Thermochemical Properties of Energy Crop Species Planted in Slovakia

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In the last decades, a new phenomenon has arisen in connection with temporary or permanent non-use of land for agricultural activity, namely the cultivation of energy crops in these localities, because of growing demand for biomass as a fuel. Farmers are expected to sell energy crops and the fuels they produce, both at home and in the surrounding countries. To choose economically efficient energy crop species to cultivate, the thermochemical parameters of the crop should be used to support decision-making process of farmers. This paper summarizes the results of small-scale laboratory tests of three energy crop species planted in Slovakia – *Sida hermaphrodita*, *Arundo donax*, and *Miscanthus* × *giganteus* – used for determination of thermal and chemical properties of the energy crop species to evaluate their suitability for energy purposes. The most suitable species for energy purposes was found to be *Miscanthus* × *giganteus* with higher heating value of 19.6 MJ/kg, lower heating value of 14.8 MJ/kg (at moisture content of 17%), and ash mass of 2.67% dry mass (d.m.). From a lignin mass and activation energy point of view, the most suitable for energy purposes was *Arundo donax*, with a lignin mass of 20.5% d.m. and an activation energy of 124.2 KJ/mol.

Keywords: Arundo donax; Ash mass; Heating value; Energy potential; Miscanthus × giganteus; Sida hermaphrodita

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INTRODUCTION

Agricultural biomass is a result of agricultural activities. It includes cereal grains, sugar crops, oilseeds, other arable crop's vegetative grasses, farm forestry, and livestock by-products. Agriculture should potentially help to meet the growing energy and raw material requirements of society. This must be done in a sustainable manner and result in lowering greenhouse gas (GHG) emissions. It should bring benefits to soil and water quality as well as biodiversity. Agricultural biomass can only be considered sustainable if it is economically efficient and profitable, socially viable, and provides a net benefit to improving environmental performance and rural development. At the same time, in the wider context of trade liberalization and sustainable development, it must also be compatible with policy goals for agriculture, environment, and energy (Petříková *et al.* 2006).

Slovakia has suitable geographical and socio-economic conditions for energy crop cultivation, *e.g.*, the total area of agricultural land is 370 thousand hectares; phytomass can be grown for approximately 100 thousand ha; cultivation of fast-growing plant cultures

(Fig. 1) is also possible on less fertile soils; there is a possibility to produce 85 PJ of energy from agricultural biomass without negative impact on undercutting, animal feeding, and soil nutrition; and cultivation and establishment of plantations is at the level of small plots, especially in the East Slovakian lowlands (Víchová 2019).

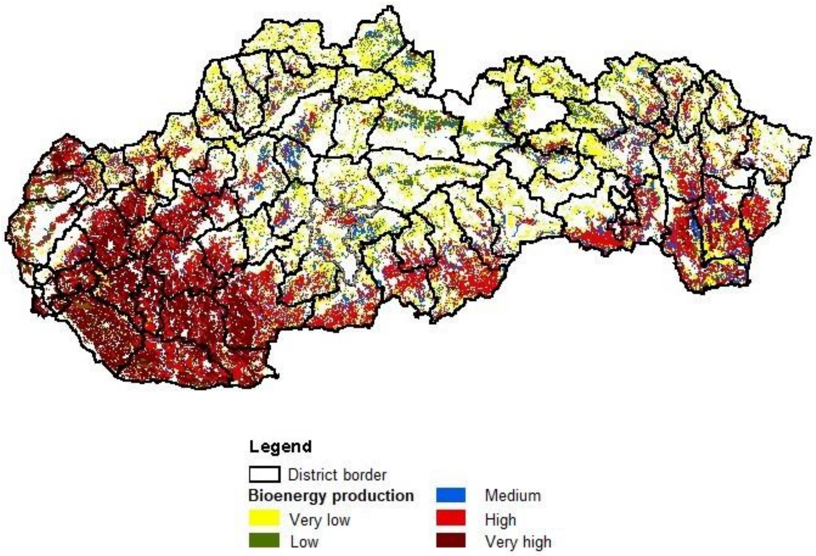

Fig. 1. Potential of fast-growing plant cultures for energy purposes in Slovakia (VUPOP 2019)

The energy potential of agricultural biomass is quite high and theoretically represents 20.4% of the annual energy consumption in the Slovak Republic, which is 800 PJ (Porvaz 2019).

