

Assessment of gross calorific value of crop and bio-energy residues

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Abstract

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This study assessed the gross calorific values (GCV) of crop and bio-energy residues. In addition, it assessed the calorific values of sweet sorghum to clarify its potential as energy crop in the region. Furthermore, it statistically analysed the ash remaining after burning three bio-energy residues, bagasse, oil cakes and fermented sludge of biogas production, to identify their potential for agricultural use. Finally, the study calculated alkali content based on nutrient content and GCVs. Significant differences were found among the GCVs of the investigated materials. Among the crop residues, the least significant difference (LSD) ($P \leq 0.05$) of the calorimetric values was 76.26 kJ/kg, and among the by-products of bio-energy production, it was 20.80 kJ/kg. Significant differences were also found in nutrient content. In the case of the alkali content of bio-energy residues, the LSD was 0.04 kJ·kg⁻¹. For the bagasse and compost, the study recommends some technical operations to avoid slagging.

Keywords: biomass; combustion; calorimeter; ash; alkali content

To support the broader use of renewable energy, the directive 2009/28/EU (Directive 2009/28/EC of the European Parliament and of the Council of April 23, 2009 on the promotion of the use of energy from renewable sources) appropriated the increase of the rate of energy that must come from renewable sources in the EU countries by 2020 to 20% of communal energy consumption. Agricultural lands being finite, hence the competition for arable land to service both the food- and energy-production sectors (SMITH et al. 2010). Therefore one prospective method of producing renewable energy is from residues. Several studies have addressed the possible uses of agricultural residues (MEGGYES, NAGY 2012; MUGERWA et al. 2012; GÁLYA et al. 2014; MALAT'ÁK, BRADNA 2014; MÉZES, TAMÁS 2015), but the most commonly investi-

gated materials in those studies were wheat straw, maize and sunflower residues. According to CHANNIWALA and PARIKH (2002), the gross calorific value (GCV) of wheat straw is 17,990 kJ·kg⁻¹, while DEMIRBAS (1996) measured it at 17,000 kJ/kg. The GCV of maize stems is 17,680 kJ·kg⁻¹ (TORTOSAMASIÁ et al. 2007; Yin 2011), and KUCUKBAYRAK et al. (1991) measured the GCV of sunflower residues as being 15,870 kJ·kg⁻¹. All these data call attention to the energy potential of agricultural by-products.

Sweet sorghum (*Sorghum bicolor* (L.) Moench), which is an adequate feedstock for producing biogas and bio-ethanol (ZHAO et al. 2009; RATNAVATHI et al. 2010; PAZDERŮ et al. 2014), can be an excellent crop for producing biomass energy by combustion, due to its high content of lignocellulosic materials (CARILLO et al. 2014). Examining the use of fodder

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sorghum as a biomass energy source, CARRILLO et al. (2014) measured GCV as being 17,840 kJ·kg⁻¹. TÜRE et al. (1995) examined nine varieties of fodder sorghum and determined their GCVs to be between 16,272 and 17,210 kJ·kg⁻¹.

In the case of bio-ethanol production based on sweet sorghum, a significant amount of biomass, so-called bagasse, is appears during mechanical preparation of the raw material. GROVER et al. (2002) measured the GCV of this bagasse as being 13,730 kJ·kg⁻¹. GRAVALOS et al. (2016) measured the GCV of oil cake, a by-product of bio-energy production, as being 21,231 kJ·kg⁻¹.

The alkali content of annual crops can cause problems during combustion because it can lower the ash-fusion temperature which can increase slagging and fouling of boilers (MILES, MILES 1995). Measures to counter this include adding chemicals to neutralize the alkali, blending high-alkali biomass with low-alkali biomass and removing of alkali using washing techniques are also acceptable operations (MILES, MILES 1995; JENKINS et al. 1996, 1998, 2003; DAVIDSSON et al. 2002; DAS et al. 2004; HIGGINS et al. 2011).

