

Pyrolysis of sewage sludge to obtain valuable products

**Szabina TOMASEK^a, Norbert MISKOLCZI^a, Csaba FÁYKÖD^b,
Andrea SOMOGYI^c**

^aFaculty of Engineering, Research Centre of Biochemical, Environmental and Chemical Engineering, Department of MOL Hydrocarbon and Coal Processing, University of Pannonia, Egyetem u. 10, H-8200, Veszprém, Hungary

^bFelső-Bacska Storage Windpark Ltd.,

^cSolver Unio Ltd.,

e-mail: tomasek.szabina@mk.uni-pannon.hu

Abstract

This paper focuses to pyrolysis of different sourced sewage sludge in a scaled-up semi-batch reactor at temperatures of 300 and 500°C. It was found that both the temperature and raw material composition had a significant effect on the product yields and properties. The highest gas and synthesis gas yield was observed in pyrolysis of distillery sewage sludge at 500°C, while composition of chicken manure favored for the formation of bio-oil (9.8 and 17.1%). The gas product was characterized by H₂/CO ratios up to 0.6; therefore further quality improvement is needed prior to use for synthesis. The bio-oil (5.2 – 17.1%) contained significant amount of oxygenated compounds, but after hydrogenation it is suitable to substitute the conventional fuels. During the pyrolysis the elemental composition of char (22.8 – 71.4%) has also changed due to carbonization and removal of functional groups.

Keywords: sewage sludge, pyrolysis, synthesis gas, bio-oil, bio-char production

Introduction

The increasing in sewage sludge production necessitates the introduction of more feasible processes to reduce the socio-economic and environmental problems associated with its current treatment. In terms of dry matter, nearly 23 million tons of municipal sewage sludge is generated annually¹. Sewage sludge contains proteins, carbohydrates, lipids or fats, organic and inorganic compounds and various harmful materials such as bacteria, viruses, dioxins and heavy metals². Nonetheless, in Bosnia and Herzegovina, Croatia, Romania, Serbia and Turkey landfilling is the most widely used sewage sludge handling method. In Bulgaria, Czech Republic, Ireland or Norway, the agricultural utilization is the mostly used method for sewage sludge treating, meanwhile that of the composting in the Baltic countries, Slovakia, Luxembourg or Hungary³. The main disadvantage of the current methods is that they can significantly increase the emission of nitrogen, phosphorous, heavy metals and various pathogens into the environment⁴.

To reduce the harmful effects of sewage sludge, pyrolysis has been proposed due to the better economic performance, greater volume reduction and higher efficiency of converting carbon rich products into energy and/or fuel^{5,6}. Pyrolysis is a degradation process carried out in an oxygen-free environment in a temperature range of 300 – 600°C. During the process, the organic constituents are transformed into bio-oil, gas product and carbonaceous residue, so-called char. Pyrolysis, like other thermochemical processes is affected by many factors, including raw material, temperature, reaction time, residence time, heating rate and catalyst⁷. Raw material has a great influence on both the quantity of products and their composition. In general, raw materials with high cellulose content result significant amount of water and other oxygen-containing components. Nitrogen, sulphur and other non-metallic elements can appear both in the gas, liquid and solid fractions, meanwhile the metals accumulate in the liquid and solid products^{8,9}. Other substances mixed with sewage sludge (e.g. biomass, plastic) also affect the reactions taking place and the product properties. During co-pyrolysis of sewage sludge and biomass, dilution and synergistic effects can also be prevailed, resulting in lower decomposition temperature and higher gas yields^{10,11}. Temperature is also a key factor for the product yields and compositions. Higher temperature promotes the formation of gas product and results in higher hydrogen

content. In addition, higher temperatures can also contribute to the more significant coke formation^{12,13}. The reaction time has also a significant effect on the products in terms of secondary reactions. High heating rates increase the amount of volatiles¹⁴. However, it is important to note that high heating rates are usually combined with short reaction times, thus the liquid yield is also higher¹³. Catalyst (e.g. alumina, silica or zeolites) can also be used to influence the yield structure and composition of the pyrolysis. However, their use should be complicated, because of the significant cost requirement or difficult recovery and regeneration¹⁵.