Crops, such as *Miscanthus* × *giganteus*, *Arundo donax*, and *Sida hermaphrodita*, meet the calorific value requirements and can be used as fuel for heating while also having positive impact on the environment. These are lignocellulosic plants with huge potential for application in industry, construction, stationery, and the pharmaceutical industry. The cultivation of energy crops is also important for the more efficient use of agricultural land with less value. They can be grown as part of greening up to an area of 5% within the area of the farmer's agricultural land. At present, the area of energy plants plantations in Slovakia is not increasing; those have a stagnant character. For example, the area of the *Miscanthus* plantations in Záhorie decreased from 120 ha to 80 ha. In Slovakia, there is not intensive, but extensive cultivation of this plant. There is still a problem with the realization of production, specifically with the sale of briquettes and pellets at economically advantageous prices. A new introduced energy plant, *Sida hermaphrodita*, grows on an area of 15 ha and is still in the stage of verification and zoning. The cultivation of plants for bioethanol is still only at a theoretical level in Slovakia. The area of these crops is limited by the interest of the processing industry. In the Prešov and Košice regions, there are higher demands for processing of post-harvest residues and phytomass of energy plants in the processing industry. Currently, *Miscanthus* × *giganteus*, *Arundo donax*, and *Sida hermaphrodita* are mostly cultivated for energy purposes in Slovakia (Porvaz 2019).

The cultivation of *Miscanthus* × *giganteus* provides several advantages, mainly high hectare yields of phytomass in the range of 20 to 40 tons/ha of absolute dry matter, depending on the agroclimatic conditions. At the same time, the low input costs of cultivation and the initial costs of establishing a plantation are rapidly decreasing due to the constant tendency to reduce the prices of rhizomes. The cultivation of this energy crop in Europe is affected by the risk of frost damage to newly established stands. From the point of view of industrial use, this energy plant is suitable to produce biomethane and bioethanol and to be used as a source of lignin cellulose, while its application is currently in the research stage. The area of cultivation areas in Slovakia is at the level of 100 to 120 ha (Porvaz 2019).

Arundo donax is originally a wild perennial grass with creeping outcrops, which is particularly widespread in Europe in the Mediterranean. Research into alternative crops for biomass production for energy has ranked it among the species that are very suitable in terms of biomass production. However, it is sensitive to winter, especially in the first years of plant establishment. In the Košice region, this energy crop is grown on an area of up to 50 ha. However, as with other perennial energy crops, chemical protection against weeds is a problem. This causes major problems in cultivation because the first two years are crucial for the sustainability and economic profitability of this crop. *Sida hermaphrodita* belongs among the promising energy plants as well; it is mainly grown on an area of 15 ha in the Prešov region (Porvaz 2019).

In relation to the process of energy conversion, biomass properties are important in its subsequent processing. Among those properties belong moisture content (intrinsic and extrinsic), calorific or higher heating value, mass of fixed carbon and volatiles, ash/residue mass, alkali metal mass, and cellulose to lignin ratio. For dry biomass conversion processes, the moisture content (intrinsic and extrinsic), calorific and higher heating value, fixed carbon and volatiles mass, and ash/residue mass are of interest. For wet biomass conversion processes, the moisture content and cellulose to lignin ratio are of prime concern (McKendry 2002).

Moisture content is a physical property of biomass that influences its thermal and energy potential. Lower biomass moisture content is required when using it for energy purposes. It also has an impact on transport and storage of biomass. There also exists a direct and strong relationship between the moisture content of fuel and its energy potential, which is expressed by calorific value (Forests Research 2020). According to Forest Research (2020), in combustion systems, any water in the fuel must be driven off even before the first phase of combustion. This requires energy and thus reduces overall system efficiency. Thermal conversion usually requires low moisture content biomass (typically less than 50%). The summary of factors influencing the energy potential of biomass has been published by Moskalik and Gendek (2019).

Cellulose, hemicelluloses, lignin, extractives, lipids, proteins, simple sugars, starches, water-soluble substances, hydrocarbons, ash, *etc.*, are contained in the biomass. Among all these components, cellulose, hemicelluloses, and lignin are the three principal components. According to Forest Research (2020), biomass contains varying amounts of cellulose, hemicellulose, lignin, and a small number of other extractives. Cellulose and lignin are determining factors in identifying the suitability of plant species for subsequent processing as energy crops. The cellulose and lignin mass contained in biomass is important only in biochemical conversion processes, while the biodegradability of cellulose is greater than that of lignin. However, overall conversion of carbon-containing plant material present as cellulose is greater than for plants with a higher proportion of lignin. Woody plant species are typically characterized by slow growth and are composed of tightly bound fibers, giving a hard-external surface, while herbaceous plants are usually perennial with more loosely bound fibers, indicating a lower proportion of lignin, which binds together the cellulosic fibers. The mass of lignin in biomass can be used as an indicator of the higher heating value due to its relatively lower oxygen mass (Demirbas 1997; Lewandowski and Kicherer 1997; Collura *et al.* 2006; Collura *et al.* 2007; Michel *et al.* 2006; Villaverde *et al.* 2009, Lourenço and Pereira 2017; Ahmad and Pant 2018).