The present study determined the GCV for winter wheat, maize, sunflower by-products and sweet sorghum. It also measured the GCVs of bioenergy by-products, including bagasse, oil cakes and compost made from the fermented sludge of biogas production. To clarify their potential to increase the nutrient content of soil and to assess their alkali content, the study also determined the element composition of ashes of the abovementioned bio-energy.

MATERIAL AND METHODS

The crop samples originated from the production sites of the Research Institute of Karcag in Hungary and were collected after harvesting. To provide representative samples for measurement, special care was taken during the collection of plant residues to ensure homogeneity.

The compost originated from a biogas plant in which the basic feedstocks are cattle slurry and crop

products. In this plant, the biogas slurry coming from the fermenter is separated into solid and liquid phases. The solid phase is composted, and this compost was the basic material used for measurements.

The oil cakes originated from an oil press plant in the region of Karcag, and the bagasse from sweet sorghum grown at the production sites of the Research Institute of Karcag. The juice content of the harvested sweet sorghum was pressed out using a spiral press, and the solid by-product of this procedure was examined as the bagasse. All samples were dried at 50°C for 3 days, and their average moisture content varied ≤ 5% (Table 1).

After chopping the samples were ground first with rough-, and then with fine grinder (Condux) to achieve sizes of from 0.1–2 mm. Precisely weighed, tablets 1.00 g tablets made of the homogenised samples were placed in the burning vessel of an adiabatic calorimeter (IKA C2000 Basic). Before each measurement, calibration was carried out using benzoic-acid tablets of a known GCV (26,470 kJ·kg⁻¹). To ensure perfect burning, the calorimeter was filled with pure oxygen at constant atmospheric pressure according to the standard method (ISO 1928:2009), Determination of gross calorific value by calorimeters bomb method.). To ensure statistically reliable data, 20 parallel measurements were taken in each series. Then, the weight of the remaining ash measured in each case to evaluate the relationship between GCV and ash remaining after combustion.

The controlled preparation of the ashes for analysis was conducted in an annealing oven (OM SZÖV Type OH 63). Exactly 6 g of each air-dry sample was put into a ceramic pot for annealing, which was conducted in three phases to prevent the samples from falling apart. First the samples were annealed to ~257°C, then to ~570°C, and finally to ~650°C. The ceramic pots containing the ash were exsiccated to protect the ash from moisture and chill it to room temperature.

The analyses were conducted in three repetitions. First, to determine P, K, Na and Mg contents, 0.4 g of ground sample was fractured with 4.0 cm³ cc of sulphuric acid at 360°C and at atmospheric pres-

Table 1. Average moisture content of the materials investigated (mean ± SD) (w/w %)

Maize	Wheat	Sunflower	Sweet sorghum	Compost	Oil cake	Bagasse
4.40 ± 0.33	4.12 ± 0.20	3.54 ± 0.22	4.23 ± 0.26	4.08 ± 0.18	4.21 ± 0.39	4.17 ± 0.27

n = 10

sure in the presence of selenium catalyst in a DK-20 block heater (VELP Scientifica) for 40 minutes. The annealing residues were produced up to a volume of 100 cm³.

Then, P content was further determined using a vanadomolybdate reagent and a Spekol 110 spectrophotometer (Carl Zeiss Jena) $\lambda = 440$ nm wave length. The K, Na and Mg contents were further determined using a flame photometer (Spectra AA-10 Varian) in air-acetylene flame.

In the case of the bio-energy residues, the alkali-metal content was calculated using the equation of MILES and MILES (1995) and CARILLO et al. (2014).

The measurement results were analysed by ANOVA to identify statistically significant difference among the materials' GCVs. For the statistical analyses, R software was used (R Core Team 2016).

RESULTS AND DISCUSSION

The results showed that the highest average GCV 17,508.85 kJ·kg⁻¹ \pm 104.32 kJ·kg⁻¹ was in maize residues, which agrees with results of Gaur and Reed (1988), while the lowest average GCV was measured for sunflower by-products, 14,388.40 \pm 210.61 kJ·kg⁻¹ (Table 2). The materials differed significantly in GCV from one another, and the least significant difference (LSD) among them was 76.26 kJ·kg⁻¹. No significant difference was found between wheat residues and sweet sorghum.

