Properties of Biochar Produced by Slow Pyrolysis of Stabilized Sewage Sludge.

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2017

PROPERTIES OF BIOCHAR PRODUCED BY SLOW PYROLYSIS OF STABILIZED SEWAGE SLUDGE

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ABSTRACT: Direct application of stabilized sewage sludge on agricultural soil is currently a big concern because of its significant content of detectable organic micropollutants. Proper sludge treatment should suppress its negative features and produce material suitable for soil amendment. Slow pyrolysis is one of such treatments. We studied the influence of pyrolysis temperature (400–800 °C) on material and energy balances and on elementary composition of the pyrolysis solid residue (biochar). Pyrolysis at higher temperatures resulted in lesser biochar yield and promoted gas yield. The macronutrient content of biochar increased with an increase in pyrolysis temperature (except for nitrogen).
Keywords: sewage sludge, biochar, pyrolysis, batch reactor, energy balance, mass balance

1 INTRODUCTION

Sewage sludge is an inevitable waste stream formed during wastewater treatment. Its direct use in agriculture has been one of the conventional methods for its disposal [1], however, it is a big concern nowadays because of increasing content of detectable organic (micro)pollutants such as POPs, pesticides, detergent residues, pharmaceuticals, antibiotics, and various compounds with endocrine-disrupting potential [2]. Prior to its application on the soil, the sludge should be treated to suppress its negative features, for example by a slow pyrolysis process aimed to produce biochar, which is a safe material with enhanced agronomic properties.

Pyrolysis is thermal decomposition of organic material at oxygen-free atmosphere. Pyrolysis products are generally divided into gas, liquid (oil) and solid residue (biochar) [3]. The process is endothermic and significant amount of heat must be provided to the process. The heat can be fully or partially provided by combustion of the oil and gas products.

With regard to relatively high content of nutrients (N, P, K, Ca, Mg), sewage sludge is potentially suitable material for production of biochar, which can partially substitute the soil fertilizers. In addition, the sludge derived biochar has significantly lower estrogenic activity [4], supposing that the thermal treatment not only successfully destroys pathogens but reduces amount of various organic (micro)pollutants as well.

In general, application of biochar to agricultural soil is advantageous also for some other reasons: biochar improves water holding capacity of the soil and it slows down the release of nutrients and prevents their fast leaching into groundwater [5, 6].

To study the influence of pyrolysis temperature on material and energy balances and on elementary composition of biochar, we performed sewage sludge pyrolysis in closed batch laboratory reactor.

2 MATERIALS AND METHODS

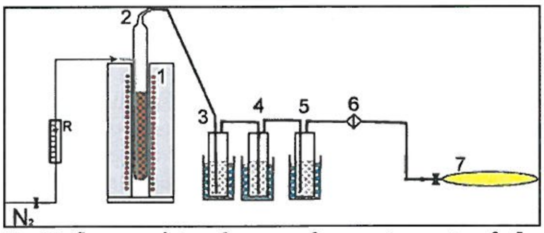
Sewage sludge used for the experiments was obtained from wastewater treatment plant with mesophilic anaerobic digestion of the sludge. The sludge was dried (final moisture content W≈9 wt. %). ground and sieved (particles size used for the experiments 0.5–2 mm) before the experiments. Proximate analysis, ultimate analysis and calorific values of the sludge used for experiments are summarized in the Table I.

Table I: Basic characteristics of the sewage sludge

Proximate analysis		
Ash, A^d	mass %	44.6
Volatiles, V^{daf}	mass %	87.3
Fixed Carbon, FC^{daf}	mass %	12.7
Calorific value		
Higher heating value, HHV^d	MJ kg^{-1}	12.8
Lower heating value, LHV^d	MJ kg^{-1}	11.8
Ultimate analysis		
C^d	mass %	28.9
H^d	mass %	4.39
N^d	mass %	4.10
S^d	mass %	1.75
Ca^d	mass %	4.46
K^d	mass %	0.607
Mg^d	mass %	0.710
P^d	mass %	3.55

Biochar was prepared by pyrolysis of approximately 60 g of the sludge in a quartz batch reactor at 400, 500, 600, 700 and 800 °C. The reactor was placed into hot furnace and the pyrolysis lasted till the end of the release of primary pyrolysis products (gas and oil), after which the reactor was removed from the furnace and cooled under oxygen-free atmosphere. Extraction of primary pyrolysis products from the reactor and inert atmosphere were secured and maintained by supplying nitrogen to the bottom part of the reactor at a flow rate of 150 ml/min through all the experiment and the subsequent cooling. Arrangement of the pyrolysis apparatus is schematically depicted in Fig. 1.