The ash mass affects both the handling and processing costs and biomass energy conversion costs. In biochemical conversion for the same material, the percentage portion of solid residue is usually greater than the ash mass that is formed in combustion. This is because the ash mass represents the recalcitrant carbon. This cannot be degraded biologically; it can only be burnt in thermo-chemical conversion.

Additionally, elemental (C, N, H, O, and S mass) analysis together with the ash mass analysis is often used. Results of those analyses show that higher proportions of oxygen and hydrogen compared to carbon reduces biomass energy potential. This is due to the lower energy contained in the carbon-oxygen and carbon–hydrogen bonds.

The thermal analysis of biomass, *i.e.*, energy crop, has been the focus of work by several investigators. They mostly used the thermal analyses results to study the combustion reaction kinetics and calculate the activation energy of the reaction.

Pyrolysis and combustion behavior are important characteristics to study biomass and its behavior at different temperatures (Carrier *et al.* 2011). Defining the biomass energy potential is usually used for numerical simulations of thermal systems to evaluate the quality of combustion.

This study presents results of study focused on the thermal and chemical properties of biomass planted in Slovakia, which are important for determination of energy crop potential for energy production.

EXPERIMENTAL

Materials

There were three energy crop species tested: *Sida hermaphrodita*, *Arundo donax*, and *Miscanthus* × *giganteus*. These crops were harvested at the experimental plantations in Dolné Saliby, Slovakia in May 2018. The experimental plantations (total area of 3.8 ha) were established in 2014. More information about energy crop species is introduced in Table 1.

Table 1. Calorific Values of the Samples

Sample	Moisture content (%)	Area (ha)	Biomass mass from harvesting (t)	Biomass dry mass (t)
Sida	21.00	1.14	21.55	14.90
Miscanthus	17.00	1.52	31.46	17.20
Arundo	36.00	1.14	27.47	15.40
Total		3.80	74.56	32.60

The biomass was harvested, sampled. In the field, the biomass moisture content was measured using the Wiltronics Fine Fuel Moisture Meter ME 2000 (Wiltronics Research Pty. Ltd., Alfredton, Australia). Biomass mass from harvesting was calculated based on the weighting the biomass fully loaded truck and the empty truck, using the LESAK MAV stable vehicle scales (LESAK s.r.o., Brno, Czech Republic), with length of 16 m, width of 3 m, load capacity of 60 t, and precision of 20 kg).

The dry mass samples were used in experiments. The samples were dried in the Memmert UFB 500 Basic dry oven (MEMMERT GmbH+Co.KG, Schwabach, Germany) and ground. Three repetitions were performed for each analysis and each sample. To analyze the thermal and chemical properties of the energy crop species, several standardized analytical methods were used.

To determine the higher heating value, an IKA C200 calorimeter (IKA®-Werke GmbH & Co. KG, Staufen, Germany) and the procedure described in ISO 1928 (2009) were used. Based on Eq. 1, which was introduced in the same standard, the calculated the lower heating value (KJ/kg) was calculated,

$$q_{\mathrm{v,net,m}} = [q_{\mathrm{v,gr,d}} - 206.0 \times w(H)_{\mathrm{d}}] \times (1 - 0.01 \times M_{\mathrm{T}}) - 23.5 \times M_{\mathrm{T}} \tag{1}$$

where $q_{\mathrm{v,net,m}}$ is the lower heating value at constant volume and containing water (kJ/kg), $q_{\mathrm{v,gr,d}}$ is the higher heating value at constant volume without water content (k/kg), $w(H)_{\mathrm{d}}$ is the percentage of hydrogen (%), and M_{T} is the total water content of the fuel for which conversion is required - relative moisture (%).

For calculation, the following moisture contents (measured during harvesting) were used: 21% for *Sida hermaphrodita*, 17% for *Miscanthus* × *giganteus*, and 36% for *Arundo donax*.

The procedure for ash determination was based on the requirements of the standard STN ISO 1171 (2003). A dry sample with a weight of 2.0 g was placed in a muffle furnace with the lid of the crucible removed. The temperature of the furnace was raised slowly to 580 to 600 °C to avoid flaming. When all the carbon was burnt, the sample was cooled and weighed. The analysis results show the average value of those measurements.

