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BIOCHAR FROM A DIGESTATE AS AN ENERGY PRODUCT AND SOIL IMPROVER

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ABSTRACT

Digestate, as bio-degradable agricultural biogas waste may be subject to the direct management as a fertilizer or, after separation of the solid and liquid phase – solid phase may be subjected to thermo-chemical transformation to biochar. Biochar is a carbonization product with high carbon concentration and relatively low decomposition susceptibility, obtained from various types of organic waste (International Biochar Initiative). Biomas carbonization takes place in the torrefaction process in the temperature from 200ºC to 320ºC. The chemical composition and utility properties of biochar depend on the substrate type and the process parameters. Biochar obtained from biodegradable waste may be an element of carbon biosequestration and used as biofuel, whereas in agriculture – as soil improver, which decomposes for a long time and which positively influences soil fertility, number of biogenic components and physical and water properties. The paper presents characteristic of the torrefaction process, process products and utility values of biochar from the point of view of energy and the agricultural value.

Introduction

Along with the development of the biogas sector, amount of the generated digestate increases. It is estimated that to 2020 approx. 2.5 thousand agricultural biogas plants will be founded, which relates to production of approx. 25 million post-fermentation residues annually (Czekała et al., 2012). Moreover, Poland prohibits storing biodegradable waste of the content above 5% of the total organic carbon, including digestate (Czekała et al., 2012).

The main trend in managing digestate is using it as a fertilizer directly to the soil, or after separation – application in the form of a solid and liquid fertilizer or also other use of the solid fraction, e.g. as energy pellet or litter (Mumme et al., 2011; Troy et al., 2013). Currently, particularly the second form of using digestate gets significance due to the potential of generating positive economic effects through the limitation of storing costs and costs of transport to the field as well as the environmental effects through limiting the loss of nutrients (leaching, oxidization, biogens drop (Lehman and Joseph, 2009; Nelissen et al., 2014; Zheng et al., 2013).

From among the perspective concepts related to the improvement or development of new technologies of processing the post-fermentation mass, conversion of the solid fraction of a digestate to biochar in a themo-chemical torrefaction process draws attention (Gołaszewski et al. 2013, Mohan et al., 2014; Sun et al., 2014).

The objective and the scope of the study

The objective of this paper is to review the literature on account of usefulness and potential of using a digestate obtained from the agricultural biogas plant for production of biofertilizer (soil improver) and energy material (biofuel). The paper presents characteristic of the torrefaction process, process products and the utility values of biochar from the point of view of energy and agricultural value.

Thermo-chemical biomass conversion - torrefaction

Biochar – according to a definition by *International Biochar Initiative* it is a carbonization product in high carbon concentration and relatively low susceptibility to decomposition, therefore it may be used as a soil improver and an element of carbon sequestration in soil (Lehman et al., 2011; Mohan et al., 2014; Sun et al., 2014; Sunil and Ajay, 2012; Zheng et al., 2013).

Production of biochar takes place in the thermo-chemical process of conversion – pyrolysis. Pyrolysis is defined as a thermal process of decomposition of the organic matter in the anaerobic conditions within the scope of temperatures 200-600ºC (Mohan et al., 2014). In relation to the parameters of the process, such as: temperature, stop time, pressure and the type of substrate, one may obtain a product, which is varied on account of the quality and quantity (Table 1) (Mohan et al., 2014; Sunil and Ajay; van der Stelt et al., 2011). The highest amounts of biochar are obtained in the slow heating processes, where biocarbonization product may constitute approx. 35%. Therefore torrefaction is considered to be the main process of biochar production (Mohan et al., 2014; van der Stelt et al., 2011).

Table 1
Types of thermo-chemical biomass conversion (modified)

Parameter	Thermo-chemical process				
	Slow pyrolysis	Torrefaction	Torrefaction	Gasification	Hydro-thermal carbonization
Temperature scope (ºC)	350-800	200-300	400-600	700-1500	175-250
Heating rate	slow (< 10ºC/min)	slow (< 10ºC/min)	very fast (~ 1000ºC/s)	fast	slow
Pressure	atmospheric	atmospheric	vacuum - atmospheric	raised atmospheric	–
Retention time	seconds - hours -	minutes-hours	seconds	seconds-minutes	hours
Product	Biochar	Biochar	Biooil	Syngas	Hydrochar

Source: Mohan et al., 2014

Torrefaction as a type of thermo-chemical biomass conversion (roasting, carbonization) is carried out the most frequently within the scope of the temperatures from 200ºC to 300ºC, in the pressure conditions similar to the atmospheric ones and in the inert environment. In the subject literature there are also other definitions of the torrefaction process, such as: roasting, slow and mild pyrolysis, high-temperature drying (Bergman et al., 2005; Kopczyński and Zuwała, 2013; van der Stelt et al., 2011).