Pyrolysis of sewage sludge can be carried out in fixed, fluidized or circulating fluidized bed reactors. Nonetheless, the degradation processes were most often investigated in thermogravimetric devices (e.g. TG-FTIR)¹⁶⁻¹⁸, which should be problematic for reproducibility and representativeness. To investigate realistic cases, there are some articles about pyrolysis carried out in larger scales (10 – 50 g). Alvarez et al. carried out pyrolysis experiments using 50 g of sewage sludge, at 450 – 600°C¹⁹. They focused exclusively on the production of bio-oil and did not provide information on the yield, composition and properties of gas and solid products. Sun et al.²⁰ pyrolyzed 35 g of raw materials as Xie et al.²¹ also conducted scaled-up pyrolysis experiments. Although information was provided on the yield and composition of gas and solid products, a catalyst (coated alumina or ZSM-5) was also used to increase the amount of volatile products and modify the product structure in a favourable direction. Based on the referenced articles, it can be concluded that bio-oil has potential to substitute conventional engine fuels, and the purified and/or conditioned gas product can also be used as feedstock of Fischer-Tropsch or methanol synthesis. The solid pyrolysis product may be suitable for use as a catalyst or sorbent. Nonetheless, there is practically no information about experiment where at least 100 g of raw material would be pyrolysed – especially thermally – and the usage for all products would be examined.

Experimental part

Based on the aforementioned, this study investigates the pyrolysis of sewage sludge in a scaled-up semi-batch reactor system (Figure 1) in terms of the yield, composition and usability of pyrolysis products. During the experiments, 100 g of sewage sludge (municipal sewage sludge (MSS), distillery sewage sludge (DSS) and chicken manure (CHM) was placed into the reactor and pyrolysed at 300 and 500°C. The heating rate was constant (25°C/min) and the reactor was kept at the target temperature for 45 minutes. In order to maintain an inert atmosphere, constant nitrogen flow (1.5 dm³/h) was established in each experiment. To control the temperatures PID controllers were used. The pyrolysis vapours were condensed in a heat exchanger at room temperature, the non-condensable gases were collected in a Tedlar bag. The amount of the liquid product and the residue was determined by weight measurement and the weight of the gas product was calculated by the difference. After the weight measurement, the liquid product was separated into an aqueous and oily phase (so-called bio-oil) by a funnel (sedimentation time: 2 hours). The amount of each phase was also determined by mass measurement.

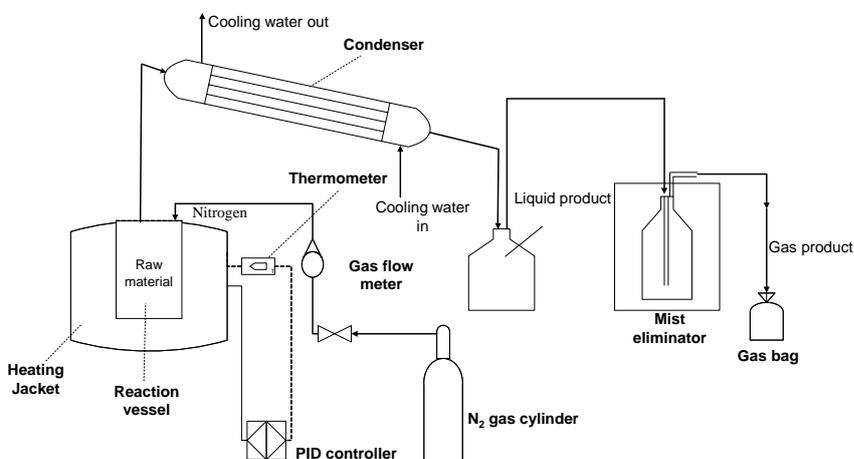


Figure 1: The scheme of the experimental apparatus

The most relevant properties of sludge samples were determined as the average of three parallel measurements and summarized in Table 1. The repeatability of the measurements has standard deviation value up to 8%. To define the water content, weight measurement was carried out for the wet and dried samples and mass differences were related to the weight of the wet samples. In order to determine the fixed carbon, ash and volatile contents proximate analysis was conducted. The detailed analysis conditions can be found elsewhere²². The carbon, hydrogen, nitrogen and sulphur contents were measured by a Carlo Erba type elemental analyser. In case of elemental analysis weight percentages of C, H, N and S were defined, and the oxygen and other element content was calculated from the difference.