The chemical analyses focused on the elemental analysis as well as the mass of extractives, lignin, hemicelluloses, and cellulose. To determine the elemental composition of the samples, the FLASH EA 1112 (Thermo Fisher Scientific Inc., Waltham, MA, USA) apparatus was used. The carbon mass (C_{daf}), hydrogen mass (H_{daf}), nitrogen mass (N_{daf}), and sulphur mass (S_{daf}) were analyzed. The oxygen mass (%) in the sample was calculated based on Eq. 2:

$$O_{\mathrm{daf}} = 100 - C_{\mathrm{daf}} - H_{\mathrm{daf}} - N_{\mathrm{daf}} - S_{\mathrm{daf}} \tag{2}$$

In chemical analysis focusing on the mass of extractives, lignin, hemicelluloses, and cellulose, the samples were disintegrated and arranged to fraction by grain size analysis to fractional pieces of 0.5 up to 1.0 mm. Extractive agents were determined according to the standard ASTM D1107-96 (2013). Lignin was determined according to the ASTM D1106-96 (2013) standard. Cellulose was determined according to Seifert (1956).

Combustion reaction kinetics were expressed by the activation energy (J/mol). To calculate them, three iso-conversional kinetic methods were used: Ozawa-Flynn-Wall, Kissinger, and ASTM-E698-05 (2018). For the Ozawa-Flynn-Wall method, the thermal analysis was performed using the Mettler TA 3000 (Mettler Toledo, Greifensee, Switzerland), the TC 10A processor (Mettler Toledo, Greifensee, Switzerland), and TG 50 thermogravimetric weights (Mettler Toledo, Greifensee, Switzerland) with an air flow rate of 200 mL/min, heating rates of 10, 15, 20, and 25 °C/min, and standard test room conditions. The thermogravimetry/derivative thermogravimetry (TG/DTG) curves obtained from the thermal analysis, provided in accredited laboratories of the Fire Research Institute of the Ministry of Interior of the Slovak Republic (Fig. 2 shows TG/DTG analysis result for *Sida*), were used to calculate the activation energy.

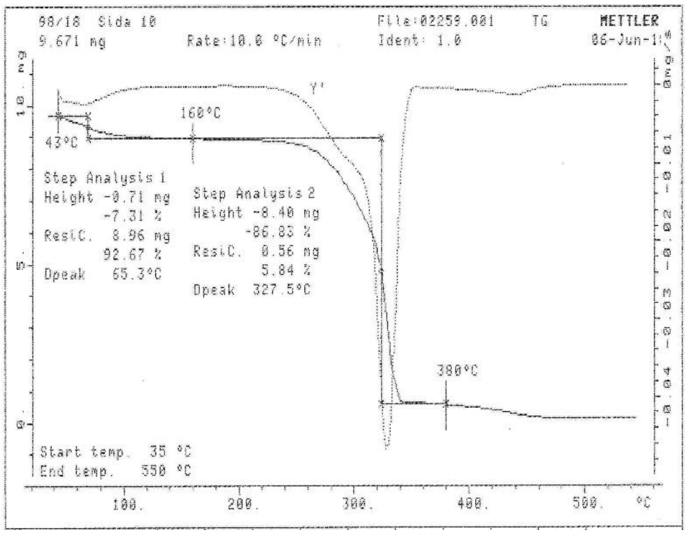

Fig. 2. TG/DTG analysis result for *Sida hermaphrodita*

At the same conversion levels, Eq. 3 was used. The activation energy value was derived from the slope of the plot log (β) *vs.* 1/T values specific for conversion levels,

$$\left[\frac{d(\log\beta)}{d(\frac{1}{T})}\right] = 0.4565\left(\frac{E}{R}\right) \tag{3}$$

where E is activation energy (J/mol), R is the ideal gas constant (8.314 J/mol·K), T is temperature (K) corresponding to the measured heating rate at the same conversion, and β is heating rate (°C/min).

Using the Kissinger method, the activation energy was calculated based on Eq. 4,

$$\left[\frac{d\left(\frac{\ln\beta}{T_p^2}\right)}{d\left(\frac{1}{T_p}\right)}\right] = -\left(\frac{E}{R}\right) \tag{4}$$

where E is activation energy (J/mol), R is the ideal gas constant (8.314 (J/mol·K), T_P is peak temperature (K), and β is heating rate (°C/min).

According to the ASTM-E698-05 (2018) method, Eq. 5 was used for the calculation of activation energy,

$$E = -2.19R\left[\frac{d(\log\beta}{d\frac{1}{T}}\right] \tag{5}$$

where E is activation energy (J/mol), R is the ideal gas constant (8.314 (J/mol·K), T is temperature (K) corresponding to the measured heating rate at the same conversion, and β is heating rate (°C/min).

RESULTS

Presented below are the results of the analyses of thermal and chemical properties of energy crop species planted in Slovakia.

Higher Heating Value, Lower Heating Value, and Ash Mass

An important property for assessing the suitability of a biomass for production of energy is the biomass moisture content. The biomass moisture content is changing in time. There is a difference in moisture content of a plant in growing phase, when harvested, stored and after drying. To utilize the biomass for energy purposes, the lowest value of moisture content is required. This value is achieved in drying process. Only after drying, the biomass should be used as an input to energy conversion, *i.e.* production process.

