Characteristics of a solid carbonaceous product of microwave torrefaction of sewage sludge

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ABSTRACT

The aim of this work is to present results of characterization of the dried sewage sludge (SS) and produced solid carbonaceous product (SCP) of microwave torrefaction (MT) for combustion energy and agricultural use. The tests reflected several variables influencing pyrolysis such as mixing SS with additives, pelletization process, pyrolysis residence time, process temperature and parameters such as yield of SCP, yield of pyrolysis oil, yield of pyrolysis gas, content of heavy metals (HMs), calorific value, C_{org}, pH, EC, and S_{BET}. The product of pretreatment is feedstock (FS) for MT process which can directly be used for energy or agricultural use. Mixing and pelletizing process improve the FS qualitative parameters for the certification of solid alternative fuel and the subsequent certification of biochar or the soil amendment substances. For certification of biochar or soil amendment substances, it is necessary to prepare mix of raw dried SS with additives to improve the feedstock qualitative parameters for the subsequent certification of biochar/soil amendment substances to increase organic matter or to improve other properties such as C_{org}, S_{BET} etc. We conclude that slow MT with SCP represents an eco-friendly way of SS disposal, which belongs among the important strategies of circular economy.

1. Introduction

In the European Union (EU), circular economy strategy of wastewater (WW) treatment postulates a search for new ways of reusing sewage sludge (SS). Thermal treatment, such as incineration, gasification, hydrothermal carbonation (HTC), pyrolysis, and torrefaction represent acceptable solutions of SS disposal. Two different ways exist, the first one is incineration of SS for energy production and the second one is SS transformation into a new product for other use, especially for agriculture. The second way represents a research challenge, especially solid carbonaceous product (SCP) after pyrolysis, torrefaction. The term biochar can be used under the assumption of strict certification thus in this paper is used SCP. The application of SCP, generally called biochar, might be today one of the most significant challenges in WW sludge management, for example in agriculture. Therefore, it is necessary to define its characteristics and compare it with guidelines certification process for application in agriculture as a soil amendment.

1.1. Disposal of sewage sludge

Currently, the disposal of SS is predominantly managed by landfilling, incineration and agricultural use. Disposal of the SS is one of the most important issues in circular economy that is a part of the waste management strategy implemented by the EU. In the Czech Republic (CR) the disposal of SS has received significant attention mainly due to the new Decree No. 437/2016 [1] strictly regulating the SS landfilling and direct application in agriculture. New incineration plants are not supported due to public and political reasons.

The landfilling of SS is not supported by the EU and is strictly restricted in several EU countries. SS contains a lot of organic matter which is decomposed at the landfill sites and generates CH_4 which contributes even more than CO_2 to the greenhouse effect. And the cost of the land needed for landfill is increasing because of its decreasing availability [2].

The incineration reduces the volume of SS up to 70% and decreases pathogens and toxic organic compounds [3,4]. Generally, SS has a calorific value similar to the energy in brown coal, thus incineration can be performed to obtain energy. Fossil fuel savings would be possible and further advantage of the incinerator is that the net CO_2 addition to the atmosphere decreases, thus contributing to overall CO_2 reduction [2]. At present, incineration of SS is carried out either directly at waste water treatment plant (WWTP) as monoincineration, or as the coincineration of SS with coal or other wastes, or the combustion of SS in cement kilns [5]. Relatively small number of incinerators of SS is located at WWTP to recover the energy of waste to the treatment process [2]. Ash of incineration of SS contains larger quantities of heavy metals (HMs), namely Cr, Cu, Ni, Pb, Zn and Fe, and is more toxic than the ash from coal combustion [6]. The reuse of the ash of SS is another topic that has to be addressed and the incineration of SS in cement kilns could solve the problem of ash disposal [2,6,7].

SS contains organic matter, nitrogen and phosphorus, which can be used as a fertilizer in agriculture [2]. The hazardous substances limiting the use of SS in agriculture are HMs [8,9], and in the near future legislation will implement also the limits for the content of organic pollutants [10] and microplastics [11].