Table 2. Main statistical characteristics of the measures of GCVs and ash in crop residues

		GCV (kJ·kg ⁻¹)	Ash (w/w %)
Maize	mean	17,508.85	2.20
	sd	104.32	0.19
	range	354.00	0.91
Wheat	mean	16,545.15	4.85
	sd	27.30	0.92
	range	98.00	4.32
Sunflower	mean	14,388.40	7.36
	sd	210.61	0.56
	range	878.00	2.74
Sweet sorghum	mean	16,573.85	5.14
	sd	51.50	0.47
	range	177.00	2.42
LSD		76.26	0.38

These differences were also determined for the masses of ash remaining after burning. The highest amount of ash (7.36 \pm 0.56 w/w %) remained in the case of the sunflower by-products, while the lowest (2.20 \pm 0.19 w/w %) remained for maize residues (Table 2). The LSD of this parameter was 0.38 w/w % among the crop materials investigated, indicating no significant difference between the residues of wheat and sweet sorghum. These measurements confirmed those of JENKINS et al. (1988). Higher GCVs reflect decreased ash content in biomass raw materials (Fig. 1), a phenomenon that can be notable when estimating GCV (SHENG, AZEVEDO 2005).

Based on data from the statistical databases of the Food and Agriculture Organization of the United Nations (FAOSTAT) for 2005 to 2014, the quantities of maize, wheat and sunflower produced in Hungary did not vary notably (Table 3). Using the Harvest Index values published by GHOLINEZHAD et al. (2009) and ASIF et al. (2012), plant specific residue amount can be calculated to determine the energy potential of agricultural by-products. A notable quantity of these residues is available in Hungary. In quantities of from 7,359.50 kt to 1,281.60 kt, differences in GCVs are detectable, enabling exact estimates of bio-energy potential. To fulfil the requirements of the 2009 EU 28 directive, effective crop residue management that is based on such estimates of bio-energy potential can be beneficial to Hungary.

Due to its oil-residue content oil cake was found to have the highest average GCV values of the materials investigated (20,576.70 \pm 203.47 kJ·kg⁻¹). (Fig. 2.). The GCVs of all the materials investigated differed significantly from each other, with the LSD being 120.80 kJ·kg⁻¹ (Table 4).

Biomass-energy residues can potentially produce energy and improve the balance of energy produced by bio-energy means. Using bio-energy residues as secondary energy feedstocks can increase energy efficiency. According to the results of PARIKH et al. (2005), CHANNIWALA and PARIKH (2002) and GAUR and REED (1988), the GCVs of such residues were competitive with the higher heating values of several solid bio-energy feedstocks, including wood chips and several species of trees, pointing to the potential of second-generation bio-energy resources. The differences among the average GCVs of all bio-energy residues investigated indicated that application of these materials as energy feed-

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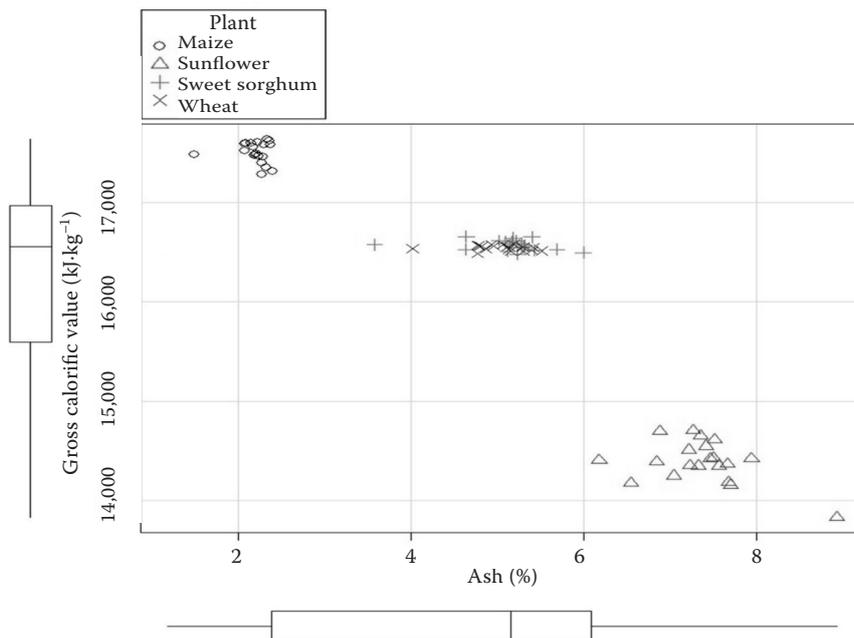