In the higher heating value analyses, all tested samples were of 0% (dry mass) according to requirements of the methodological approaches and standards used. The moisture content value needs to be stated for quoting lower heating values. The samples calorific values (Table 2) were expressed in the form of higher and lower heating values.

Table 2. Calorific Values of the Samples

Sample	Moisture content (%)	Higher Heating Value at 0% moisture content (MJ/kg)	Lower Heating Value (MJ/kg)
Sida	21.00	18.75 ± 0.362	13.35 ± 0.362
Miscanthus	17.00	19.60 ± 0.144	14.85 ± 0.144
Arundo	36.00	18.85 ± 0.091	10.45 ± 0.091

The highest energy potential was shown by *Miscanthus* × *giganteus* (19.60 ± 0.144 MJ/kg; 14.85 ± 0.144 MJ/kg). The lowest energy potential, *i.e.*, lowest lower heating value, was shown by *Arundo donax* (18.75 ± 0.091 MJ/kg; 10.45 ± 0.091 MJ/kg). This is because higher moisture content reduces the amount of available energy from the biomass. The results also showed that mostly *Miscanthus* × *giganteus* and *Sida hermaphrodita* were more suitable to be used for energy purposes. *Miscanthus* × *giganteus* seems to be the most suitable when looking at both the higher and the lower heating values.

The lower heating value is also related to the ash mass. This fact confirmed the ash mass analysis. The highest ash mass was achieved by *Arundo donax* (3.46 ± 0.112 wt%). The lowest values of ash mass showed *Miscanthus* × *giganteus* (2.67 ± 0.084 wt%).

In Table 2, the proximate analysis of sample moisture content, lower heating value, and ash mass is introduced (Table 3).

Table 3. Proximate Analysis of Sample Moisture Content, Lower Heating Value, and Ash Mass

Sample	Moisture Content (%)	Lower Heating Value (MJ/kg)	Ash Mass (% d.m.)
Sida	21.00	13.35 ± 0.362	2.93 ± 0.113
Miscanthus	17.00	14.85 ± 0.144	2.67 ± 0.084
Arundo	36.00	10.45 ± 0.091	3.46 ± 0.112

The highest ash mass was achieved by *Arundo donax* (3.46 ± 0.112 % d.m.). *Miscanthus* × *giganteus* (2.67 ± 0.084 % d.m.) showed the lowest ash mass values.

Chemical Properties

According to the elemental composition analysis results, it was found that the best results were obtained by *Miscanthus* × *giganteus*; see results in Table 4.

Table 4. Carbon (C), Hydrogen (H), Nitrogen (N), Oxygen (O), and Sulfur (S) Dry Mass in the Energy Crop Samples

Sample	C (wt%)	H (wt%)	N (wt%)	S (wt%)	O (wt%)
Sida	43.74 ± 0.036	5.68 ± 0.011	0.77 ± 0.043	0.24 ± 0.018	50.96 ± 0.422
Miscanthus	45.28 ± 0.765	5.74 ± 0.031	0.29 ± 0.017	0.08 ± 0.034	51.60 ± 0.695
Arundo	44.19 ± 0.041	5.70 ± 0.028	1.29 ± 0.022	1.29 ± 0.001	52.47 ± 0.039

The highest carbon mass was found in *Miscanthus* × *giganteus*, while the lowest was in *Arundo donax*. The highest values of hydrogen mass were found in *Miscanthus* × *giganteus*, and the lowest were found in *Arundo donax*. The highest values of nitrogen mass were found in *Arundo donax*, and the lowest values were found in *Miscanthus* × *giganteus*. The highest values of oxygen mass were found in *Sida hermaphrodita*. The lowest values of oxygen mass were found in *Miscanthus* × *giganteus*. From the sulfur mass point of view, the lowest mass was found in *Miscanthus* × *giganteus*, and the highest mass was found in *Arundo donax*.

Table 5 shows the results of lignin, cellulose, hemicelluloses, and extractives analyses.

Table 5. Lignin, Cellulose, Hemicelluloses, and Extractives Mass (% d.m.) in the Energy Crop Samples

Species	Lignin (% d.m.)	Cellulose (% d.m.)	Hemicelluloses (% d.m.)	Extractives (% d.m.)
Sida	17.92 ± 0.455	36.30 ± 0.172	44.00 ± 0.240	1.78 ± 0.013
Miscanthus	20.17 ± 1.988	39.53 ± 0.011	37.89 ± 0.012	2.71 ± 0.010
Arundo	20.49 ± 0.020	34.95 ± 0.019	32.31 ± 0.012	12.25 ± 0.016

The highest mass of lignin was found in *Arundo donax* (20.49 ± 0.020 % d.m.). The lowest values were found in *Sida hermaphrodita* (19.92 % d.m.). From the lignin mass point of view, the most suitable for energy production (including biochemical processes) use is *Arundo donax*. However, the difference in lignin mass value between *Arundo donax* and *Miscanthus* × *giganteus* was not very large. Based on this fact, *Miscanthus* × *giganteus* should also be suitable for energy purposes and biochemical processes. It is also the most suitable species for production of bioethanol due to high cellulose mass.