The torrefaction products, depending on the physical state may be divided into three groups: solid, liquid and gas. The solid phase which constitutes the main product of the reaction contains the torrefaction product, ash and additionally sugar structures. The sas phase is composed of permanent gases (H_2, CO_2, CO, CH_4) as well as aromatic components, such as benzene and toluene. The liquid components (non-condensing) may be divided into three subgroups: water, organic (generated mainly during degassing) and lipid (remains after raw biomass) (Bergman et al., 2005).

During the torrefaction process, many chemical reactions take place in biomass, as a result of which the increase of the condensation and aromatization degree takes place, which translates into the change in mol relations O/C and H/C (Jinig et al., 2014; Sunil and Ajav, 2012). Relation of H/C may serve as an index of aromatization degree, whereas O/C relation constitutes index of carbonization degree (Jinig et al., 2014). It is commonly recognized that biochar has an element relation O/C below 0.4 and H/C below 0.6. Moreover, the content of the condensed aromatic groups, which increases during the process, known as black carbon, directly influences the increase of the biochar stability in the environment (Jinig et al., 2014; Sunil and Ajay, 2012).

Biochar and its utility values in agriculture

Biochar may be used in many fields. In agriculture it may be used as an organic fertilizer that decomposes for a long time, which positively influences the soil fertility, the amount of biogenic components, physical and water properties as well as biological properties (Galvez et al., 2012; Gołaszewski et al., 2013; Lehman et al., 2011; Mohan et al., 2014; Zheng et al., 2013).

The main function of biochar is regulation of dynamics of changes and circulation of C and N in soil (Galvez i in., 2012; Zheng i in., 2013), due to which it may impact the increase of the organic matter content. High content of stable fraction of organic carbon causes that biochar may take part in the biosequestration of carbon in soil (Mohan et al., 2014). As reservoir of carbon, which is mineralized slowly, it causes decrease of the greenhouse effect caused by excessive emission of the greenhouse gases, including CO_2 (Mohan et al., 2014). Taking into account that the average time of biochar decomposition in soil (MRT, Mean Residence Time) is estimated as approx. 1300-4000 years (Sunil and Ajay, 2012), it was assumed that through biochar, used on cultivation fields one may permanently depose 428 Gt C (Sunil and Ajay, 2012). Whereas a considerably small content of labile fraction, biochar which may be subject to fast decomposition, additionally influences the increase the amount of organic matter in soil (SOM, Soil Organic Matter) and the number of mineralized nutrients available for plants (Sunil and Ajay, 2012).

Biochar participates also in a biogeochemical cycle of nitrogen. The research proves that biochar addition influences the decrease of the nitrification level (decrease of NH_3 oxidization); moreover, it influences the increase of the number of the ammonification bacteria, whereas through stimulation of nitrogen immobilization influences the reduction of N_2O emission to atmosphere (Zheng et al., 2013). According to the research carried out by Ding et al. (2010) application 0.5% of biochar to the external layer of soil influenced the decrease of NH_4^+ leaching by 15.2%, through absorption of ammonium ions on the surface of biochar (Zheng et al. 2013). Reduced washing out of NO_3 – from soil after the application of biochar fertilization was also proved by Knowles et al. (2011). Similarly a positive impact on nitrogen management was proved in the research carried out by Nelissen et al. (2014), where limitation of N_2O emission by 52-84% and NO by 47-67% was reported.

