Evaluation of burning and reutilization parameters of different crop production by-products

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Abstract

Nowadays covering the permanently increasing energy demand is a serious challenge of the energy management. In the Central and Eastern European Region it is necessary to integrate energy sources into practical applications that do not need the reorganisation the infrastructural systems.

In our work the determination and assessment of the Higher Heating Value (HHV) released from burning some secondary products of crop and bioenergy production were done. Analytical examination of the ash remained after the burning of three by-products (bagasse, oil cakes, fermented sludge of biogas production) of biomass energy production were done in order to reveal its agricultural utilization possibilities regarding its nutrient content.

Significant differences were found in the HHV of the investigated by-products of crop production. The least significant difference (p=0.05) of the calorimetric heats among the by-products of crop production was 86.51 KJ kg^{-1}, while 120.80 KJ kg^{-1} was among the by-products of bioenergy production.

In the case of the nutrient contents significant differences (p=0.05) were found. According to the high nutrient contents found in the ash remained after the burning of the by-products of bioenergy production it can be suitable to increase the nutrient stocks of the soil.

Keywords: bioenergy, higher heating value, crop production, byproduct, ash

1. Introduction

The energy demand has been increased like never before all over the world (IEA, 2011), so there is more emphasis on the accommodation to the changing conditions both in the agricultural sector and in the energy supply. Recently 19% of the total energy consumption of the world originates from renewable energy resources, and approximately half them is of biomass origin (REN21, 2013). The 2009/28/EU directive appropriates the increase of the rate of renewable energy up to 20% in communal energy consumption of the EU countries by 2020 in order to support the broader dissemination of renewable energy.

The importance of energy produced from biomass is high as their use is in balance with the principles of sustainable development, does not need the radical reorganization of the actual infrastructure, but does not impede the application of new, sustainable technologies in the Central and Eastern European Region.

The economy of biomass energy production is principally determined by the basic materials applied hence energy production from secondary products can be significant in the fields of renewable energy use. Several options exist for the utilisation of secondary products of agricultural origin. These materials are characteristically reutilized by working them into the soil, but burning them can be a potential direction of utilization as well. This kind of materials is generated in huge quantities year by year providing a potential base for bioenergetical utilization.

Several studies were published regarding the utilization possibilities of agricultural residues (Mézes *et al*., 2015), but the most commonly studied basic materials appearing in the field of plant production are wheat straw, maize and sunflower residues. According to Channiwala and Parikh (2002) the HHV of wheat straw is 17990 KJ kg^{-1}, Demirbas (1996) measured 17000 KJ kg^{-1}, Gaur and Reed (1998) 17510 KJ kg^{-1}, while Parikh *et al*. (2005) 17360-18910 KJ kg^{-1}. The HHV of maize stem is 17680 KJ kg^{-1} (Tortosa-Masiá *et al*., 2007; Yin, 2011), while Kucukbayrak *et al*. (1991) published 15870 KJ kg^{-1}HHV for sunflower residues. All these data call the attention to energy potential of agricultural by-products.

In the case of the utilization of sweet sorghum for bioethanol production, significant amount of biomass of plant origin as a secondary product, so called bagasse, is generated during the preparation of the basic material. Grover *et al*. (2002) measured 13730 KJ kg^{-1} as the HHV of this bagasse.If bagasse is utilized through biomass burning as well, two ways of the production of renewable energy are ensured from the same plot.

Beyond the sorghum bagasse starts up during bioethanol production, the solid phase of the fermented sludge generated during biogas production can be an energy source as well. By-products are often used as the source of useful nutrients, but they are of great importance from the point of view of covering system demands, just like in the case of the by-products remaining after biodiesel production which has a high energy content. Nearly 60%

of the harvested sunflower remains back as oil cake which has HHV of 20990 KJ kg^{-1} (Kobayashi *et al*., 2008).