Generally, the term SS waste from WWTP with organic content can also be defined as biosolids. Thermochemical treatment processes can be classified into two main categories such as thermochemical oxidative processes and thermochemical reductive processes. Thermochemical oxidative treatment processes include combustion in which oxygen is present in stoichiometric or larger amounts. Thermochemical reductive processes include pyrolysis, gasification and hydrothermal carbonization [12].

1.2. Pyrolysis and torrefaction of solid carbonaceous product

Pyrolysis is the thermochemical reductive process of converting biosolids into carbon rich SCP, having yield above 10-80% carried out under a wide temperature range 100-1 300°C, at wide residence time 0.05s-12h under low or atmospheric pressure [13-16]. The other products of pyrolysis are pyrolysis oil, thus bio-oil mixed with water, and pyrolysis gas, thus syngas which mainly contains CO, CO_2, CH_4 and H_2.

Selected literature suggests torrefaction [15,17-21], which can be described as a mild pyrolysis, when biosolids are heated in an inert atmosphere at temperature about 200-300°C for residence time 30min-4h. Torrefaction produces primarily 60-80% solid, 20-40% gases, and a relatively small amount of liquid that can be burned together with gases.

The pyrolysis process can be further divided into two classes such as conventional and microwave assisted pyrolysis (MAP) [22,23] / microwave torrefaction (MT) [24]. MAP and MT are the most efficient thermal treatment under which process conditions are more favorable in energetic and economic terms [25]. This technology can have advantages associated with faster production and a significant reduction in energy losses compared to conventional methods [26].

Thermal pyrolysis transformation of biosolids including SS produces pyrolysis oil, pyrolysis gas and SCP called either charcoal or biochar. The term char or carbon is used for the solid substances of the decomposition of natural and synthetic organic material [27]. Lehmann and Joseph [28] reported that charcoal is used as fuel for heat, as a filter, as a reductant and biochar is used in environment management, agricultural and carbon sequestration.

1.3. Solid carbonaceous product produced by microwave torrefaction

Raw SS generated at sludge management of WWTPs shows typically the content of a dry solid (DS) between 1-5% depending on the origin, and the average DS content of digested SS is 4% [29]. Generally, the next step as dewatering in combination with chemical management can achieve 25% DS of SS. The final step for pretreatment of SS prior to the pyrolysis is drying. The drying temperature of SS is an important parameter, as low-temperature drying ensures a less explosive environment. Generally, the most commonly used drying SS systems are fluidized convection ovens, belt dryers, and solar dryers. Conventional slurry fluid and belt dryers provide a unified granule size with the following properties: dry matter around 85-95%, dusty to coarse-grained granulate or without dusty particles, bulk density 400-900 $kg \cdot m^{-3}$ depending on the shape of the SS particles [30].

Based on the type of MT, the dried SS may require mixing with additives [24]: catalyst and organic additives. The catalyst represents the additive with theoretically catalytic effect, thus various types of zeolites was added and mixed with SS to absorb microwave radiation after evaporation of moisture and to support catalytic cracking of specific hydrocarbons. The organic additives represented by organic matter, such as wood sawdust, lignin, and hay, was mixed with SS in order to adjust physical properties of pellets, to increase the ratio of organic matter and surface area in the SCP.

The next step after mixing SS with additives is pelletization. Based on the literature data [31], the parameters of pellets should comply with the depth of microwave radiation and batch height. Generally, the knowledge of penetration depth is important for homogeneously irradiated MT processed output. Thus, SS was mixed with additives and consequently pelletized for MAP and MT process. The pellets with 6 mm diameter were pressed and passed through a hot die of the pelletizing press, the surface became smooth and partially "baked". Such an encapsulated pellet thus formed a kind of "micro-reactor" and processes during MAP and MT were similar to the so-called "pop-corn" effect responsible for pores formation [24]. Another considerable benefit of such pelletization is the ease of handling the produced SCP, which otherwise leads to problem with dust. On the contrary, the disadvantage of pelletizing of SS is energy demanding treatment process.