Fig.1. Gross calorific values and remaining ash masses in crop residues investigated

Table 3. Main data regarding plant production and residue amounts in Hungary (kt)

	Maize	Wheat	Sunflower
Average quantity of production	7,359.50	4,568.45	1281.60
SD of production quantity	1,785.13	642.80	203.47
Estimated minimum quantity of residue	7,359.50	7,778.72	2,091.04
Estimated maximum quantity of residue	17,172.17	9,707.96	2,487.81

stocks, especially oil cake, which is commonly used as fodder in Hungary, could be beneficial.

Regarding the alkali-metal content used to classify burning feedstocks by their potential to foul and

slagboilers the LSD, 0.04 kg·GJ⁻¹ was determined among the bio-energy residues investigated.

Regarding slagging potential, compost provided a 1.04 kg·GJ⁻¹ average alkali content with a stan-

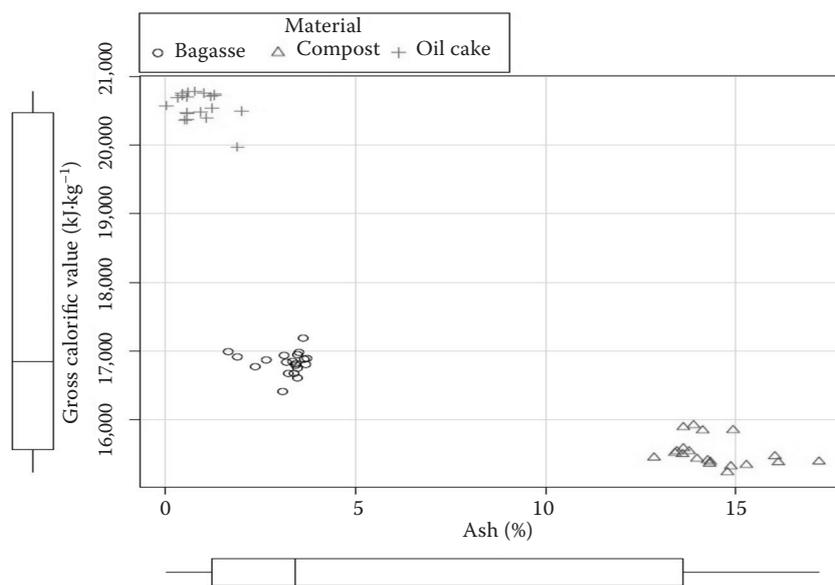


Fig. 2. Gross calorific values and remaining ash masses in the bio-energy by-products investigated

Table 4. Main statistical characteristics of the measure of GCVs and ash in bio-energy residues

		GCV (kJ·kg ⁻¹)	Ash (w/w %)
Oil cake	mean	20,576.7	0.86
	sd	203.47	0.51
	range	813.00	1.98
Compost	mean	15,514.55	14.42
	sd	202.78	1.07
	range	686.00	4.34
Bagasse	mean	16,830.8	3.16
	sd	163.28	0.58
	range	776.00	2.07
LSD		120.80	2.00

