BATCH REACTOR PYROLYSIS OF STABILIZED SEWAGE SLUDGE: PRODUCT ANALYSIS AND SULPHUR BALANCE

JAROSLAV MOŠKO[1,2,*], MICHAEL POHOŘELÝ[1,2], SIARHEI SKOBLIA[2], ZDENĚK BEŇO[2], OLGA BIČÁKOVÁ[3], ŠÁRKA VÁCLAVKOVÁ[1], MICHAL ŠYC[1] & KAREL SVOBODA[1]
[1]Institute of Chemical Process Fundamentals of the Czech Academy of Sciences, Czech Republic
[2]Department of Power Engineering & Department of Gaseous and Solid Fuels and Air Protection, University of Chemistry and Technology Prague, Czech Republic
[3]Institute of Rock Structure and Mechanics of the Czech Academy of Sciences, Czech Republic

ABSTRACT

Prior to sewage sludge application to agricultural soil, the sludge should be treated appropriately to suppress its negative features like content of microorganic pollutants or leaching heavy metals. Pyrolysis has been investigated as one way of producing sewage sludge-derived biochar (solid pyrolysis residue) which is stable and less toxic than sewage sludge. A significant amount of heat must be provided to the pyrolysis process due to its endothermic character. To make the process economically and energy efficient, the necessary heat can be obtained by the combustion of primary pyrolysis products (pyrolysis oil and gas), however in the case of sewage sludge, attention must be paid to the resulting gaseous pollutants due to high nitrogen and sulphur content. Slow pyrolysis of stabilized sewage sludge in inert helium atmosphere was performed at temperatures 400–800°C in order to examine the influence of pyrolysis temperature on the properties of pyrolysis products and sulphur distribution amongst these products. Pyrolysis at higher temperatures resulted in lesser biochar yield and promoted gas yield. At temperatures of 500°C and higher, over 50% of energy bound in the input sewage sludge was transformed to liquid and gas products. Finally, the effect of pyrolysis temperature on sulphur distribution amongst pyrolysis products was only marginal.

Keywords: sewage sludge, pyrolysis, sludge-derived biochar, mass balance, energy balance, sulphur balance, sulphur species.

1 INTRODUCTION

Disposal of sewage sludge on agricultural soil is a reasonable solution due to its organic matter content, high nitrogen content, and considerable content of phosphorus which has been listed on the List of Critical Raw Materials for the EU in the form of phosphorus and phosphate rock [1]. On the other hand, such sludge utilization is challenged because of pollutants contained in the sludge, lately the contents of pathogens, persistent organic pollutants and residues from various pharmaceuticals and personal care products are of concern [2].

Pyrolysis of the sludge may be considered as a suitable process for the removal of organic pollutants. In addition, thermal treatment significantly reduces the amount of the sludge [3], [4] and the solid pyrolysis residue (sludge-derived biochar /SDBC/) can be with advantage applied on the soil [5]. Due to the endothermic nature of pyrolysis, a significant amount of heat must be provided to the process, which can be fully or partially provided by the combustion of other pyrolysis products – pyrolysis gas and oil. However, combustion of those products may result in flue gas containing SO_2 originating from the combustion of sulphur containing compounds released from the sludge.

*ORCID: https://orcid.org/0000-0002-4371-6661

www.witpress.com, ISSN 1743-3541 (on-line)
doi:10.2495/WM180331

Sulphur in sewage sludge is present in both organic and inorganic forms (sulphates, sulphides). The reduction of sulphates and decomposition of organic sulphur leads to the formation of H_2S, CH_3SH, COS, CS_2 which are unpleasant compounds and can be easily converted to SO_2 during combustion [6], [7]. Additionally, transformation of sulphur in the sludge was observed by XPS analysis, suggesting that a part of organic sulphur may be transformed into inorganic sulphide and sulphate during pyrolysis [8].

To study the influence of pyrolysis temperature on material and energy balances, biochar elementary composition, and sulphur speciation in pyrolysis gas and biochar, we performed sewage sludge pyrolysis in closed batch/fixed bed laboratory reactor using helium as carrier gas.