Activation Energy

Table 6 also shows the activation energy values of the tested samples of energy crop species obtained by application of three different iso-conversional methods.

Table 6. Activation Energy Values Calculated for the Energy Crops Using the Iso-conversional Methods

Method/Species	Activation Energy					
	Sida		*Miscanthus*		*Arundo*	
	(kJ/mol)	(kJ/kg)	(kJ/mol)	(kJ/kg)	(kJ/mol)	(kJ/kg)
Ozawa-Flynn-Wall	196.17	0.086	191.50	0.084	201.75	0.089
Kissinger-Akahira-Sunos	114.54	0.050	102.80	0.045	115.35	0.051
ASTM-E698-05 (2018)	123.45	0.054	112.01	0.049	124.17	0.055
St Dev	± 36.82	± 0.020	± 39.93	± 0.021	± 38.84	± 0.021

From the activation energy point of view, the best results were obtained with *Miscanthus* × *giganteus*. The activation energies calculated by different methods showed remarkable differences, which were caused by the application of different approaches for determination of the thermal degradation process and different equations for setting the activation energy. Those are still developing to find an approach that will be more appropriate and precise and will exclude the known errors that present methods include. The overall difference of activation energy calculation results was ± 38.53 kJ/mol on average. According to the results, it can be stated that energy crops are suitable for energy purposes. The advantage of crop biomass, compared to woody biomass, is that it has higher and mostly annual yields with very similar energy properties.

DISCUSSION

The experiments were focused on the investigation of the selected thermal and chemical properties of three crops (*Sida hermaphrodita*, *Arundo donax*, and *Miscanthus* × *giganteus*), which are mostly planted and harvested on energy plantations in Slovakia. The results of this study are compared with the results of other authors dealing with similar issues.

The calorific value and lower heating value of the energy crop samples were investigated. To calculate these values, the moisture content needed to be stated. This is because higher moisture content reduces biomass energy potential. According to McKendry (2002), quoting both the calorific value and crop yields expressed in dry matter tons (dmt) is usually required. If any moisture is present in biomass, it leads to a reduction in its calorific value (proportional to the moisture content). Biomass heating value is tightly connected with elemental composition and is affected by the variation in cell wall composition and ash. In this study, the higher heating values of tested crop species ranged from 18.8 to 19.6 MJ/kg. Those results are correlated with results of Morales (2017), who stated that higher heating value of a plant dry matter is *ca.* 19.0 MJ/kg. In general, this value is more than the calorific value of brown coal, which is commonly used for heating. Its higher heating values range from 12.0 to 14.0 MJ/kg. That is the reason why herbaceous biomass is valuable. It is valuable not only from the efficiency and economic point of view, but even from an environment protection point of view.

Jablonowski *et al.* (2016) studied *Sida hermaphrodita* and determined the calorific (higher heating) value of *Sida hermaphrodita* at 17.0 MJ/kg. In this study, the higher heating value of *Sida hermaphrodita* was 18.75 ± 0.362 MJ/kg and the lower heating value was 13.35 ± 0.362 MJ/kg (at a moisture content of 21%).

Another factor affecting the quality and energy potential of crop is the ash mass. Ash is a by-product generated during biomass burning. As stated in Nuamah *et al.* (2012), higher ash mass indicates a lower biomass energy potential. In this study, the highest ash mass was achieved by *Arundo donax* (3.46 ± 0.112 % d.m.). *Miscanthus* × *giganteus* (2.67 ± 0.084 % d.m.) showed the lowest values and therefore the highest energy potential. The 2.0% to 3.5% mass of the fuel remaining after *Miscanthus* combustion was also found by Lanzerstorfer (2019). *Arundo donax* ash mass was studied by Dragoni *et al.* (2015), who found its ash mass at 3.4 to 4.8 % d.m. and by Jeguirim *et al.* (2010), who determined the ash mass of *Arundo donax* at 5.0 % d.m. In the study of Krička *et al.* (2017), the value of *Arundo donax* ash mass was 3.56 % d.m. Jeguirim *et al.* (2010) also studied the ash mass of *Miscanthus* × *giganteus* and determined it to be 2.7 % d.m. In the study of Howaniec, Smolinski (2011), the value of *Miscanthus* × *giganteus* ash mass was found at 1.60 % d.m., and in the study of Krička *et al.* (2017) the value was 1.20 % d.m. Stolarski *et al.* (2014) studied the ash mass of *Sida hermaphrodita* and determined it to be 2.56 % d.m. In the study provided by Krička *et al*. (2017), the value of *Sida hermaphrodita* ash mass was 2.84%. In this study, the ash mass of *Sida hermaphrodita* was 2.93%.