Table 1: Main properties of dried sewage sludge samples

Sample	MSS	DSS	CHM
Water content, % ⁽¹⁾	55.36	47.42	35.28
Fixed carbon, %	7.75	23.23	15.07
Ash content, %	47.61	24.19	20.21
Volatiles, %	44.64	52.28	64.72
C	23.4	42.3	34.7
H	3.4	5.2	4.5
N	3.8	0.8	4.6
S	2.0	0.0	1.6
O+Other	67.4	51.7	54.6

(1) Water content before the analysis (this water content was evaporated at 110°C prior to the analysis).

The produced gases were analysed by a Dani type gas chromatograph comprising flame ionization and thermal conductivity detectors. The equipment contained two columns (Rtx-1 PONA (100 m x 0.25 mm x 0.5 µm) and Carboxen TM 1006 PLOT (30 m x 0.53 mm)). In case of PONA column isotherm conditions and 230°C of injector and detector temperature was applied. For Carboxen TM 1006 PLOT column the applied heating program was the follows: 35°C for 18 min, heating to 120°C with a heating rate of 15°C/min and held at 120°C for 2 min. The retention times of the components were determined using gas mixtures and individual components.

Heating value of obtained gases was calculated from the gas chromatographic results according to the following equation:

$$\text{Heating value, } \frac{\text{MJ}}{\text{m}^3} = H_2 \times 10.283 + CO \times 12.663 + CH_4 \times 35.949 + CO_2 \times 0.589 + C_{2-5} \times 70$$

Similar to analysis of gas products, composition of the bio-oil was also determined by a Dani type gas chromatograph. For the analysis Rtx-1 column (30 m x 0.53 mm x 0.25 µm) was used. Both the injector and detector temperature were 340°C, and the applied heating program was the follows: 40°C for 5 min and heating to 340°C (heating rate: 15°C/min) and held at 340°C for 30 min. Before the gas chromatographic analysis, bio-oil samples were diluted with carbon disulphide.

Results and discussion

During the pyrolysis gas, liquid and solid products were also formed (Figure 2). As expected, gas and liquid product yields increased with the temperature and the amount of char varied along the opposite trend. The increasing gas and decreasing char yields were attributed to the lower thermal stability of components at higher temperatures. In addition to temperature, pyrolysis reactions and thus the product yields were also affected by the raw materials. The highest gas yields were observed in pyrolysis of DSS sample, while it seems that the composition of CHM favoured the formation of liquid products.

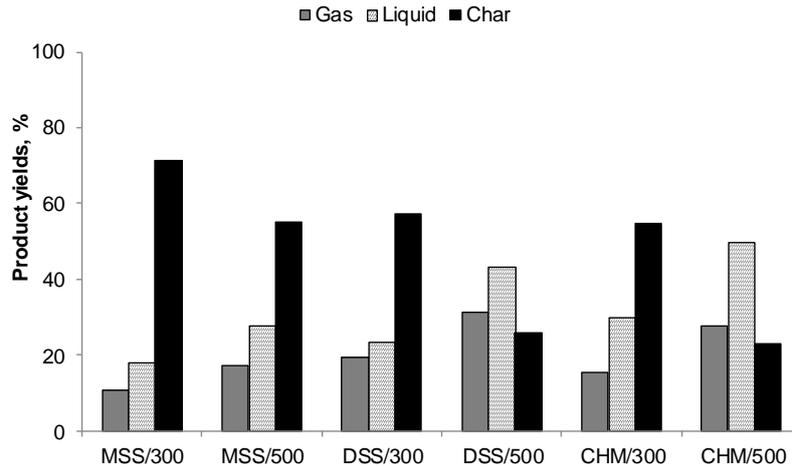


Figure 2: Product yields of pyrolysis in function of the raw material and temperature

Gas product

The composition of gases was determined by GC-FID and GC-TCD methods (Figure 3). Based on the results, there are clear differences in the composition of the gas products using different raw materials and reaction temperatures. At 300°C, no hydrogen was produced and the share of carbon monoxide was also below 10%. At the same time, the most dominating compound of the gas product was the carbon dioxide. In contrast, at 500°C a higher degree of synthesis gas production (mixture of CO and H₂) also took place. This also proves that thermal degradation is a series of complex reactions. In general, only the moisture content of sewage sludge is removed up to 200°C. The slow degradation of hemicellulose and cellulose begins only in the torrefaction stage (T=200 – 350°C), where the main product is the solid carbonaceous material, the so-called bio-char. Above 350°C, the pyrolysis reactions become dominant and result in synthesis gas production, as confirmed by our experimental results.