The primary pyrolysis products (diluted by nitrogen) flowed through 3 collectors (cooled in ice baths) for condensable part (oil + water) collection, then through porous filter and finally non-condensable (gas) part was collected in Tedlar bags. The mass of biochar and condensable products was obtained by measuring the weights of the apparatus components before and after the experiments. The mass of water and organic oil fractions were individually measured after their separation from the first oil collector. The mass and heating value of gas were calculated from its volume and its composition determined by GC-TCD/FID analyses. Heating values of biochar and oil were measured calorimetrically.



R - N_2 flow regulator, 1 - oven, 2 - quartz reactor, 3–5 - tar (oil) collectors, 6 - porous filter, 7 - tedlar bag

Figure 1: Scheme of the pyrolysis apparatus

3 RESULTS

Both mass and energy balances are basic and important characteristics defining the quality of pyrolysis process. Due to endothermic character of pyrolysis, significant amount of heat must be provided to the process. To make the process more energy-self-sufficient, the necessary heat can be obtained by combustion of the primary pyrolysis products. Therefore, the knowledge of mass and energy balances is important for proper construction and operation of the pyrolysis facility.

3.1 Mass balance

The mass balance of the sludge pyrolysis at different temperatures is displayed in Fig. 2. The biochar mass yield continuously decreased from 61 mass % (400 °C) to 45 mass % (800 °C) due to the release of more stable species at higher temperatures. Consequently, the gas mass yield continuously increased with the increase in the temperature. The oil mass yield firstly increased, however, it decreased at temperatures over 500 °C due to more intensive cracking of the oil vapors released from the sludge, which resulted in steeper increase in the gas mass yield.

The overall sum of the mass yields of pyrolysis products was below 100 %. The partial loss of mass can be attributed to two main reasons: 1) Aerosol particles penetrated the porous filter, therefore they were not weighed. The presumption about the penetration of aerosols particles through the porous filter is based on a visual inspection of the Tedlar bags which were connected after the filter. 2) Nitrogen content of the sludge is significantly high (Table I), however, the nitrogen released from the sludge was not calculated because the mass yield of gas was calculated from nitrogen balance (nitrogen as carrier gas).

3.2 Energy balance

Energy balance describes the amount of energy in individual products that are produced by pyrolysis of reference amount of the sewage sludge. The yields of energy transformed to gas, oil and biochar products, expressed as % of energy in dry sewage sludge, are displayed in Fig. 3.

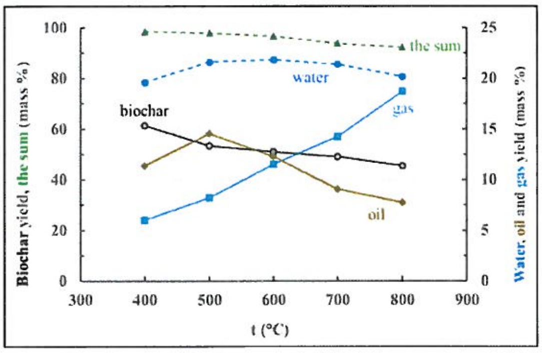


Figure 2: Mass balance of the sludge pyrolysis at different temperatures

Due to the fact that the energy yield is strongly dependent on the mass yield, the trends of the dependence on temperature are the same for both yields. Nevertheless, the important fact is that the sum of energy transformed to gas and oil products (which is essential for sustainability of pyrolysis facility) increased up to 500 °C and it leveled over 50 % at temperatures above 500 °C. Such amount of energy extractable by the combustion of these products should provide enough heat to cover the heat demands of the pyrolysis of sewage sludge with moisture content up to 15 %.

The loss of energy and uncertainty in the measurement and calculation are due to the same reasons as in the case of the mass balance. Moreover, part of the oil energy is lost in the water fraction of condensable part of the primary pyrolysis gas because some organic compounds remained dissolved in the water and were not separated.