2 MATERIALS AND METHODS

2.1 Stabilized sewage sludge

Stabilized sewage sludge was obtained from municipal wastewater treatment plant with mesophilic anaerobic digestion of the sludge. The sludge was air-dried (average moisture content within all experimental runs: W≈9 wt.%), ground, and sieved prior to experiments. Particles size used for the experiments was 0.5–2 mm. Following tables describe main properties of the sludge (Table 1) and the composition of the sludge ash (Table 2).

2.2 Sewage sludge pyrolysis

Sludge-derived biochar was prepared by pyrolysis of approximately 100 g of the sludge in a quartz batch reactor at 400, 500, 600, 700 and 800°C. Arrangement of the pyrolysis apparatus is schematically described in Fig. 1. The reactor (2) was placed into hot furnace (1) preheated to pyrolysis temperature and the experiment ended when the release of primary pyrolysis products (gas and condensate) stopped. Subsequently the reactor was removed from the furnace and cooled under oxygen-free atmosphere. The exhaust of primary pyrolysis products from the reactor and inert atmosphere were secured and maintained by supplying helium to the bottom of the reactor at a flow rate of 150 ml min^{-1}.

Table 1: Proximate analysis, ultimate analysis and calorific values of the sludge.

Proximate analysis		
Ash, A^d	wt.%	43.3
Volatiles, V^{daf}	wt.%	86.8
Fixed carbon, FC^{daf}	wt.%	13.2
Calorific values		
Higher heating value, HHV^d	MJ kg^{-1}	12.7
Lower heating value, LHV^d	MJ kg^{-1}	11.8
Ultimate analysis		
C^d	wt.%	28.8
H^d	wt.%	4.20
N^d	wt.%	4.22
O^d	wt.%	18.4
S^d	wt.%	1.10

Table 2: Sewage sludge ash speciation determined by XRF analysis.

Species	wt.%
Al_2O_3	16.0
CaO	14.0
Fe_2O_3	13.9
K_2O	1.64
MgO	2.64
P_2O_5	18.2
SiO_2	28.5
Sum	94.9

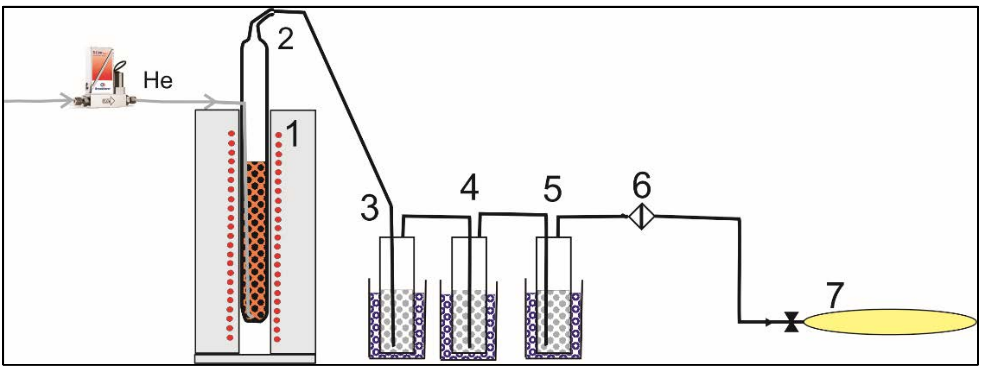

Figure 1: Scheme of the pyrolysis apparatus: 1 – oven; 2 – quartz reactor; 3–5 ice water cooled impingers; 6 – porous filter; 7 – tedlar bag.

Primary pyrolysis products (diluted by carrier gas–helium) flowed through 3 impingers (3–5) cooled in ice baths to collect condensable vapours, then through porous filter (6) and finally permanent gases were collected in Tedlar bags (7).

The mass of biochar and condensable products was obtained by measuring the masses of apparatus components before and after the experiments. The mass of water and organic oil fractions were individually measured after their separation from the first impinger. The mass and heating value of gas were calculated from gas volume and its composition.