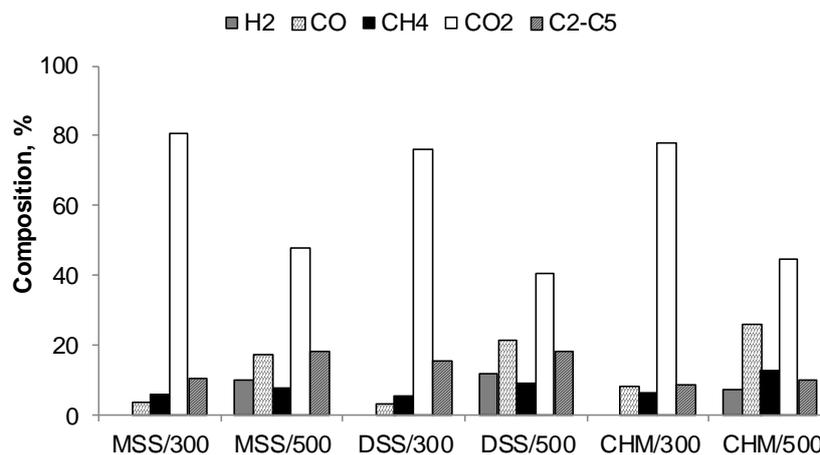


Figure 3: Composition of gas products in function of the raw material and temperature

In order to evaluate the usability of the gas product, synthesis gas yields, H₂/CO ratios (Figure 4) and heating values (Figure 5) have also been calculated. As Figure 4 depicts, the highest synthesis gas yield was observed in pyrolysis of DSS and followed by CHM and MSS raw materials.

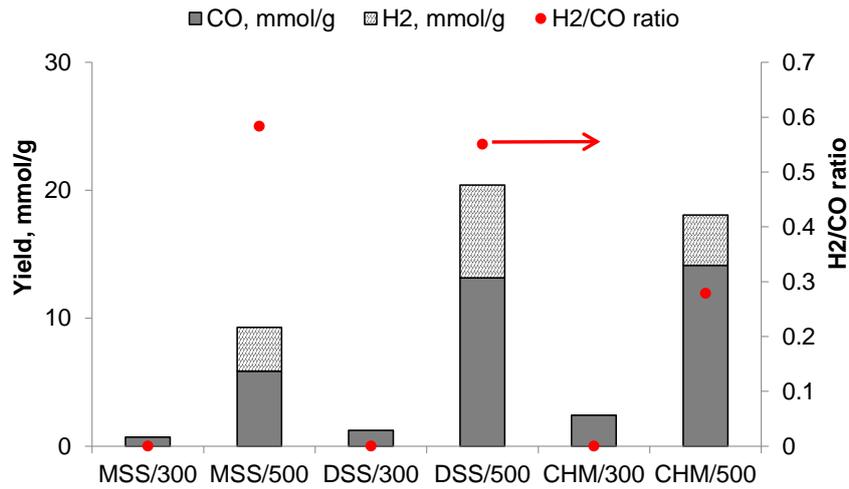


Figure 4: Synthesis gas yields and H₂/CO ratios

The H₂/CO ratios changed between 0.3 and 0.6; thus the produced gases require further quality improvement prior to the use for chemical synthesis. The reason for this is that theoretical H₂/CO ratio of synthesis gas for cobalt catalysed Low Temperature Fischer-Tropsch synthesis is around 2:1, 1.5:1 for aldehydes, higher alcohols and dimethyl ether, 1:1 for acetic acids and 1:2 for polycarbonate production^{23,24}. Heating value can also be a valuable characteristic for energetic purposes. The heating values were in the range of 9.5-19.9 MJ/m³. Not surprisingly, the highest heating value was observed where smaller hydrocarbons were present in the highest percentage (DSS/500). These smaller hydrocarbons as individual components provide a higher heating value than the other compounds present in the mixture.