Further, there was investigation of the elemental composition of energy crop samples. Results of this study showed that *Miscanthus* × *giganteus*' elemental composition was represented by 45.28 % d.m. carbon, 5.74 % d.m. hydrogen, 0.08 % d.m. sulfur, and 51.60 % d.m. oxygen. Similar results were introduced in the studies of Lewandowski and Kircherer (1997), Hodgson *et al*. (2011), and Lygin *et al.* (2011), which showed that the major elemental composition of *Miscanthus* dry matter was 47.1 to 49.7% carbon, 5.38 to 5.92% hydrogen, and 41.4 to 44.6% oxygen. Licursi *et al.* (2015) investigated nitrogen mass in *Arundo donax*. Its mass was around 0.3 % d.m. In the current study, the nitrogen mass of *Arundo donax* was set to 1.29% d.m. The elemental composition of *Arundo donax* was also investigated by Krička *et al.* (2017), who found the carbon mass at 45.67%, the hydrogen mass at 6.17 % d.m., the oxygen mass at 47.13 % d.m., and the nitrogen mass at 0.74 % d.m. In the current study, the *Arundo donax* the carbon mass was 44.19 % d.m., the hydrogen mass was 5.70 % d.m., the sulfur mass was 1.29 % d.m., and the oxygen mass was 52.47 % d.m. Those authors also studied *Sida hermaphrodita*'s elemental composition, which was found as the following: 50.08 % d.m. carbon, 6.10 % d.m. hydrogen, 42.95 % d.m. oxygen, and 0.65 % d.m. nitrogen. In this study, the elemental composition of *Sida hermaphrodita* was found as follows: 43.74 % d.m. carbon, 5.68 % d.m. hydrogen, 0.24 % d.m. sulfur, 50.96% oxygen, and 0.77% nitrogen. The carbon mass of *Sida* biomass of 49 % d.m. was also stated by Stolarski *et al.* (2014). There were specified carbon mass values in two other studies (Wróblewska *et al*. 2009; Michalska *et al.* 2015) as well. The carbon masses were set to 45.9 % d.m. and 47 % d.m., and the nitrogen masses were set to 0.3 % d.m. and 0.2 % d.m.

As stated above, cellulose and lignin are determining factors in identifying the suitability of plant species for subsequent processing as energy crops. That is also the reason to know the lignocellulose composition of the energy crop. This study showed the following lignocellulose content of *Sida hermaphrodita*: 36.30 % d.m. cellulose, 44.00 % d.m. hemicelluloses, 17.92 % d.m. lignin, and 1.78 % d.m. extractives. The lignocellulose content of *Miscanthus* × *giganteus* is as follows: 39.53 % d.m. cellulose, 37.89 % d.m. hemicelluloses, 20.17 % d.m. lignin, and 2.71 % d.m. extractives. The lignocellulose mass of *Arundo donax* is as follows: 34.95 % d.m. cellulose, 32.31 % d.m. hemicelluloses, 20.49 % d.m. lignin, and 12.25 % d.m. extractives. In general, higher lignin indicates a better energy source (McKendry 2002). In the present study, the highest lignin mass was found in *Arundo donax* (20.49 % d.m.). The lowest values were found in *Sida hermaphrodita* (17.92 % d.m.). From a lignin mass point of view, the most suitable for energy production (including biochemical processes) use was *Arundo donax*. The lignocellulose content of *Arundo donax* was also studied by Raspolli Galletti *et al.* (2015), who determined the following contents: 41.60 % d.m. cellulose, 23.60 % d.m. hemicellulose, and 24.60 % d.m. lignin. The lignocellulose content of *Miscanthus* × *giganteus* was investigated by Wróblewska *et al.* (2009): 43.20 % d.m. cellulose, 25.20 % d.m. hemicellulose, and 23.00 % d.m. lignin. Wróblewska *et al.* (2009) also studied the lignocellulose content of *Sida hermaphrodita*: 41.00 % d.m. cellulose, 17.10 % d.m. hemicellulose, and 26.00 % d.m. lignin. The differences in the investigated values were mostly caused by the difference in soil, location, and harvest time.