2.3 Analytical tools

Moisture content (W) of the sludge was determined according to the Czech/European standard ČSN EN 15414-3, the sludge was dried in analytical dryer to constant weight at temperature 105±2°C. The ash content (A) of the sludge and biochars was established according to the standard ČSN EN 15403, the sample was burned in an open crucible in an oven to constant weight at temperature 550±10°C. The volatile content (V) of the sludge and biochars was established according to the standard ČSN EN 15402, sample was gasified in a closed crucible in an oven for 7 minutes at temperature 900±10°C. Higher heating value (HHV) of the sludge, biochars, and condensates was determined according to the standard

www.witpress.com, ISSN 1743-3541 (on-line)

ČSN EN 15400 by means of the calorimeter IKA C 2000 and lower heating value (LHV) was calculated according to the same standard. The ultimate analysis of sludge and biochars was performed in Flash EA 1112 device in CHNS/O configuration where content of C, H, and N was measured by analysis of gaseous products from combustion by oxygen (CO_2, H_2O and N_2) in thermal conductivity detector. Total sulphur content and sulphur speciation in the sludge and biochar samples were determined according to Czech/International standards ČSN ISO 351 and ČSN ISO 157 respectively. The content of oxygen (O) was calculated by difference.

Composition of the sludge ash was determined by X-Ray fluorescence (XRF) on device ARL 9400 XL (Thermo ARL, Switzerland).

Permanent gases (composition of gas in Tedlar bag) were determined by GC-TCD/FID analysis. The composition of gaseous pyrolysis products was then calculated without including carrier gas. Content of sulphur containing compounds in the gases was determined by GC-SCD analysis and is expressed as concentration of elementary sulphur.

3 RESULTS

3.1 Mass and energy balances

Mass and energy balances are integral and important characteristics defining the quality of pyrolysis process and pyrolysis products. To make the process partially or fully energy-self-sufficient, the necessary heat can be obtained by combustion of primary pyrolysis products. Therefore, the knowledge of mass and energy balances is important for proper construction and operation of the pyrolysis facility. In addition, mass balance is the first indicator of good or bad biochar quality.

3.1.1 Mass balance

Due to enhanced volatilization of the sludge at elevated temperatures, the biochar yield decreased considerably from 61.7% to 52.9% when temperature increased from 400 to 500°C. With further increase in pyrolysis temperature ($T_{pyrolysis}$), biochar yield decreased slightly to 46.3% at 800°C (Fig. 2). As anticipated, the release of sludge matter resulted in increase in primary pyrolysis gas amount. Primary pyrolysis gas consists of condensable vapours (after condensation divided into water liquid fraction and pyrolysis oil) and permanent gases – pyrolysis gas. When pyrolysis temperature increased, there was observed a slight increase in pyrolysis oil yield followed by slight decrease, with maximum yield at pyrolysis temperature 600°C – yield 14.1%. The yield of pyrolysis gas increased from 7% at $T_{pyrolysis}$= 400°C to 16.2% at $T_{pyrolysis}$= 800°C. The overall sum of product yields was satisfactory and ranged between 96–99%. The loss of mass is primarily attributed to penetration of aerosol particles through porous filter.

3.1.2 Energy balance

Energy balance (Fig. 3) describes the absolute amount of energy in individual products related to energy contained in input sludge. Consequently, the product energy yields are strongly dependent on products mass yields, therefore the dependence of product energy yield on pyrolysis temperature is very likely the same as the dependence of product mass yield. The important fact is that the sum of energy transformed to pyrolysis gas and oil products (which is essential for sustainability of pyrolysis facility) levelled over 50% at temperatures above 500°C. Combustion of these products should provide enough heat to cover process demands for pyrolysis of sewage sludge with moisture content up to 15%.

www.witpress.com, ISSN 1743-3541 (on-line)