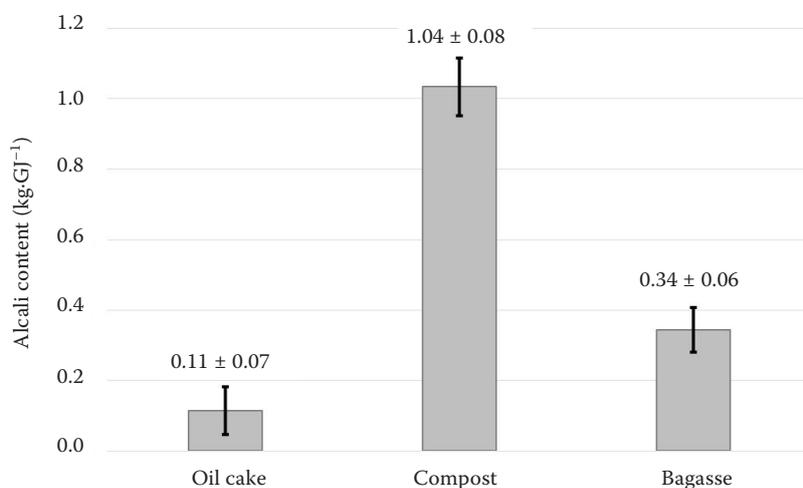
standard deviation (SD) of 0.08 kg·GJ⁻¹ which was the highest among the bioenergy residues evaluated and is probably related to its secondary biomass

content. The alkali content of bagasse was 0.34 ± 0.06 kg·GJ⁻¹ which was lower than the alkali content of sweet sorghum measured by CARILLO et al. (2014). According to MILES and MILES (1995), who indicated that alkali levels above 0.34 kg·GJ⁻¹ increase the potential for fouling and slagging, bagasse and compost merit more attention, due to their high alkali content during combustion. To mitigate risks caused by slagging and fouling, further technical operations are recommended. Oil cake's risks of slagging and fouling were not determined.

In addition to having potentially high alkali contents, ashes are good sources of phosphorus and potassium and contain sufficient calcium and magnesium to be useful in reclaiming soil. The three by-products of bio-energy production that were investigated differed significantly in phosphorus content (Table 5). The least significant difference among the

Table 5. P, K, Na, Ca and Mg content of the ashes investigated (w/w %)

		P	K	Na	Ca	Mg
Compost	mean	10.57	9.53	1.60	9.08	4.30
	sd	0.45	1.68	0.12	0.26	0.00
	range	0.90	3.00	0.21	0.50	0.00
Oil cake	mean	34.53	27.20	0.13	5.73	9.56
	sd	1.50	1.74	0.01	0.23	0.25
	range	3.00	3.20	0.02	0.33	0.50
Bagasse	mean	2.92	18.00	0.24	5.46	1.31
	sd	0.03	1.97	0.08	0.39	0.17
	range	0.06	3.80	0.15	0.78	0.42
LSD		1.81	3.60	0.17	0.61	0.36

Fig. 3. Alkali content of the bio-energy by-products investigated (mean \pm SD)

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investigated ash materials was 1.81%, although the value was higher in the case of potassium. Oil cake had the highest quantity of phosphorus and potassium because it contains sunflower seeds. Bagasse had remarkable K content as well.

Regarding the Ca content of the by-products of bio-energy production that were investigated the LSD was 0.61%. The LSD for Mg was 0.36%. All three materials investigated had high Ca and Mg content which, can be important for improving the porosity of soils especially those with high sodium content.

CONCLUSION

All by-products evaluated from the fields of plant or bio-energy production were adequate to produce energy by combustion. Some of the materials investigated had remarkable GCVs, making them prospective feedstocks for producing solid-biomass energy. The GCV and ash values determined by the study showed significant differences, not just between sweet sorghum and wheat residues. Thus, the amount of potential energy depends on the type of by-product. Regarding K and Na contents, only the oil cake can be recommended for burning without specific treatments to reduce alkali content.

Due to its high P and K content, ash remaining from the combustion of bio-energy by-products was adequate to enhance the nutrient content of soils. Most importantly the results showed that these ashes contained significant amounts of other nutrients, including Ca and Mg, indicating that applying them can enhance the nutrient stocks of soils is an adequate method in the case of acidic soils.

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