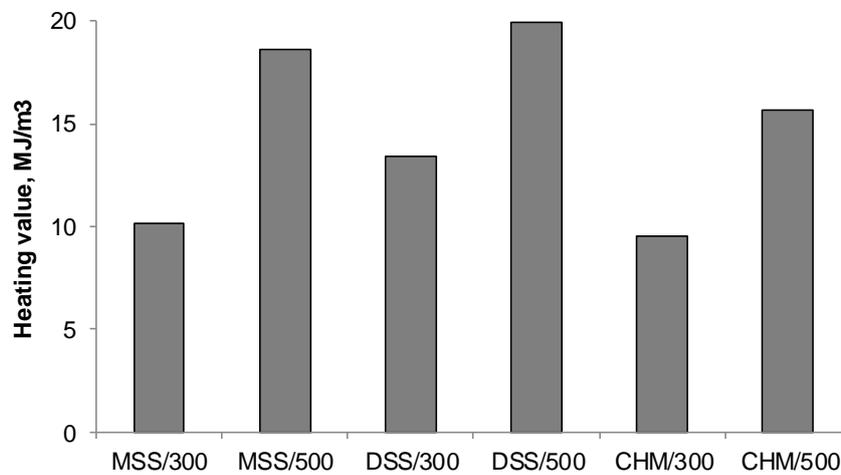


Figure 5: Heating values of the produced gases

Liquid product

The liquid products consisted of aqueous and organic phase (Figure 6). Their main component was the water (yield: 12.7 – 32.6%), which resulted from the dehydration reactions and the secondary cracking of oxygen containing, high molecular weight compounds, especially at higher temperature²⁵. The organic phase, i.e. the bio-oil contained aldehydes, ketones, carboxylic acids, phenols and their derivatives, alcohols and aromatic or aliphatic hydrocarbons (Figure 7).

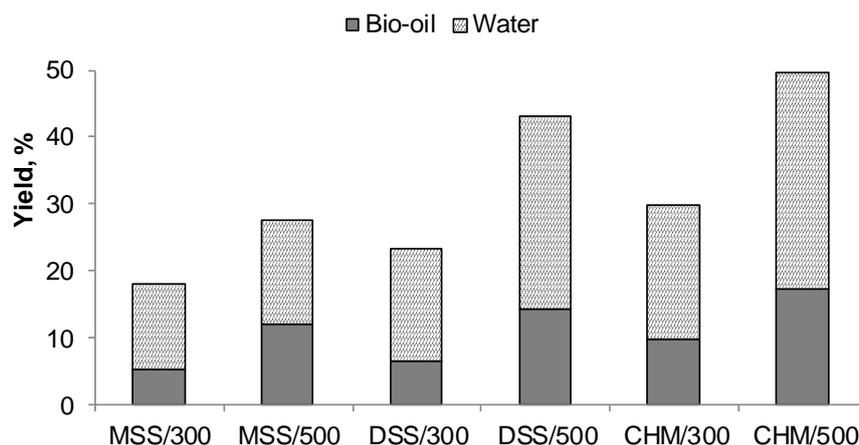


Figure 6: Bio-oil yield

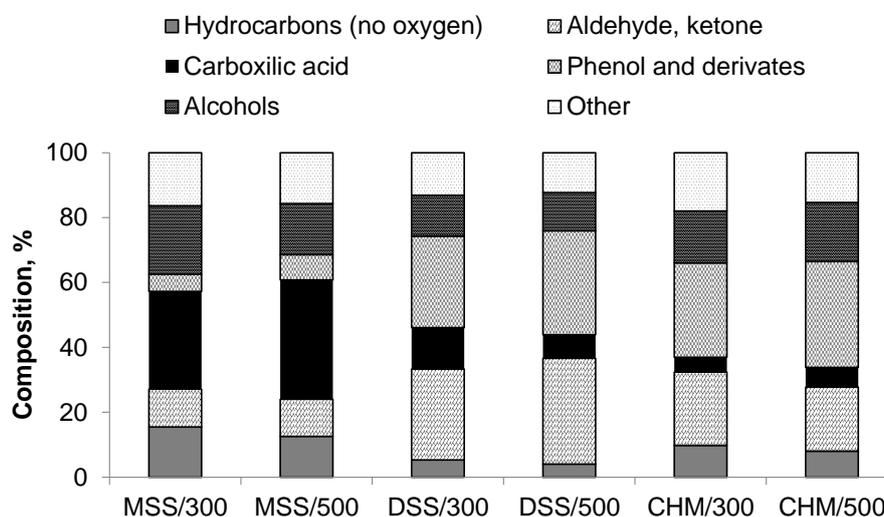


Figure 7: Composition of the bio-oil

The oxygen-containing compounds were mainly formed from the cellulose and lignin; and their major representatives were phenols and their derivatives, as was also found by other researchers^{26,27}. The concentration of aldehydes and ketones decreased with the temperature; while the share of the phenolic compounds varied along the opposite trend. The decrease in yield of aldehydes and ketones was attributed to the secondary cracking reactions. Due to the high share of oxygenated compounds, heating value of the produced bio-oils is lower than that of the conventional fuels. In addition, oxygen may also promote the polymerization reactions and increase the viscosity, therefore prior to use as engine fuel or engine fuel blending component it is needed to improve the quality of bio-oil by catalytic hydrodeoxygenation.