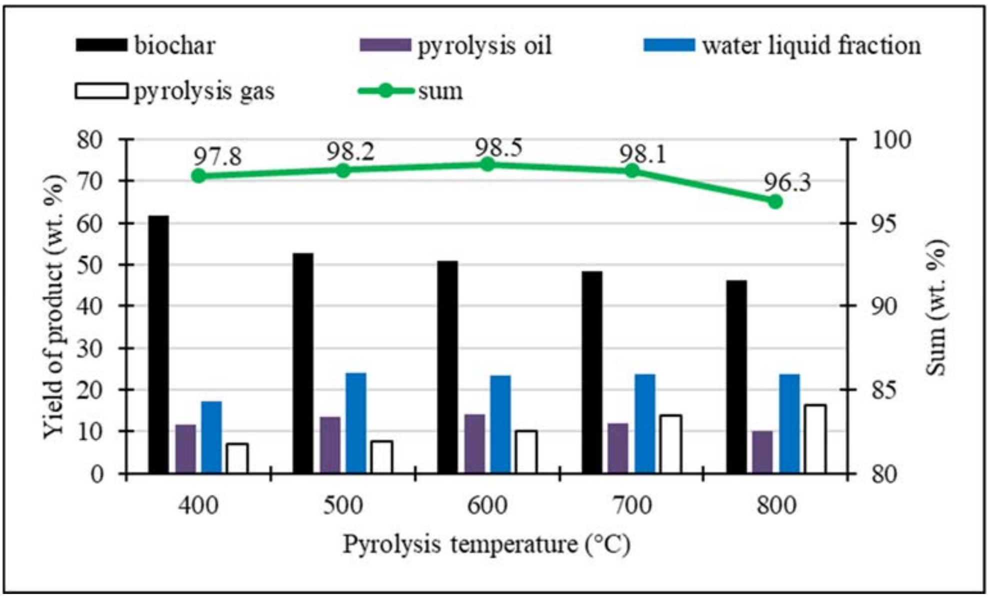

Figure 2: Mass balance of pyrolysis.

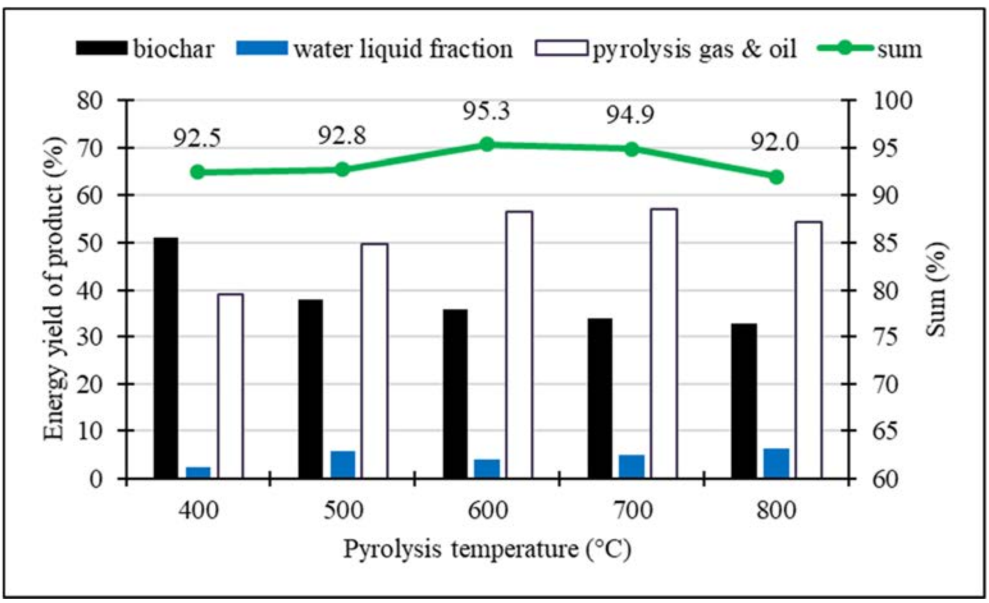

Figure 3: Energy balance of pyrolysis.

