

Integrated Waste Treatment System Combining Biogas Technology and Pyrolysis

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Anaerobic digestion allows combining waste treatment and energy production from biomass, but lignin and lignocellulosic fractions, which typically make up 10-25 wt. % of biomass can't be converted efficiently. Another treatment pathway for bio-waste (including lignocellulosic biomass) are thermochemical processes such as gasification and pyrolysis which prevent technical and environmental issues related to solid biomass combustion and generate gas as an energy carrier. In this paper the method of low-temperature pyrolysis (torrefaction) of sewage sludge which is formed during anaerobic digestion is investigated. The torrefaction temperature is 220 °C and 300 °C. The data on mass balances of torrefaction process, specific volume yield, composition and calorific value of gas mixture formed in torrefaction, characteristics of torrefied material (mass loss, proximate and ultimate composition, calorific value, hygroscopicity limit) are presented. The effect of the initial sludge ash content on the calorific value of the torrefied material is calculated. Based on the obtained data the torrefaction process conditions of sewage sludge after anaerobic digestion are determined.

1. Introduction

As it is known, the sewage sludge formed in water treatment facilities as a result of mechanical and biological waste water purification has a high moisture content (up to 98 wt. %) which is why it has a large volume and contains a pathogenic microflora that pollutes the environment. Among the methods of its treatment aimed at solving these problems there is anaerobic digestion which produce biogas (calorific value is 21-23 MJ/m³ (Kosov et al., 2015)). However, residue whose mass is practically equal to the mass sewage sludge before digestion is remained. Since only 40-50 % of the sludge organic mass passes to biogas (Caoa, Pawlowski, 2012). Thus, the sewage sludge after digestion still contains energy potential (the lower calorific value is 11-12 MJ/kg (Fonts et al., 2009)), has a significant volume and contains a part of the pathogenic microflora that not lost in the process of anaerobic treatment (Caoa, Pawlowski, 2012). Such residue is often used as fertilizer or buried. But the risk of soil contamination with a pathogenic microflora and the need to search for a land for burial make these methods not optimal.

One of the possible further use ways of sewage sludge after anaerobic digestion is thermochemical treatment – torrefaction. Torrefaction is pyrolysis process that carried out at temperatures up to 300 °C. With respect to wood fuel, this process makes it possible to improve its consumer properties – to increase the calorific value and reduce the hygroscopicity limit. In addition, lignin containing 25-35% of the energy presented in the biomass can't be processed due to anaerobic digestion (Lukehurst et al., 2010; Appels et al., 2008). The process of thermochemical conversion will make it possible.

In this paper the investigation results of the torrefaction process at the two extreme temperatures – 220 °C and 300 °C – of sewage sludge after anaerobic digestion are presented. The aim of the work was to determine the practicability of applying this method to the sewage sludge after anaerobic digestion in order to estimate the possibility of the anaerobic digestion process and thermochemical conversion combining.

2. Materials and methods

2.1 Materials

In this work a sewage sludge obtained after the anaerobic digestion process was used as initial raw material (Table 1)

Table 1: Characteristics of sewage sludge after anaerobic digestion (on dry basis)

Parameter	Value	Analytical method
Proximate analysis:		
Volatile matter (VM), wt. %	60.7	thermogravimetric analysis
Ash (A), wt. %	31.5	thermogravimetric analysis
Fixed carbon (FC), wt. %	7.8	--
Ultimate analysis:		
C, wt. %	37.61	Element Analyzer «Elementar Vario Macro Cube»
H, wt. %	5.23	
N, wt. %	5.97	
S, wt. %	1.43	
O, wt. %	18.25	
A, wt. %	31.50	
Calorific values:		
Higher calorific value, MJ/kg	17.54	calorimetric measurements
Lower calorific value (calculated by ultimate composition), Q_L^{el} , MJ/kg	16.31	--
Lower calorific value (calculated on the basis of higher calorific value), Q_L^{val} , MJ/kg	16.68	--

The discrepancy of the lower calorific values obtained by two methods is 2.2 %. The initial moisture content of the fermented sludge was 70 wt. %. For the experimental studies the sludge was dried in a drying oven to a moisture content not more than 2 wt. %.