Using the energy gained by burning agricultural wastes and by-products is an effective method of the utilisation of secondary raw materials, but it raises an environmental protection problem due to the ash remain of the burning. The ash contains concentrated amounts of volatile and non-volatile elements and aerosols getting into the air. Nevertheless the non-volatile components can be utilised further as chemical amendments and nutrients in soil reclamation and plant nutrition if the strict technological rules are kept, therefore there is an opportunity to use ashes to increase the nutrient content of soil, as in the case of liquid biogas by-products (Gálya *et al*., 2014). Biomass ashes are nearly free of nitrogen, but they are significant sources of potassium and rich in calcium with a low content of heavy metals compared with ashes produced from coal (Pels *et al*., 2005; Eijk *et al*., 2012)

In this study the HHV was determined in the case of the by-products of winter wheat, maize and sunflower. HHVs of bioenergetical by-products (bagasse, oil cakes andcompost made from fermented sludge of biogas production) were also measured.In order to clarify their potential role in the increase of the nutrient content of the soil, the element composition of the ashes of the bioenergetical by-products was determined.

2. Material and methods

After chopping the air-dry crop samples were grinded first with a rough-, then a fine grinder (Condux) in order to achieve the size from 0.1 mm to 2 mm. The precisely weighed tablets (1.00 g) made of the homogenised samples were put into the burning vessel of an IKA C2000 Basic adiabatic calorimeter. Before each measurement calibration was carried out with benzoic acid tablet of known HHV (26470 KJ kg^{-1}). In order to ensure perfect burning, the calorimeter was filled with pure oxygen of constant atmospheric pressure according to the standard method (ISO, 2009). The software we used for the measurements was the CalWin Version 2.00.030.from 1999. In order to have statistically reliable data, 20 parallel measurements were taken in each series.

The controlled preparation of the ashes for the analytical examinations was carried out in an OM SZÖV Type OH 63 annealing oven. Exactly 6 g of air-dry samples were put into ceramic pots for the annealing, which was carried out in three phases in order to avoid the samples falling apart. In the first phase the samples were annealed up to ~257°C, then to ~570°C, and finally ~650°C was the temperature. The ceramic pots containing the ashes were exsiccated in order to protect the ash from moisture and chill down to room temperature.

The analytical examinations were done in three repetitions. For the determination of P, K, Na and Mg contents 0.4 g grinded sample has been fractured with 4.0 cm^3 cc. sulphuric acid at 360°C and at atmospheric pressure at the presence of selenium catalyst in a DK-20 blockheater (VELP Scientifica) for 40 minutes. The annealing residue were completed up to 100 cm^3 volume.

The P-contents were determined with vanadomolybdate reagent by means of a Spekol 110 spectrophotometer (Carl Zeiss Jena) λ = 440 nm wave length. The K, Na and Mg contents were determined by means of a flame photometer (Spectra AA-10 Varian) in air-acetylene flame. For the determination of the Cu, Zn, and Mn contents 0.5 g quantity of the samples were digested in a HNO_3-H_2O_2 compound and put into a MARS Xpress (CEM) microwave destructor at 190°C, 27 bar pressure with 30 minutes of reaction time. The element contents of the samples were determined by an AA220FS atomic absorption spectrophotometer (Varian) in air-acetylene flame.

The measurement results were analysed by ANOVA in order to determine if there are statistically significant difference among the HHVs of the investigated materials. For the statistical analyses R statistical software on R Studio user surface was used (R Core Team, 2016).

3. Results and discussion

On the base of the HHVs of the investigated by-products of crop production it can be established that the highest HHV value had been determined in the case of maize residues (17508.85 KJ kg^{-1}), while 14388.40 KJ kg^{-1} was measured for sunflower by-products giving the lowest value (Table 1.). According to the results some of the examined materials differed significantly from one another, the least significant difference among them was 86.51 KJ kg^{-1}.

These determined differences were characteristic to the mass of ashes remained after burning as well. The highest amount of ash (7.36 w/w %) remained in the case of the by-products of sunflower, while this value was 4.85 w/w % for wheat and 2.2 w/w % for maize. In the case of maize it must be emphasized that the lowest average amount of ash with a low standard deviation and variance values were characteristic to this crop residue. The least significant difference of this parameter was 0.401 w/w %.