A positive influence of the biocarbonization product is also reflected in the biological properties of soil, through the influence on the quality and quantity properties of the soil microflora (Galvez et al., 2012; Nelissen et al., 2014; Tang et al., 2013; Zheng et al., 2013). Due to the biocarbonization product properties, such as a big specific surface (approx. 400-800 $m^2 \cdot g^{-1}$) and a porous structure, good living conditions and development conditions for the soil microflora are created (Galvez et al., 2012; Sunil and Ajay, 2012). In the research carried out by Steiner et al. (2004) a considerable increase of the microbiological activity after the use of biochar fertilization was proved. It could be seen in both the increase of the amount of biomass of microorganisms, as well as the increase of the biodiversity of the soil microflora (which additionally may influence stability of the ecosystem and had a nature of protection against pathogenic microorganisms). The increased microbiological activity influences the raise of the rate of mineralization, and thus the increase of bioavailability of nutrients for plants (Sunil and Ajay, 2012).

Physical and chemical properties, such as a developed specific area and porosity positively influence not only the biological properties (microbiological) but also improvement of the chemical properties and water relations of soil. Through the increased water retention (improvement of water-air relations), indirectly influences the decrease of the level of leaching biogenic components along with soil solution. Biochar acts as a modification filter for the retention time and the flow of soil solution (Sunil and Ajay, 2012; Zheng et al., 2013). Moreover, a positive influence of biochar addition on the pH increase and total cation capacity (CEC) was proved and thus availability of nutrients for plants (Galvez et al., 2012; Nelissen et al., 2014; Tang et al., 2013; Zheng et al., 2013).

The biocarbonization product may be used not only on cultivated soils as a biofertilizer, but also may be used in the remediation process of polluted and reduced soils, inter alia through inactivation of polyaromatic hydrocarbon and heavy metals bioavailability (Jinig et al., 2014; Mohan et al., 2014; Tang et al., 2013;). As Mohan et al. (2014) state biochar may play a role of a sorbent of the toxic organic compounds, such as pesticides, polycyclic aromatic hydrocarbons and synthetic chloro- and phospohorus – organic compounds. The use of carbon as a toxic sorbent is also presented in Sun et al. (2011), who shows ability to remove the phenatren (Phen), bisphenol A (BPA) and estradiol (EE2) compounds from water. Moreover, the potential use of the biocarbonization product. Moreover, possible use of biocarbonization product for removal of non-organic pollution, due to high sorptive properties in relation to heavy metals such as Pb^{2+}, Cu^{2+}, Ni^{2+}, and Cd^{2+}, was proved by Inyang et al. (2012) and Han et al. (2013).

Biochar as biofuel

In the power industry, drying digestate limits humidity, which constitutes ballast during storing and transport and also during the combustion processes or co-combustion of the dehydrated digestate in a heating plant, heat and power station, power stations and other industrial facilities (Kopczyński and Zuwała, 2013; Liu et al., 2013). High biomass humidity influences not only the increase of the transport costs but also the decrease of energy concentration (lower energy density). A high level of the water content during storing favours the biodegradation processes of the organic matter and thus from the point of view of power industry – lowering energy value. Moreover, hydrated biomass creates favourable conditions for pathogenic microflora development, which is dangerous for human and animal health. Fresh or dried digestate is a problematic fuel also from the point of view of installation, influencing its faster exploitation, therefore also in the co-firing processes, participation of this type of biomass is admissible and it should constitute up to 10% (Kopczyński and Zuwała, 2013). It means that energy potential of the remains from biogas plant may be increased through biomass torrefaction, which next to the processes such as drying of briquetting or pelleting may determine the wider energy use (Kopczyński and Zuwała, 2013; Liu et al., 2013; Troy et al., 2013).

During the torrefaction process, the loss of mass takes place in biomass (decrease of humidity) and chemical energy of raw material. The obtained product of carbonification – torrefaction product characterizes with an increased uniformity of material, grinding susceptibility and energy density (concentration), obtains also a hydrophobic nature. As a result of loss of mainly oxygen and hydrogen, it resembles carbons with its physical and chemical properties (Kopczyński and Zuwała, 2013; van der Stelt et al., 2011). Parameters of the selected biochars as biofuels were presented in Table 2.