2.2 Experimental set up and conditions

A laboratory set up shown in Figure 1 was used for experimental investigations. The laboratory set up includes a pyrolysis reactor (1), a gas pipe (2) and a condenser (3). The pyrolysis reactor into which 80 g of initial raw material is put is a cylindrical pipe 142 mm long with an outer diameter of 60 mm and a wall thickness of 1.5 mm. The gas pipe connects the pyrolysis reactor and the condenser. The condenser is made of a cylindrical pipe 250 mm in length with an outer diameter of 48 mm and a wall thickness of 2 mm. It is used to collect pyrolysis liquid at the bottom of the condenser. Non-condensable gases go further to the heat exchanger (4) which is cooled by flow water at a temperature of 10 °C. A gas flowmeter (5) and a gasholder (6) of 45 liters are installed behind the heat exchanger to collect the non-condensable pyrolysis gases. Depending on the experimental research purpose the valves can switch gas flows. The temperature is measured by means of thermal couples in the places shown in the Figure 1. After installation, the laboratory set up is purged with argon. A gas pipe is heated to a temperature of $T_4=270\pm 10$ °C the first. This temperature remains constant throughout the experiments. Then, the heating of the pyrolysis reactor to the torrefaction temperature T_1 at a heating rate of 4 °C/min is started. For these experimental studies, the two extreme temperatures of torrefaction – 220 and 300 °C – were used. After reaching the temperature T_1 , the feedstock was kept under these conditions for 20 minutes. The condenser temperatures was $T_3 = 20\pm 5$ °C throughout the experiments.

As a result of the torrefaction process, three products were formed: solid residue (torrefied material), pyrolysis liquid (tar), non-condensable gases. Experimental studies at different temperatures were carried out in two stages. In the first stage, a volume yield of non-condensable gases was measured using a gas flowmeter. In the second stage, the composition of the non-condensable gas mixture (H_2 , CO, CO_2 , C_nH_m , N_2) was measured with a flow gas analyzer connected to the gasholder.

