which burns wood biomass with different moisture content and composition (waste from wood processing in forests and cuttings from orchards).

With gradual expansion of biomass combustion, the given conditions will decline (availability of suitable biomass). The results of wood show a high content of combustible from 99.889% to 96.869%. The impact of bark in case of cherry wood sample causes an increase in ash content of 0.955%. Softwood pellets (90% spruce, 10% fir) have the same content of combustible and can be considered as equivalent substitutes. The samples taken from boiler room (Vráble) had a high initial moisture (woodchips up to 58.782%), but the combustible content in dry matter was 98.407%. Cuttings from coniferous trees contained various additives, the combustible content decreased to 88.402%. The heat source also enabled the combustion of these fuels.

We have carried out dozens of experimental measurements with various biofuels, even in combination with coal dust (Mikulová et al., 2014). The method according to STN ISO 1171 has been approved to evaluate moisture, combustible and ash content. The unavailability of the originally intended fuel leads to the use of substitutes, where it is necessary to know their properties and to set up the adequate process of combustion and ash production (cleaning of the boiler). In addition, it is necessary to know the proportion of volatile and solid combustible, which has an impact on the combustion (supply of secondary and tertiary air). Further research is carried out in this area.

Similar results obtained from samples of another fuels are presented in the work (Vitázek & Vitázková, 2012) which shows processed gravimetric measurements of selected types of biofuels. In terms of ash content, pellets from rape waste and cereals contain 7.988%, maize straw pellets contain 5.194%, corn flake pellets contain 4.708%, corncob pellets contain 4,378%, softwood pellets contain 1.029% and softwood pellets without bark contain 0.462%. The results obtained in the paper (Mikulova et al., 2014) show that the highest ash content was found in sample from cuttings from coniferous trees – 11.59% and the lowest ash content has spruce wood – 0.11% and therefore confirm the results presented in this work. Similar results are presented also in the work (Chrastina et al., 2015) – distillery refuse from corn distiller's dried grain has ash content of 4.64%.

Research of biofuels includes other works from this field. Impact of the physical properties of solid biofuels on the design of combustion devices is discussed in (Vítěz & Trávníček, 2010). Influence of the input raw material properties on the quality and energetic demand in briquette production is presented in the paper (Muntean et al., 2017). Usage of additives has significant impact on the properties of wood pellets, which include combustion and production of emissions (Jandačka et al., 2011; Jandačka et al., 2015). The article (Ivanova et al., 2015) provides comparison of selected types of solid biofuels for heating private houses. Efficiency of boilers and the production of gaseous emissions is also observed. The work (Kirsanova et al., 2016) deals with the thermodynamic model of biomass gasification and the impact on tar and char production.

In all cases, it is necessary to know the physical properties of the particular biofuels.

#### CONCLUSION

Various types of biomass are used for the purpose of combustion. In small devices, piece wood is often used. In the case of bigger devices, different types of woodchips, cuttings or waste from wood processing are used. For this reason, the article is focused on selected types of wood (pure and with bark) and fuels collected from the boiler room in Vráble, Slovakia (cuttings from coniferous trees and woodchips). High moisture of fuel (woodchips 58.78%) was observed. The second fuel indicated the highest content of ash (cuttings from coniferous trees 11.598%). The heat source in question allows combustion of these fuels without operational problems. Pure wood indicates the highest content of combustible, bark additives increase the ash content. For small combustion devices, a lower content of combustible may have an impact on the operation, for example the increased need of cleaning. Apart from high combustible content, proportion of volatile combustible and its rate of release also affects the quality and properties of the fuel. The obtained results enable easy decision making when replacing the type of fuel.

The experiments continue with further examination of biofuels and their combinations with fossil fuels (pellets from sawdust and coal dust) and with analysis of the content of volatile and solid combustible and its rate of release. Results of thermal analysis of samples by DSC method will be subject to further examination and other fuels will be analyzed.

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