3.2 Pyrolysis gas composition

The composition of pyrolysis gas (Fig. 4) is strongly dependent on pyrolysis temperature because of the influence of temperature on release of volatiles, cracking of vapours, and water gas reactions in homogeneous and heterogeneous phase. Increase in gas energy yield suggests the increase in combustible gases content in pyrolysis gas. That was confirmed by significant decrease in CO_2 gas content from 62.3 vol.% ($T_{pyrolysis}$= 400°C) to 23.6 vol.% ($T_{pyrolysis}$= 800°C). On the other hand, content of H_2 and CO increased significantly from 10 to 27.9 vol.% and 8.2 to 24.5 vol.%, respectively. Methane content increased slightly from 7.8 vol.% ($T_{pyrolysis}$= 400°C) to 12.7 vol.% ($T_{pyrolysis}$= 600°C) and then decreased to 10.7 vol.% ($T_{pyrolysis}$= 800°C).

The main sulphur containing compounds in the pyrolysis gas (Table 3) were hydrogen sulphide (H_2S), methanethiol (CH_3SH), carbonyl sulphide (COS) and carbon disulphide (CS_2). Concentration of these compounds decreased significantly as pyrolysis temperature increased from 400 to 800°C, which can be attributed mostly to dilution as the result of increase in gas yield.

3.3 Biochar properties

The ash content of biochar (Table 4) increased with an increase in pyrolysis temperature due to volatilization of more stable species of the sludge at higher temperatures. It may as well be supposed that valuable elements (P, K, Ca and Mg) bound preferably to mineral/ash part will also be concentrated in biochars to greater extent at higher pyrolysis temperatures. On the other hand, content of elements bound mostly to organic matter, hydrogen and nitrogen, decreased steeply from 1.6 to 0.3 wt.% and 3.0 to 0.9 wt.% respectively in biochars prepared at 400 and 800°C. Carbon content slightly decreased with an increase in pyrolysis

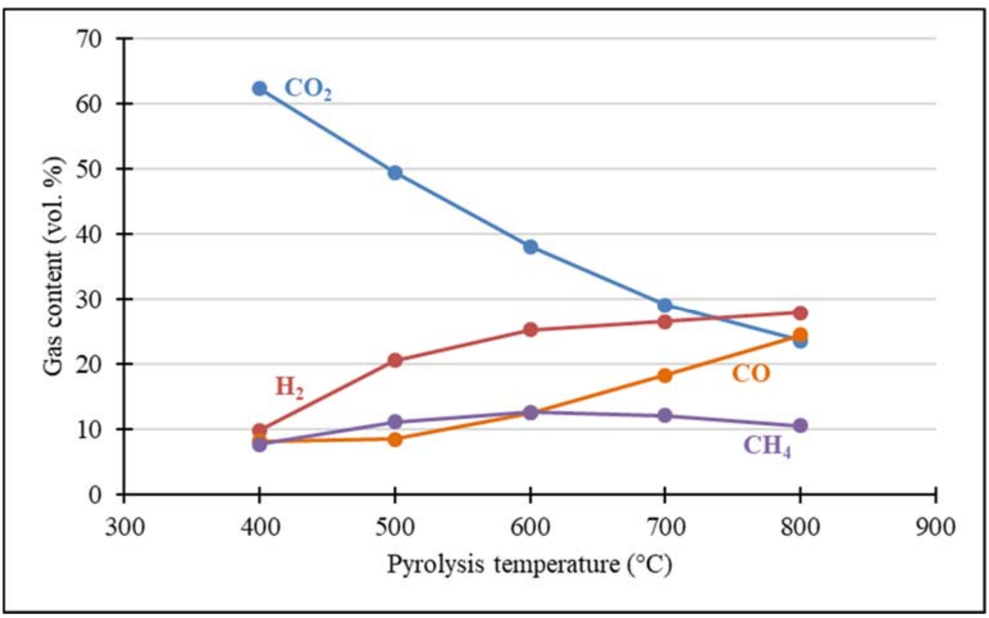

Figure 4: Major components in pyrolysis gas.

Table 3: Sulphur species in pyrolysis gas – expressed as grams of sulphur per normal cubic meter of pyrolysis gas.