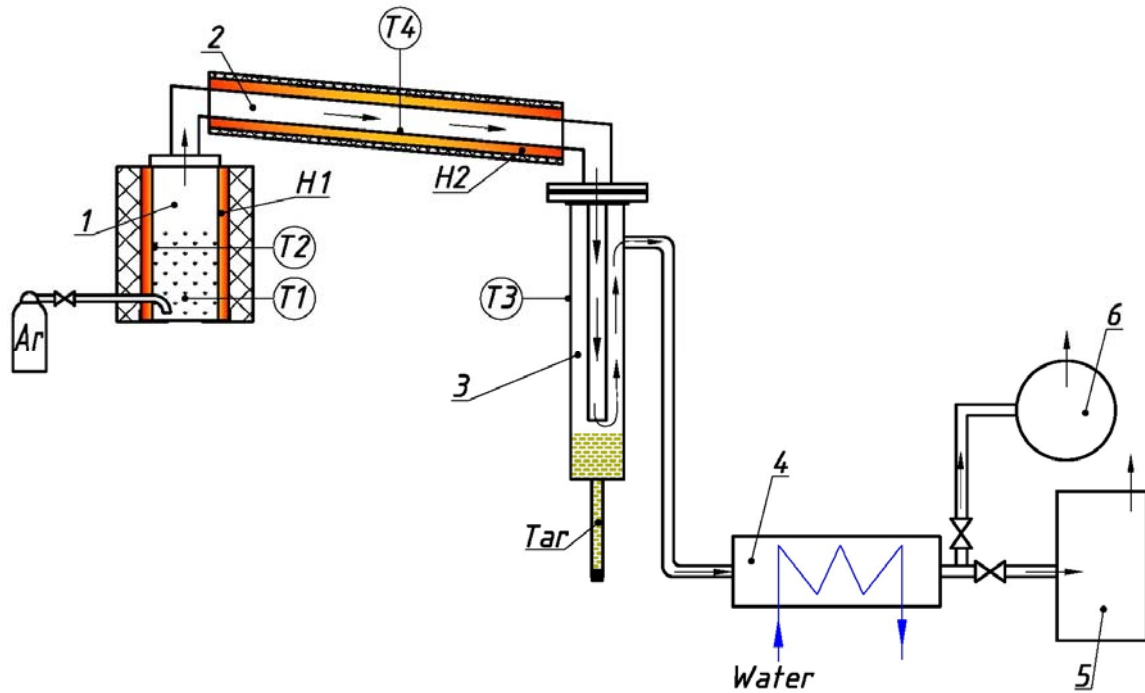


Figure 1: Laboratory set up (1 – pyrolysis reactor, 2 – gas pipe, 3 – condenser, 4 – heat exchanger, 5 – gas flowmeter, 6 – gasholder, H1, H2 – heater, T1...T5 – position of thermal couples, Ar - argon)

Table 2: Formulas for calculating the characteristics of torrefaction products

Formula	Designation	Description
$O = 100 - (C + H + N + S + A)$	(1)	C, H, N, S, A – content in the sample of carbon, hydrogen, nitrogen, sulfur and ash content of raw materials (on dry basis), wt. %
$FC = 100 - VM - A$	(2)	--
$Q_L^{el} = 0.001 \cdot (339 C + 1030 H - 108(O - S) - 25W)$	(3)	--
$Q_L^{val} = Q_H - \frac{24,42 \cdot (8,94 \cdot H + W)}{1000}$	(4)	--
$A_{sr} = A_{im} \cdot \frac{m_{im}}{m_{sr}}$	(5)	A_{sr} – ash content of feedstock, wt. %; m_{im} – feedstock mass, g; m_{sr} – solid residue mass, g
$V_{sp} = \frac{V}{m_{im}}$	(6)	V – volume of non-condensable gases, l.
$Q_g = 126,44 \cdot CO + 107,6 \cdot H_2 + 358,18 \cdot CH_4,$	(7)	H_2, CO, C_nH_m – gas content in mixture, vol. %.

2.3 Methods of torrefaction product characteristic investigation

The characteristics of the initial raw material and solid residue after torrefaction includes moisture, ash and volatile matter contents, ultimate composition, amount of fixed carbon, calorific value and hygroscopicity limit. Moisture content (W, wt. %) was measured by the Ohaus MB45 moisture analyzer. Ash content (A, wt. %) and volatile matter (VM, wt. %) were determined using thermogravimetric analysis with SDT Q600 thermal analyzer. The value of the highest calorific value (Q_H , MJ/kg) was determined using the combustion calorimeter. Before determining the ash content, volatile matter, elemental composition and calorific value the samples were dried to the moisture content of 0.1 wt. %. The elemental composition (C, H, N, S, wt. %) was determined on the Elementar Vario Macro Cube element analyzer. The oxygen content (O, wt. %) was calculated from the Eq1 (Table 1). The amount of fixed carbon on dry mass (FC, wt. %) was determined by Eq2. The lower calorific values based on the ultimate composition data (Q_L^{el} , MJ/kg) and based on the experimental values of the highest calorific value (Q_L^{val} , MJ/kg) were calculated by the Eq3 and Eq4, subsequently. The ash content of the solid residue (A_{sr} , wt. %) was calculated from Eq5. The hygroscopicity

limit was determined according to (GOST, 1977). The specific volume yield of the gas mixture (V_{sp} , l/kg) was calculated by Eq6. The composition of the gas mixture (H_2 , CO, CO_2 , C_nH_m , N_2) was measured by a flow gas analyzer Vario Plus Industrial "SYNGAS". The calorific value of the gas mixture (Q_g , kJ/m³) was calculated from Eq7.

3. Results and discussion

3.1 Torrefaction of sewage sludge after anaerobic digestion

The results of mass balance calculating and the characteristics of the obtained gas mixtures are presented in Table 3.