SCP may represent the main product of pyrolysis included MT of SS which can be consequently one of the most significant challenges in WW management for energy and agricultural use.

Fonts et al. published that the calorific value of biochar after pyrolysis is 5-21 $MJ \cdot kg^{-1}$ [2]. Furthermore, unlike other thermochemical processes such as combustion or gasification, pyrolysis is an endothermic reaction, and this means that the pyrolysis products may have higher calorific value than the raw material. Kim and Parker

[32] found that the pyrolysis oil and the biochar of pyrolysis at 300 °C of thickened waste activated sludge (TWAS) had combustion energy content higher than the raw SS. In the CR, dried SS and SCP can be certificated as solid alternative fuel according Decree No. 415/2012 [33] and Czech standard ČSN EN ISO / IEC 17067 [34].

SS is a renewable source of valuable compounds for agricultural use such as carbon, phosphorus, nitrogen, potassium etc. [35]. SS is an important strategy source of phosphorus because the natural sources are estimated to be exhausted around 2 300 [36]. But SS can also be a source of hazardous substances such as HMs, pathogens, organic pollutants, microplastics etc. [8-11]. To produce certified biochar from SS, the thermochemical reductive treatment process should be defined together with pretreatment procedures of raw SS. The description of analyses includes determination of the solid yield of biochar, immobilization of HMs in SS by the production of biochar, and other parameters according to the two guidelines: The International Biochar Initiative (IBI) [37] and The European Biochar Certificate (EBC) [38]. Selected parameters for biochar certification according to guidelines IBI [37] and EBC [38] are reported in Table 1, the requirements are divided into biochar of category A/B (IBI) and biochar premium/basic (EBC). For biochar of category A and premium biochar the limits of selected parameters are stricter. The selected parameters are divided into main general parameters such as toxicant assessment, maximum allowed thresholds and other parameters.

Table 1 Selected parameters for biochar certification according to guidelines [37,38]

			Guidelines to biochar certification			
General parameter	**Selected parameter**	**Unit**	**International Biochar Initiative (IBI)** [37]		**European Biochar Certificate (EBC)** [38]	
			Category A	**Category B**	**Premium**	**Basic**
Toxicant assessment, maximum allowed thresholds - HMs	As	mg·kg^{-1} dry wt-mass	13	100	13	13
	Cd		1.4	20	1	1.5
	Cr		93	100	80	90
	Cu		143	6 000	100	100
	Pb		121	300	120	150
	Hg		1	10^{a}	1	1
	Ni		47	400	30	50
	Zn		416	7 400	400	400
Other parameters	C_{org}	%	≥60	≥30	≥50	
	pH	pH	Declaration		Declaration	
	Electrical conductivity	dS·m^{-1}	Declaration		Declaration	
	S_{BET}	m^{2}·g^{-1}	-		≥150	

Notes: C_{org} - organic carbon; ^{a} methyl mercury 10 mg·kg^{-1} and inorganic mercury 40 mg·kg^{-1}.

In the CR, other options for certification of SCP of MT is certification according to the Regulation No. 156/1998 [39] which defined the soil amendment substances as substances without a number of nutrients, which biologically, chemically or physically affect the soil, improve its state or increase the efficiency of fertilizers. The characteristics of biochar pyrolysis of SS for agricultural use were presented in a separate review publication the authors of this article [paper in press 40].

Based on a previous biochar review of SS, this paper presents new results and develops the characterization of the produced SCP for combustion energy and agricultural use. The analyses included determination of the following parameters: mixing SS with additives, pelletization process, pyrolysis residence time, process temperature, yield of SCP, yield of pyrolysis oil, yield of pyrolysis gas, content of HMs, calorific value, C_{org}, pH, EC, and S_{BET}. This paper aims to increase the knowledge of the SCP/biochar of SS after MT and the conclusions may serve as the basis for biochar certification. The product of pretreatment is feedstock for MT process which can be used for energy or agricultural use. Mixing and pelletizing process improve the feedstock qualitative parameters for the certification of solid alternative fuel and the subsequent certification of biochar or the soil amendment substances. For certification of biochar or soil amendment substances, it is necessary to prepare mix of raw dried SS with additives to improve the feedstock qualitative parameters for the subsequent certification of biochar/soil amendment substances to increase organic matter or to improve other properties such as C_{org}, S_{BET} etc.