$T_{pyrolysis}$	°C	400	500	600	700	800
H_2S	g m^{-3}	6.9	4.3	5.3	2.5	2.1
COS	g m^{-3}	1.9	1.1	1.2	0.8	0.7
CH_3SH	g m^{-3}	6.6	3.7	4.2	1.8	1.6
CS_2	g m^{-3}	0.28	0.19	0.15	0.092	0.072
Other	g m^{-3}	2.6	1.2	1.0	0.57	0.29
Sum	g m^{-3}	18	10.5	11.9	5.7	4.7

Table 4: Biochar ultimate analysis, ash content and calorific value.

$T_{pyrolysis}$	C^d	H^d	N^d	S^d	O^d	A^d	HHV
°C	wt.%						MJ kg^{-1}
400	23.1	1.62	3.04	0.76	3.59	67.88	9.49
500	21.4	1.04	2.66	0.81	1.40	72.65	8.23
600	20.5	0.716	2.26	0.77	–	75.8	8.04
700	19.3	0.497	1.55	0.85	–	77.8	8.01
800	17.2	0.310	0.939	0.84	–	80.8	8.10

Table 5: Sulphur speciation in sewage sludge and the sludge-derived biochars.

$T_{pyrolysis}$	$S^d_{sulphate}$	$S^d_{organic}$	S^d_{pyrite}	$S^d_{sulphide}$
°C	wt.%			
Sewage sludge	0.45	0.55	0.10	–
400	0.14	0.47	0.10	0.05
500	< 0.05	0.67	< 0.05	0.09
600	< 0.05	0.62	< 0.05	0.07
700	< 0.05	0.43	< 0.05	0.40
800	< 0.05	0.21	< 0.05	0.60

temperature and the content of sulphur was levelling which suggests small effect of pyrolysis temperature on total sulphur content in sludge-derived biochar.

The determination of sulphur species – organic-S, sulphate-S, pyrite-S, sulphide-S – in the sludge and biochars (Table 5) suggests a strong effect of pyrolysis temperature on sulphur speciation in biochars. There was obvious decrease in sulphate-S content after sludge pyrolysis. At first, the organic-S content slightly increases with pyrolysis temperature, up to 600°C, however at higher temperatures, the content decreases significantly. Pyrite-S content decreased extensively when pyrolysis temperature increased from 400 to 500°C and the content of sulphide-S increased when pyrolysis temperature increased, especially at pyrolysis temperature 700 and 800°C.

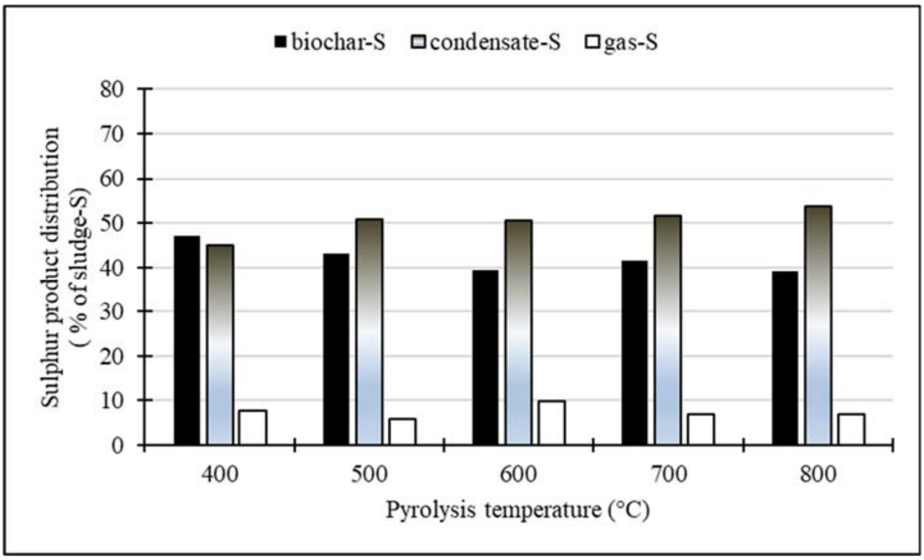

Figure 5: Sulphur distribution amongst pyrolysis products.