Table 3: Mass balance of initial raw material torrefaction at temperatures of 220 °C and 300 °C

Parameter	T _t =220 °C	T _t =300 °C
Mass balance:		
solid residue, wt. %	83.5	68.6
tar, wt. %	12.6	23.3
non-condensing gas, wt. %	3.7	6.2
imbalance, wt. %	0.2	1.9
total, wt. %	100	100
Non-condensable gas:		
CO ₂ , vol. %	99.58	93.41
CO, vol. %	0.42	4.91
CH ₄ , vol. %	0	1.68
H ₂ , vol. %	0	0
N ₂ , vol. %	0	0
total, vol. %	100	100
V _{sp} , l/kg	18.8	32.1
Q _g , kJ/m ³	52.7	1223.2

From the table It can be seen that the mass loss during the torrefaction was 16.5 wt. % and 31.4 wt. % for temperatures of 220 °C and 300 °C, respectively. As the temperature was risen, the yield of the pyrolysis tar was increased. The low specific volume yield of non-condensable gases and its low calorific value due to the large content of CO₂ make it unnecessary to use such a gas mixture for own needs and also to obtain synthesis gas from it, as described in the work (Antropov et al., 2011).

3.2 Characteristics of solid residue from sewage sludge

Characteristics of the solid residue obtained at torrefaction of sewage sludge after anaerobic digestion are presented in Table 4.

Table 4: Characteristics of torrefied sewage sludge after anaerobic digestion (on dry basis)

Parameter	T _t =220 °C	T _t =300 °C	Analytical method
Proximate analysis:			
Volatile matter (VM), wt. %	54.3	41.6	thermogravimetric analysis
Ash (A), wt. %	37.7	45.9	thermogravimetric analysis
Fixed carbon (FC), wt. %	8.0	12.5	--
Ultimate analysis:			
C, wt. %	42.08	42.66	Element Analyzer
H, wt. %	4.93	4.14	«Elementar Vario Macro Cube»
N, wt. %	6.30	5.70	
S, wt. %	1.27	1.10	
O, wt. %	7.72	0.51	
A, wt. %	37.70	45.90	
Calorific values:			
Higher calorific value, MJ/kg	19.57	19.81	calorimetric measurements
Q _L ^{el} , MJ/kg	18.64	18.79	--
Q _L ^{val} , MJ/kg	18.67	19.06	--

From the data presented in the table it is seen that with increasing temperature the fixed carbon content is increased and the residue ash content is increased significantly. Compared to the initial raw material, the ash content of the solid residue obtained at $T_t=300\text{ }^\circ\text{C}$ is grown almost 1.5 times. The volatile matter content depending on the temperature rising is decreased by 1.12-1.5 times. The carbon content isn't almost changed, but the oxygen content is decreased sharply in 2.4-35.8 times. According to the oxygen and hydrogen content the sewage sludge after anaerobic digestion and sewage sludge after torrefaction is approached the solid fuel with a high energy density (the oxygen and hydrogen content in anthracites is about 1.5 wt. %). Therefore, this torrefied material is suitable for co-firing with coal.

Compared with the feedstock the lower calorific value of material torrefied at $220\text{ }^\circ\text{C}$ was increased by 12 %. A further increase of the process temperature to $300\text{ }^\circ\text{C}$ does not lead to a significant rising in the calorific value (Figure 2a). For plant origin biomass (wood), the lower calorific value due to torrefaction is grown by 20-30% compared to the initial material (Kuzmina et al., 2016).

The torrefaction process allows to reduce the hygroscopicity limit of the feedstock (Figure 2b). At $T_t = 220\text{ }^\circ\text{C}$ it is 10 wt. %, that is 3.4 times less than the initial sludge. Increasing the process temperature leads to an even greater reduction in the hygroscopicity limit. And for $T_t=300\text{ }^\circ\text{C}$ this value is 3 wt. %. Thus, the characteristics of the torrefied material show that in the case of a sewage sludge after anaerobic digestion, it is effectually to carry out the torrefaction at the lowest temperature of $220\text{ }^\circ\text{C}$.