Table 1. Statistical parameters of the HHVs and the amount of the ash of the by-products of crop production

Type of by-product	HHV (KJ kg^{-1})			Ash (w/w %)		
	Mean	SD	s^2	Mean	SD	s^2
Sunflower	14388	210.6	44356	7.36	0.56	0.31
Maize	17508	104.3	10882	2.20	0.19	0.04
Wheat	16545	27.30	745.5	4.85	0.92	0.85
LSD (p=0.05)		86.51			0.401	

Table 2. Statistical parameters of the HHVs and the amounts of ash of the by-products of bioenergy production

Type of by-product	HHV (KJ kg^{-1})			Ash (w/w %)		
	Mean	SD	s^2	Mean	SD	s^2
Oilcake	20576	203.47	41400	0.86	0.51	0.26
Compost	15514	202.78	41119	14.42	1.07	1.15
Bagasse	16830	163.28	26661	3.16	0.58	0.34
LSD (p=0.05)		120.80			2.00	

Measuring the HHVs of the investigated by-products of bioenergy production oil cake was found to have the highest average values (20576.70 KJ kg^{-1}) probably due to its oil residue content while compost had the lowest values with the value of 15514.55 KJ kg^{-1} (Table 2.).

The HHVs of the investigated materials differed significantly from each other with the least significant difference of 120.80 KJ kg^{-1}. This well determined difference was characteristic to the mass of ashes remained after burning as well. The highest amount of ash (14.42 w/w %) remained in the case of compost, while this value was 3.16 w/w % for the bagasse and 0.86 w/w % for oil cake. The value of the least significant difference was 2.00 w/w %.

During ash formation the element concentration of the initial products is considerably increasing, therefore high amount of certain elements can remain in the ash. Ash residues are good phosphorus and potassium sources and also contain sufficient amount of calcium and magnesium, therefore they can be utilised in soil reclamation. From the point of view of soil reclamation the P and K content, which are the dominant nutrients of the ashes, is important as they can contain as much P and K substances as phosphorus- and potassium fertilizers. Regarding their average phosphorus contents and the standard deviations the three investigated by-products of bioenergy production were considerably differed (Fig. 1).

In the case of the P-content the least significant difference among the investigated ash materials was 1.81%, while this value was 3.6% for potassium.Oil cake had the highest average K-content (27.2%), the bagasse had 18%, while the compost had only 9.53%.Generally a soil has sufficient AL-soluble P_2O_5-content if it reaches the value of 160 mg kg^{-1}, while regarding K-content 200 mg kg^{-1} is considered sufficient. Oil cake has the highest amount of these two elements due to the fact it contains sunflower seeds. Nevertheless the bagasse had remarkable K-content (18.1%) as well.

Ca and Mg can have important role in the improvement of the porosity status of the soils especially if their sodium content is high. Regarding the Ca-content of the investigated by-products of bioenergy production the least significant difference was 0.61%, while this value was 0.36% for Mg.

The ashes of all three materials had high Ca- and Mg-content. The highest Ca-content was measured for the compost (9.08%), while oil cake had the highest Mg-content (9.56%).

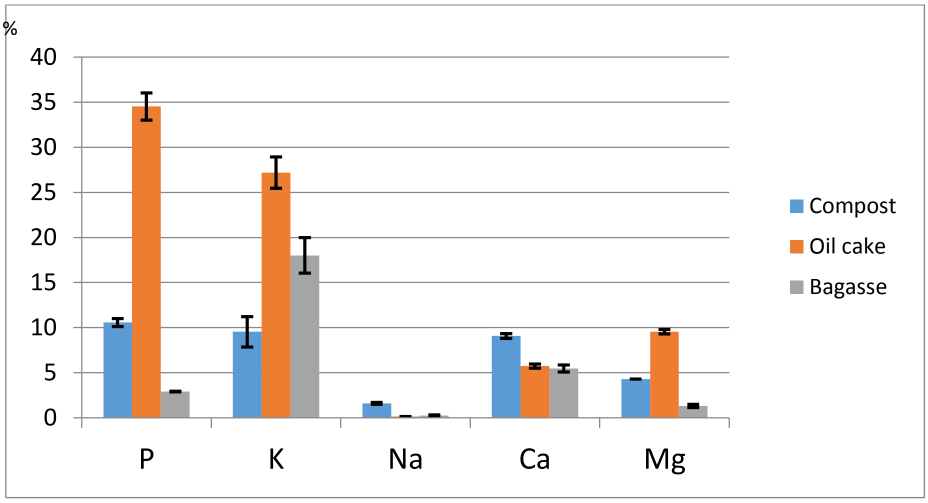

Figure 1.P-, K-, Na-, Ca-, and Mg-content of the investigated ashes (mean±SD)