Solid product

The elemental composition of char samples are summarized in Table 2. The repeatability of the measurements has standard deviation value up to 8%. During the pyrolysis, the hydrogen content of MSS (3.4%), DSS (5.2%) and CHM (4.2%) raw materials decreased to 1.4 – 2.9, 1.6 – 2.8 and 1.5 – 2.7%, respectively. The nitrogen contents (MSS: 3.8%, DSS: 0.8%, CHM: 4.6%) also became less, as well as there was a significant decrease in sulphur content of MSS and CHM raw materials (2.0 and 1.6%). As the elemental composition shows, chemical composition has changed due to carbonization and removal of functional groups.

Table 2: Main properties of char samples

	MSS/300	MSS/500	DSS/300	DSS/500	CHM/300	CHM/500
HHV, MJ/kg	7.1	5.3	8.4	6.2	7.3	5.7
C, %	18.4	23.7	19.3	22.9	16.1	22.1
H, %	1.4	2.9	1.6	2.8	1.5	2.7
N, %	1.9	1.6	1.1	0.8	1.7	1.8
S, %	0.8	0.9	0.0	0.0	0.0	0.0

Conclusions

In this study, municipal sewage sludge (MSS), distillery sewage sludge (DSS) and chicken manure (CHM) was pyrolysed in a scaled-up semi-batch reactor at temperature of 300 and 500°C. During the experiments, the effects of raw material and reaction temperature were investigated on the yields and composition of pyrolysis products. During the experiments, 10.7 – 31.1% gas, 17.9 – 43.0% liquid and 22.8 – 71.4% solid product was formed. The gas and liquid product yields increased with the reaction temperature and the amount of the char varied along the opposite trend. The highest gas and synthesis gas yield was observed in pyrolysis of DSS raw material at 500°C, while composition of CHM favored the formation of liquid products, especially the bio-oil (yield: 9.8 and 17.1%). In terms of gas product it was found that higher temperature than 300°C is needed to produce synthesis gas and due to the lower H₂/CO ratios (<0.6) further quality improvement is needed before use for synthesis. The liquid product contained aldehydes, ketones, carboxylic acids, phenols and their derivatives, alcohols and hydrocarbons. However, after hydrogenation it can be suitable to use as fuel. The char may be suitable for use as a catalyst or sorbent, after its elemental composition was changed due to carbonization and removal of functional groups.

Acknowledgment

This project (2019-2.1.13-TÉT_IN-2020-00071) was financed by the Ministry of Innovation and Technology from the National Research Development and Innovation Fund, within the 2019-2.1.13-TÉT_IN program.

References

1. Lee S., Kim Y-M., Siddiqui M. Z., Park Y-K.: Environ Pollut 285, 117197 (2021).
2. Fytili D., Zabaniotou A.: Renewable Sustainable Energy Rev 12(1), 116 (2008).
3. Buta M., Hubeny J., Zieliński W., Harnisz M., Korzeniewska E.: Ecotoxicol Environ Saf 214, 112070 (2021).
4. Gao N., Kamran K., Quan C., Williams P. T., Prog Energy Combust Sci 79, 100843 (2020).
5. Campoy M., Gómez-Barea A., Ollero P., Nilsson S.: Fuel Process Technol 121, 63 (2014).
6. Jaramillo-Arango A., Fonts I., Chejne F., Arauzo J.: J Anal Appl Pyrolysis 121, 287 (2016).
7. Kan T., Strezov V., Evans T. J.: Renewable Sustainable Energy Rev 57, 1126 (2016).
8. Bridgwater A. V.: Biomass Bioenergy 38, 68 (2012).
9. Ma R., Huang X., Zhou Y., Fang L., Sun S., Zhang P., Zhang X., Zhao X.: Bioresour Technol 238, 616 (2017).
10. Alvarez J., Amutio M., Lopez G., Bilbao J., Olazar M.: Fuel 159, 810 (2015).
11. Zaker A., Chen Z., Zaheer-Uddin M., Guo J.: J Environ Chem Eng 9(1), 104554 (2021).
12. Alvarez J., Amutio M., Lopez G., Barbarias I., Bilbao J., Olazar M.: Chem Eng J 273, 173 (2015).
13. Akhtar J., Amin N. S.: Renew Sustain Energy Rev 16(7), 5101 (2012).
14. Fonts I., Juan A., Gea G., Murillo M. B., Sánchez J. L.: Ind Eng Chem Res 47(15), 5376 (2008).
15. Huang Z., Qin L., Xu Z., Chen W., Xing F., Han J.: J Energy Inst 92(4), 835 (2019).