3.4 Sulphur balance

Sulphur balance (Fig. 5) was determined according to measurements of total sulphur content in sewage sludge, biochars and sulphur content in pyrolysis gas. The sulphur content in condensate (water liquid fraction and pyrolysis oil) was calculated by difference because of the difficulties of its measurement. A minor decrease in biochar sulphur content was observed when pyrolysis temperature increased from 400 to 800°C. In addition, the increase in pyrolysis temperature barely influenced the distribution of sulphur amongst gas and condensate. We may conclude that, unlike sulphur speciation, the distribution of sulphur contained in stabilized sewage sludge amongst pyrolysis products is marginally dependent on pyrolysis temperature.

4 CONCLUSIONS

Sewage sludge from a wastewater treatment plant with mesophilic anaerobic digestion of the sludge was pyrolyzed in a batch (fixed bed) laboratory reactor at temperatures 400, 500, 600, 700 and 800°C under inert helium atmosphere. With an increase in pyrolysis temperature: 1) sludge-derived biochar yield decreased, 2) gas yield increased and 3) oil yield firstly increased then decreased. The main sulphur containing compounds in pyrolysis gas were hydrogen sulphide (H_2S), methanethiol (CH_3SH), carbonyl sulphide (COS), and carbon disulphide (CS_2) and their concentration decreased significantly due to dilution effect when pyrolysis temperature increased from 400 to 800°C and the effect of pyrolysis temperature on sulphur distribution amongst pyrolysis products was marginal.

ACKNOWLEDGEMENTS

Financial support from Technology Agency of the Czech Republic – project TH03020119, Ministry of Agriculture of the Czech Republic – project QK1820175, AV 21 – Efficient energy transformation and storage, and specific university research MSMT No 20-SVV/2018.

REFERENCES

[1] Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions on the 2017 list of Critical Raw Materials for the EU; European Commission, COM(2017) 490 final.
http://eur-lex.europa.eu/legal-content/en/ALL/?uri=CELEX:52017DC0490.
Accessed on: 10 Apr. 2018.

[2] vom Eyser, C., Palmu, K., Otterpohl, R., Schmidt, T.C. & Tuerk, J., Determination of pharmaceuticals in sewage sludge and biochar from hydrothermal carbonization using different quantification approaches and matrix effect studies. *Analytical and Bioanalytical Chemistry*, **407**(3), pp. 821–830, 2015.
DOI: 10.1007/s00216-014-8068-1.

[3] Zhang, L. & Zhang, J., Biochar from sewage sludge: preparation, characterization and ammonia-phosphorus capture. *Advanced Materials Research*, **830**, pp. 473–476, 2014. DOI: 10.4028/www.scientific.net/amr.830.473.

[4] Agrafioti, E., Bouras, G., Kalderis, D. & Diamadopoulos, E., Biochar production by sewage sludge pyrolysis. *Journal of Analytical and Applied Pyrolysis*, **101**, pp. 72–78, 2013. DOI: 10.1016/j.jaap.2013.02.010.

[5] Faria, W.M., de Figueiredo, C.C., Coser, T.R., Vale, A.T. & Schneider, B.G., Is sewage sludge biochar capable of replacing inorganic fertilizers for corn production? Evidence from a two-year field experiment. *Archives of Agronomy and Soil Science*, **64**(4), pp. 505–519, 2018. DOI: 10.1080/03650340.2017.1360488.

[6] Shuai, L. et al., Release of organic sulfur as sulfur-containing gases during low temperature pyrolysis of sewage sludge. *Proceedings of the Combustion Institute*, **35**(3), pp. 2767–2775, 2015. DOI: 10.1016/j.proci.2014.06.055.

[7] Zhang, J., Zuo, W., Tian, Y., Chen, L., Yin, L. & Zhang, J., Sulfur transformation during microwave and conventional pyrolysis of sewage sludge. *Environmental Science & Technology*, **51**(1), pp. 709–717, 2017. DOI: 10.1021/acs.est.6b03784.

[8] Shan, C. et al., Effect of alkali addition on sulfur transformation during low temperature pyrolysis of sewage sludge. *Proceedings of the Combustion Institute*, **36**(2), pp. 2253–2261, 2017. DOI: 10.1016/j.proci.2016.06.124.

www.witpress.com, ISSN 1743-3541 (on-line)