Table 2
Characteristics of biochars as biofuel. Designations of substrates used for biochar production and temperature of the process: 1. Solid fraction of the digestate from pig manure (600°), 2. Coconut fibre (220ºC), 3. Coconut fibre (250ºC), 4. Coconut fibre (300°C), 5. Digestate from corn silage (190ºC) 6. Digestate from corn silage (230ºC) 7. Digestate from corn silage (270ºC)

Parameter	Substrate						
	1	2	3	4	5	6	7
Volatile substances (% d.m.)	69.7	69.8	67.9	53.6	-	-	-
Ash (% d.m.)	22	6.2	5	4.3	11.45	10.68	13.1
Combined carbon (%)	8	24	27.1	42.1	-	-	-
Total carbon (% d.m.)	45.2	-	-	-	30.72	19.71	12.34
Higher calorific value ($kJ \cdot mol^{-1}$)	19.1	24.7	26.7	29.4	25.4	30.3	33.8
Energy density	-	1.34	1.45	1.6	-	-	-
Energy capacity (% d.m.)	-	76.67	65.7	65	-	-	-
The molar ratio H/C	1.37	-	-	-	1.37	1.17	1.13
The molar ratio O/C	-	-	-	-	0.39	0.21	0.12
Biochar yield	-	-	-	-	71.8	46.2	41.3

Source: Liu et al., 2013; Mumme et al., 2011; Troy et al., 2013

In the research carried out by Liu et al. (2013), Mumme et al. (2011) and van der Stelt et al. (2011) decrease of the product- torrefaction product efficiency of yield was proved. On the other hand, research prove that along with the increase of the process temperature, increase of the calorific value takes place and grindability of the torrificated biomass (Liu et al., 2013; Mumme et al., 2011; Troy et al., 2013). Moreover, with the decrease of the the molar ratio of hydrogen and carbon and oxygen and carbon (indexes of aromatization and carbonization degree) calorific value of torrefaction product increases ($MJ \cdot kg^{-1}$). Efficiency of biochar production is within 46-76%, whereas energy efficiency 77-90% (Kopczyński and Zuwała, 2013; Liu et al., 2013; Mumme et al., 2011; Troy et al., 2013).

Conclusion

Based on the literature review which was carried out, one may state that digestate mass may constitute a valuable substrate for biochar production.

Biochar due to its properties, may be used as soil improver, decomposing for a long time, which positively influences soil fertility, abundance in biogenic components and physical and water properties. Additionally, it may constitute an element of carbon biosequestration, thus contributing to the reduction of a greenhouse effect.

Use of biochar as biofuel through reduction of the waste amount and the increased participation of energy generated from the renewable sources, contribute to the decrease of the greenhouse gases emission. Additionally, the torrefaction process may constitute a stage of preconditioning (initial processing) before such processes as gasification and production of the 2nd generation biofuels.

To sum up, one should state that the process of torrefaction of the digestate and the application dimension of biochar are relatively weakly researched, which opens new areas for the research and development works on the possible use and meaning of biochar in the process of carbon biosequestration.

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BIOWĘGIEL Z MASY POFERMENTACYJNEJ BIOGAZOWNI ROLNICZEJ JAKO PRODUKT ENERGETYCZNY I POLEPSZACZ GLEB

Streszczenie. Masa pofermentacyjna, jako biodegradowalny odpad biogazowni rolniczej może podlegać zagospodarowaniu bezpośredniemu jako nawóz lub też, po separacji fazy stałej i ciekłej – faza stała może być poddana termochemicznej transformacji do biowęgla. Biowęgiel jest karbonizatem o wysokiej koncentracji węgla i względnie małej podatności na rozkład, pozyskany z różnego rodzaju odpadów organicznych (International Biochar Initiative). Uwęglenie biomasy następuje w procesie toryfikacji w temperaturze od 200ºC do 320ºC. Skład chemiczny oraz właściwości użytkowe biowęgla uzależnione są od rodzaju substratu oraz parametrów procesu. Pozyskiwany z odpadów biodegradowalnych może być elementem biosekwestracji węgla i wykorzystany jako biopaliwo, zaś w rolnictwie – jako długo rozkładający się polepszacz gleby pozytywnie wpływający na żyzność gleby, zasobność w składniki biogenne oraz właściwości fizyczne i wodne. W pracy przedstawiono charakterystykę procesu toryfikacji, produkty procesu oraz walory użytkowe biowęgla z punktu widzenia wartości energetycznej i rolniczej.

Słowa kluczowe: biowęgiel, toryfikacja, bionawóz, biosekwestracja, biopaliwo