To calculate the activation energies of the energy crops, the thermal analyses (thermogravimetry and differential scanning calorimetry) were provided. Hideno (2018) studied correlations between *Miscanthus* × *giganteus* and *Miscanthus* × *sinensis*. The thermal decomposition temperature of *Miscanthus* × *giganteus* was found at 225.5 °C and 341.5 °C (TG peaks) and at 341.5 °C and 327.2 °C (DTG peaks). *Miscanthus* × *giganteus* had a characteristic shoulder peak near 292 °C. Majlingová *et al.* (2019) found TG peaks of *Miscanthus* × *giganteus* planted in the Slovak republic at 160 and 370 °C. The shoulder peak was found at 322 °C. Thermal processes of *Miscanthus* × *giganteus* and *Arundo donax* were also studied by Jeguirim *et al.* (2010). Thermogravimetric analyses were performed under air atmosphere at a temperature rate of 5 °C/min. The rates of thermal degradation in devolatilization and the combustion phase were studied. The initial degradation temperature and the residual mass were determined. Results of this study showed that the initial degradation temperature for *Arundo donax* was lower than for *Miscanthus* × *giganteus*, although the thermal degradation rate was higher for *Miscanthus* × *giganteus*. Apparent activation energy was calculated for devolatilization and for the char oxidation phase. In the devolatilization phase, the apparent activation energy value for *Arundo donax* was 107.2 kJ/mol and in the char oxidation phase it was 253.6 kJ/mol. For *Miscanthus* × *giganteus*, in the devolatilization phase, the apparent activation energy was calculated as 96.4 kJ/mol. In the char oxidation phase, the value of apparent activation energy was 279.9 kJ/mol. Results of thermal analyses performed in the framework of this study showed that under air atmosphere the degradation temperature for *Arundo donax* was lower than for *Miscanthus* × *giganteus*. This was found only in the second phase of thermal degradation, *i.e.*, in the pyrolysis phase.

In this study, the activation energies were determined only for the second phase of the thermal degradation process. When using the Kissinger-Akahira-Sunos method for activation energy calculation, the activation energy of *Arundo donax* was set to 115.35 kJ/mol and *Miscanthus* × *giganteus* was set to 102.80 kJ/mol. Jeguirim and Trouvé (2009) studied the activation energy of two energy crops species (*Arundo donax* and *Miscanthus* × *giganteus*) in the devolatilization and char oxidation steps. In their study, they calculated the activation energies of *Arundo donax* and *Miscanthus* × *giganteus* as 107.2 kJ/mol and 96.4 kJ/mol. Different results were achieved by Kok and Özgür (2013), who applied the Ozawa-Flynn-Wall, Kissinger, and ASTM E698-05 (2018) method to calculate activation energies of *Miscanthus* × *giganteus*. Those methods required to perform the thermal analyses. Activation energy values for *Miscanthus* × *giganteus* were as follows: 229.4 kJ/mol for the Ozawa-Flynn-Wall method, 135.8 kJ/mol for the Kissinger method, and 143.2 kJ/mol for the ASTM-E698-05 (2018) method. In the current study, the activation energy values of *Miscanthus* × *giganteus* ranged from 102.8 kJ/mol (Kissinger-Akahira-Sunose method) to 191.5 kJ/mol (Ozawa-Flynn-Wall method).

To compare the activation energy results only *Miscanthus* × *giganteus* and *Arundo donax* were used. We compared results achieved in this study, then achieved by Jeguirim and Trouvé (2009), Jeguirim *et al*. (2010). The values of calculated activation energy were mutually compared and results of the comparison showed that our results are close to those achieved by Jeguirim and Trouvé (2009), *i.e.* activation energy of 112.0 kJ/mol achieved in this study using the ASTM method and 96.4 kJ/mol achieved by Jeguirim and Trouvé (2009) for *Miscanthus* × *giganteus* as well as 124.2 kJ/mol to 107.2 kJ/mol achieved for *Arundo donax.*

CONCLUSIONS

To study the thermal and energy properties of selected energy crop species, several standardized and progressive analytical methods were applied. According to the results of the study, the following conclusions can be drawn:

1. According to the higher HHV, lower LHV, and low ash content, the most suitable species for energy plantations in Slovakia is *Miscanthus* × *giganteus*. Its suitability to be planted as an energy crop is confirmed also by its biomass yields, which were the highest (17.2 t/ha d.m). Also, its lowest moisture content (17 %) on input to energy production process was an important factor to assign *Miscanthus* × *giganteus* to be the most suitable energy crop, when compared with the other tested species.
2. From lignin content and activation energy points of view, the most suitable crop for energy purposes is *Arundo donax*. This is due to its good lignin properties that can also be utilized for flexible polyurethane foams production (Bernardini *et al.* 2017).
3. Thermochemical properties of tested Slovak crop species are fully comparable with results of studies provided abroad.
4. Results of the study showed that all the tested species of energy crop are suitable to be used as a source of energy.
5. In general, energy crops, compared to woody biomass, are more suitable to be used as renewable energy sources, not only from the energy potential point of view, but due to the yields, which can be harvested each year.

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