16. Naqvi S. R., Tariq R., Hameed Z., Ali I., Naqvi M., Chen W-H., Ceylan S., Rashid H., Ahmad J., Taqvi S. A., Shahbaz M.: *Renew Energ* 131, 854 (2019).
17. Sobek S., Werle S.: *Renew Energ* 161, 972 (2020).
18. González A. J., Gil M., Fernández R., Martínez J., Fernández C., Papaharalabos G., Gómez X.: *Environ Sci Pollut Res* 7, 32603 (2020).
19. Alvarez J., Lopez G., Amutio M., Artetxe M., Barbarias I., Arregi A., Bilbao J., Olazar M.: *Fuel Process Technol* 149, 169 (2016).
20. Sun Y., Jin B., Wu W., Zuo W., Zhang Y., Zhang Y., Huang Y.: *J Environ Sci* 30, 1 (2015).
21. Xie Q., Peng P., Liu S., Min M., Cheng Y., Wan Y., Li Y., Lin X., Liu Y., Chen P., Ruan R.: *Bioresour Technol* 172, 162 (2014).
22. Miskolczi N. Tomasek S.: *Energies* 15, 5116 (2022).
23. Hua Y., Wang J., Min T., Gao Z.: *J Power Sources* 535, 231453 (2022).
24. Zhao S., Li H., Wang B., Yang X, Peng Y., Du H., Li Z.: *Fuel* 321, 124124 (2022).
25. Karayildirim T., Yanik J., Yuksel M., Bockhorn H.: *Fuel* 85(10-11), 1498 (2006).
26. Sánchez M. E., Menéndez J. A., Domínguez A., Pis J. J., Martínez O., Calvo L. F., Bernad P. L.: *Biomass Bioenerg* 33(6-7), 933 (2009).
27. Tsai W-T., Lee M-K., Chang J-H., Su T-Y., Chang Y-M.: *Bioresour Technol* 100(9), 2650 (2009).

Pyrolýza čistírenských kalů k získání cenných produktů

Szabina TOMASEK^a, Norbert MISKOLCZI^a, Csaba FÁYKÖD^b, Andrea SOMOGYI^c

^a *Technická fakulta, Výzkumné centrum biochemického, environmentálního a chemického inženýrství, Katedra zpracování uhlovodíků a uhlí MOL, University of Pannonia, Egyetem u. 10, H-8200, Veszprém, Maďarsko,*

^b *Felso-Bacska Storage Windpark Ltd.,*

^c *Solver Unio Ltd.,*

e-mail: tomasek.szabina@mk.uni-pannon.hu

Abstrakt

Tento článek se zaměřuje na pyrolýzu odpadních kalů z různých zdrojů ve zvětšeném semi-vsádkovém reaktoru při teplotách 300 a 500 °C. Bylo zjištěno, že jak teplota, tak surovinové složení měly významný vliv na výtěžnost a vlastnosti produktu. Nejvyšší výtěžnost plynu a syntézního plynu byla pozorována při pyrolýze kalu z lihovarů při 500 °C, zatímco složení kuřecího hnoje upřednostňovalo tvorbu biooleje (9,8 a 17,1 %). Plynný produkt byl charakterizován poměry H₂/CO do 0,6; proto je před použitím pro syntézu zapotřebí další zlepšení kvality. Bioolej (5,2 – 17,1 %) obsahoval značné množství kyslíkových sloučenin, ale po hydrogenaci je vhodný jako náhrada konvenčního paliva. Během pyrolýzy se také změnilo elementární složení polokoksu (22,8 – 71,4 %) v důsledku karbonizace a odstranění funkčních skupin.

Klíčová slova: čistírenský kal, pyrolýza, syntézní plyn, bioolej, výroba biouhlu