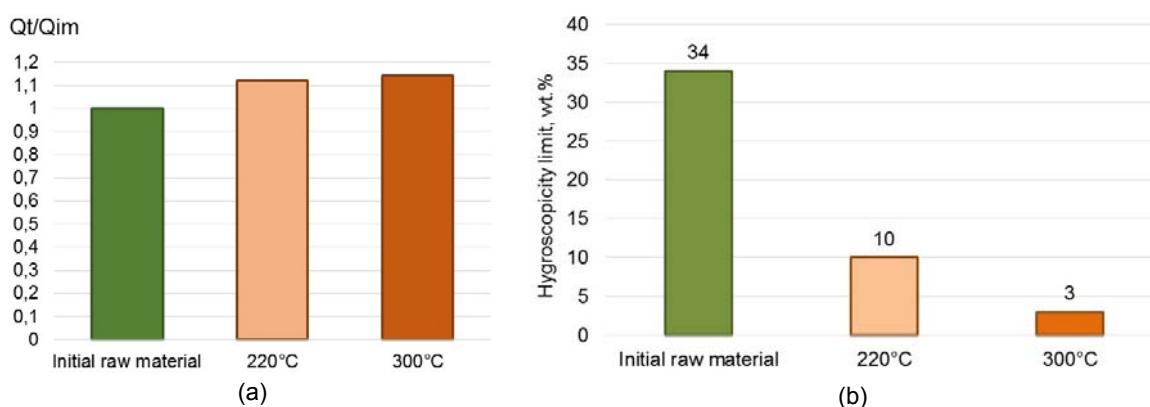


Figure 2: Change of the lower calorific value (a) and the hygroscopicity limit (b) of the sewage sludge after anaerobic digestion at two temperatures of the torrefaction (Q_t – the lower calorific value calculated by elemental composition of torrefied material, Q_{im} – the lower calorific value calculated by elemental composition of initial raw material)

The torrefaction of raw materials with high ash content is a special task compared for example with wood. Ash content of wood is no more than 1 wt. %, so its increase even 1.5 times will not have a particularly significant effect on the calorific value (Lavrenov et al, 2016). For materials with high ash content such as sewage sludge an increase in ash content due to torrefaction leads to a significant reduction of the calorific value. Figure 3 shows the effect of the ash content of the initial sewage sludge after anaerobic digestion (on a dry basis) on the change in the lower calorific value of the material at two torrefaction temperatures. The calculation was made on the basis of the ultimate composition of the material torrefied at $220\text{ }^\circ\text{C}$ and $300\text{ }^\circ\text{C}$. From the figure it is seen that even with the ash content of the initial material 30 wt. % the calorific value practically does not increase with the growth of the torrefaction temperature. With the ash content of the initial sludge of 20 wt. % an increase in calorific value by 30% compared to the feedstock can be achieved at a temperature of $300\text{ }^\circ\text{C}$, that is comparable to plant biomass. Further decrease in ash content of the feedstock leads to even better indicators – an increase of 23% at a temperature of $220\text{ }^\circ\text{C}$. With an ash content of 40 wt. % growth of calorific value at $220\text{ }^\circ\text{C}$ is only 9%. With an ash content of more than 40 wt. % it is not advisable to carry out the process of torrefaction. On average, the ash content of the sewage sludge in its original form is 20-45 wt. % (Appels et al, 2008; Kosov et al, 2016).