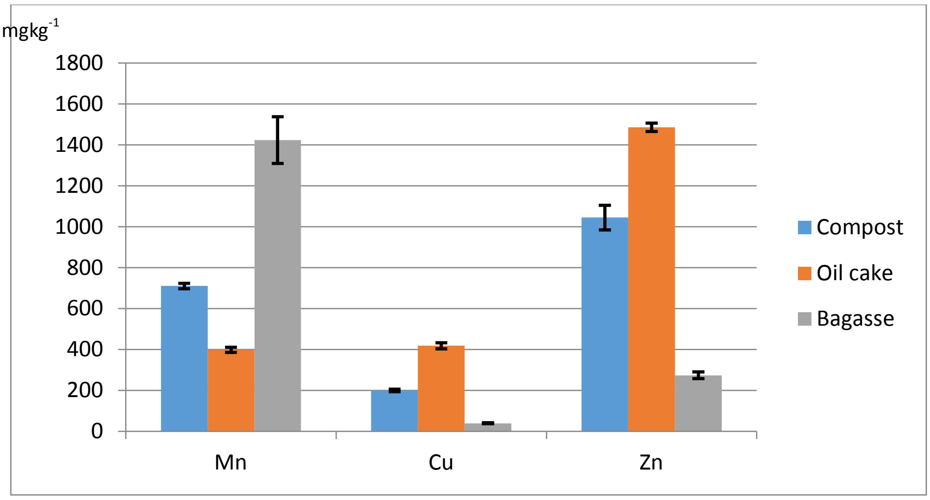

Figure 2. Mn-, Cu-, and Zn-content of the investigated ashes (mean±SD)

Regarding the manganese content of the investigated ashes considerable differences were found, which is justified by the high value of the least significant difference (133.72 mg kg^{-1}). Bagasse had the highest Mn-content with its 1424.06 mg kg^{-1} value, while 710.53 mg kg^{-1}Mn was found in the compost and 398.22 mg kg^{-1} in the oil cake (Fig. 2.).

The average copper content of oil cake was 418.33 mg kg^{-1}giving the highest value among the ashes. The compost had 199.93 mg kg^{-1}, while 39.33 mg kg^{-1}Cu was measured in the bagasse (LSD=19.36 mg kg^{-1}).

Regarding the zinc contents 75.55 mg kg^{-1} least significant difference was determined among the investigated ashes. With 1486.67 mg kg^{-1} average Zn-content oil cake had the highest value, while 1045.67 mg kg^{-1} Zn was measured in the ash of the compost and only 273.83 mg kg^{-1} in the bagasse.

Microelements have low concentration in the soils, so if the dose of the chemical amendment is calculated to the desired concentration of the major nutrients (P and K), no overdose of the accompanying microelements can occur.

According to the results of Etigéni and Campbell (1991) and Füzesi (2014) these ashes had higher nutritional values from the viewpoint of the investigated elements, therefore the application of them as fertilizer of the acidic soils can be prospective.

The humus content of the soil must be taken into consideration, beyond its pH value, if we want to avoid the overdosage of Cu, due to its complex forming ability. It is important to know the clay mineral composition of the soil when Mn and Zn containing ashes are used for plant nutrition, as these elements can be built in the interlamellar layers of the clay minerals.

4. Conclusions

The evaluated by-products appearing in the field of plant production and bioenergy can be adequate materials to produce energy by combustion. Some of the investigated materials gave a respectful HHV, therefore these materials can be prospective feedstocks to produce solid biomass energy. Regarding to the HHV and ash values determined in this study significant differences were determined among the investigated residues. Thus a respectful potential energy amount is depending on the type of the applied by-product.

Ashes remaining form the combustion of bioenergy by-products, containing a considerable amount of nutrients. Based on the measured data it can be fixed up that ashes are adequate materials to enhance the nutrient content of the soils due to their high P- and K-content. Above all, according to the results these ashes contain a respectful amount of other nutrients like Ca, Mg, Mn, Cu and Zn, therefore the application of this ashes to enhance the nutrient stocks of soils is an adequate method in the case of acidic soils.

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