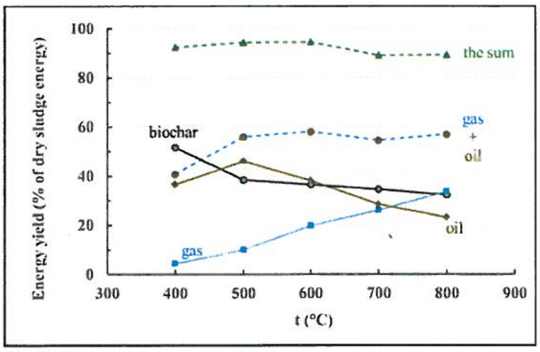


Figure 3: Energy balance of the sludge pyrolysis at different temperatures

3.3 Influence of pyrolysis temperature on biochar composition

The comparison of elementary composition and ash content of dry sewage sludge and biochars prepared at different temperatures is displayed in Table II.

The ash content of biochar increased with an increase in pyrolysis temperature due to volatilization of more stable species of the sludge at greater temperatures. Consequently, the hydrogen and nitrogen content decreased significantly in biochar prepared at 400 °C and steeply decreased from 1.7 to 0.25 mass % and from 3.1 to 1.0 mass % respectively in biochars prepared at 400 and 800 °C.

Unlike hydrogen and nitrogen, elements such as P, K, Ca and Mg are mostly bound to the ash, therefore their content increased significantly in biochar prepared at 400 °C and gradually increased in biochars prepared at higher pyrolysis temperatures.

Table II: Elementary composition of dry sewage sludge and biochars prepared at different pyrolysis temperatures

		Dry sludge	Pyrolysis temperature (°C)				
			400	500	600	700	800
Ash	mass %	45	67	72	73	76	78
C	mass %	29	24	21	21	21	21
H	mass %	4.4	1.7	1.1	0.72	0.43	0.25
N	mass %	4.1	3.1	2.7	2.4	1.6	1.0
S	mass %	1.8	0.49	0.44	0.51	0.51	0.60
Ca	mass %	4.5	7.0	7.5	7.4	7.8	7.9
K	mass %	0.61	0.86	0.99	0.94	0.99	1.0
Mg	mass %	0.71	1.2	1.3	1.3	1.3	1.4
P	mass %	3.6	6.5	7.0	7.1	7.4	7.7

4 CONCLUSIONS

Sewage sludge from a wastewater treatment plant with mesophilic anaerobic digestion of the sludge was pyrolyzed in a batch laboratory reactor at temperatures 400, 500, 600, 700 and 800 °C under inert nitrogen atmosphere. With an increase in pyrolysis temperature: 1) biochar yield decreased, 2) gas yield increased, 3) oil yield firstly increased then decreased and 4) macronutrient content of biochar increased (except for N).

Due to relatively high nitrogen content of the sludge leading to noticeable uncertainty in determination of mass and energy of the gas, pyrolysis experiments will be performed in the batch reactor under inert helium atmosphere. A set of experiments will be performed as well in a continuous through flow reactor to simulate real pyrolysis facility without utilization of inert carrier gas.

5 REFERENCES

[1] E. Agrofioti, G. Bouras, D. Kalderis, E. Diamadopoulos; Biochar production by sewage sludge pyrolysis. Journal of Analytical and Applied Pyrolysis, 101 (2013), 72–78.

[2] S.R. Smith; Organic Contaminants in Sewage Sludge (Biosolids) and Their Significance for Agricultural Recycling. Philosophical Transactions of the Royal Society A, 367 (2009), 4005–4041.

[3] A.M. Ji, Y. Cui, H.Y. Liu, Z.G. Qian;A Review on Pyrolysis Technology and Characters of Products from Sewage Sludge, Applied Mechanics and Materials, Vols. 295–298 (2013), 1419–1424.

[4] T.C. Hoffman, D.H. Zitomer, P.J. McNamara; Pyrolysis of wastewater biosolids significantly reduces estrogenicity. Journal of Hazardous Materials, 317 (2016), 579–584.

[5] D.A. Laird, P. Fleming, D.D. Davis, R. Horton, B. Wang, D.L. Karlen; Impact of biochar amendments on the quality of a typical Midwestern agricultural soil. Geoderma, 158 (2010), 443–449.

[6] D.A. Beck, G.R. Johnson, G.A. Spolek; Amending greenroof soil with biochar to affect runoff water quantity and quality. Environmental Pollution, 159 (2011), 2111–2118.

6 ACKNOWLEDGEMENTS

This research was financially supported from project AV 21 - Efficient energy transformation and storage, specific university research (MSMT No 20-SVV/2017) and IGA ICPF CAS 2017.