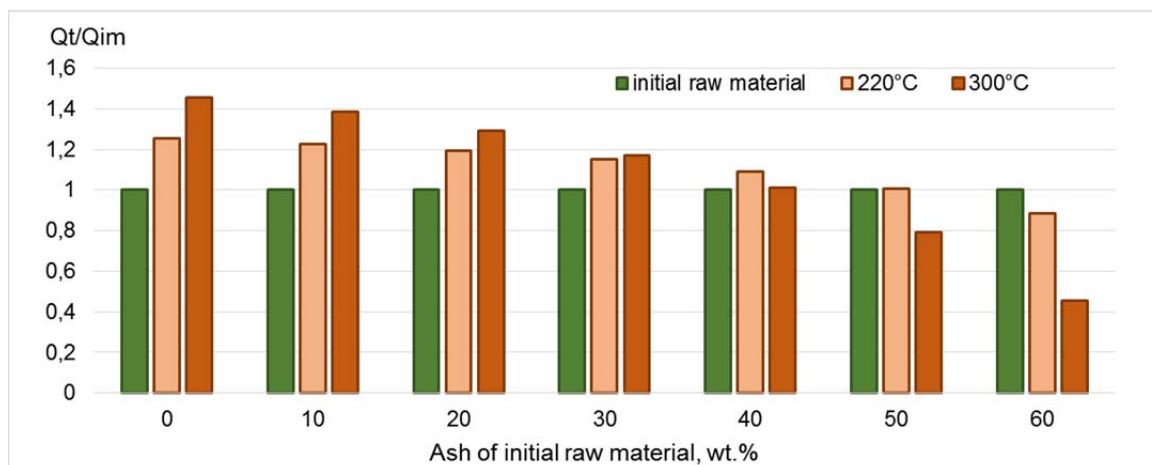


Figure 3: Change of the lower calorific value of torrefied material in dependence to ash of initial raw material (Q_t – the lower calorific value calculated by elemental composition of torrefied material, Q_{im} – the lower calorific value calculated by elemental composition of initial raw material)

4. Conclusions

Experimental studies of the torrefaction process of sewage sludge after anaerobic digestion showed that the optimum process temperature is 220 °C with a residence time of 20 minutes. The lowest calorific value of the torrefied material at this condition (on a dry basis) is increased by 12 % compared to the feedstock. The hygroscopicity limit of torrefied material is reduced by 3.4 times in comparison with the initial one. According to the oxygen and hydrogen content the sewage sludge after anaerobic digestion and sewage sludge after torrefaction is approached the solid fuel with a high energy density. Therefore, this torrefied material is suitable for co-firing with coal. Such method can be considered as a promising method of utilization of this waste type.

Acknowledgments

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References

- Antropov A., Isyemin R., Kosov V., Kosov V., Sinelshchikov V., 2011, Synthesis gas production as a result of biomass torrefaction, *ISJAEE*, 10, 42-46
- Appel L., Baeyens J., Degre've J., Dewil R., 2008, Principles and potential of the anaerobic digestion of waste-activated sludge, *Progress in Energy and Combustion Science*, 34, 755–781.
- Caoa Y., Pawłowski A., 2012, Sewage sludge-to-energy approaches based on anaerobic digestion and pyrolysis: Brief overview and energy efficiency assessment, *Renewable and Sustainable Energy Reviews*, 16, 1657-1665.
- Fonts I, Azuara M, Gea G, Murillo M.B., 2009, Study of the pyrolysis liquids obtained from different sewage sludge, *J. Anal. Appl. Pyrolysis*, 85, 184–91.
- GOST 16483.32-77 Wood. Method for determination of ultimate hygroscopicity, 1977, 7.
- Kosov V., Lavrenov V., Larina O., Zaichenko V., 2016, Use of Two-stage Pyrolysis for Bio-waste Recycling, *Chemical Engineering Transactions*, 50, 151-156.
- Kosov, V., Umnova O., Zaichenko V., 2015, The pyrolysis process of sewage sludge, *Journal of Physics: Conference Series*, 653, 012032.
- Kuzmina J., Sytchev G., Zaychenko V., 2016, Torrefaction. Prospects and Application, *Chemical Engineering Transactions*, 50, 265-270.
- Lavrenov V., Larina O., Sinelshchikov V., Sytchev G., 2016, Two-Stage Pyrolytic Conversion of Different Types of Biomass into Synthesis Gas, *High Temperature*, 54, 892–898.
- Lukehurst C., Frost P., Al Saedi T., 2010, Utilisation of digestate from biogas plants as biofertilizer, *IEA Bioenergy*, 37.