2. Materials and methods

Current applied research of MT at AdMaS Research Centre, BUT in the CR is performed in a laboratory and under full-scale conditions. For this paper, the pretreatment of SS samples for MT consists in two consequent steps: mixing dried SS with additives and pelletizing this mixture according Fig. 1. For experiments were used dried SS from two WWTPs, dried SS from a contact blade paddle dryer in the form of dust particles and dried SS from a conventional belt dryer in the shape of noodles. SS was mixed in different ratios with the following additives: catalyst and organic additive.

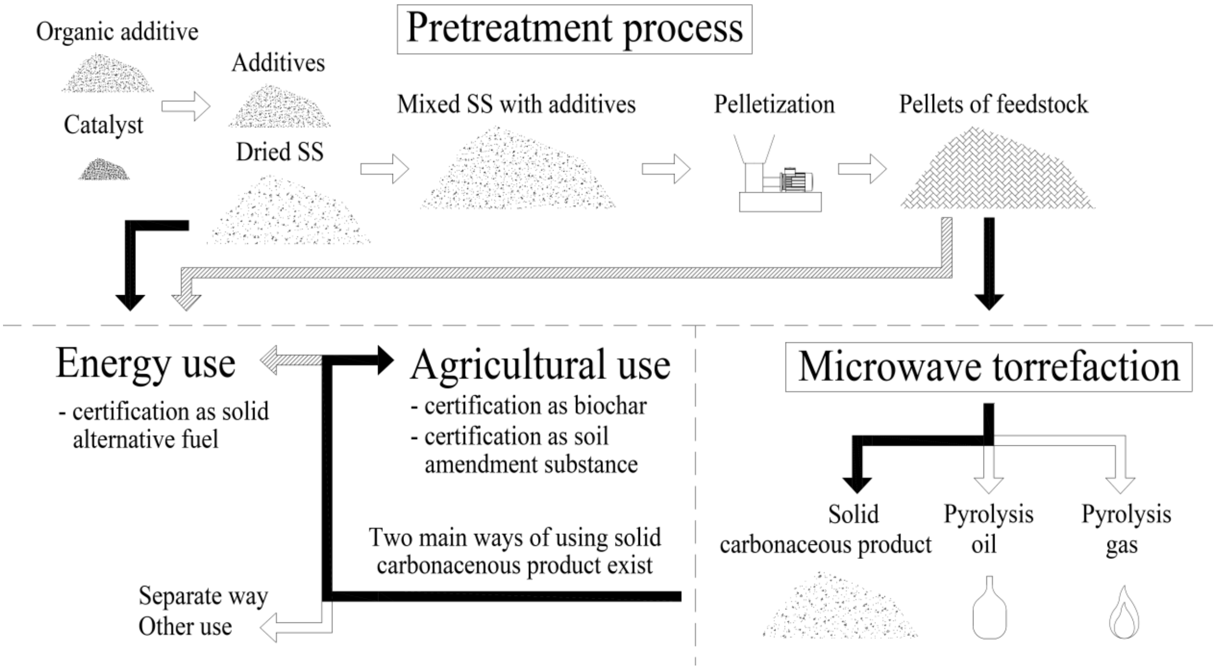

Fig. 1 Scheme of pretreatment and MT process, the main direction is indicated by solid arrows

2.1. Low temperature slow MT unit setting

Current applied research of MT is performed in a laboratory and under full-scale conditions, there are available 3 MT units [41]. For these experiments were used small full-scale MT unit which works at low pressure 800 hPa. Microwave was generated by magnetron with 3.0 kW input power and with 2.45 GHz. This unit works discontinuously, and the maximum capacity is approx. 12 kg·batch^{-1} of feedstock. The glass condensator attached to the pyrolyzer was used for separation of gaseous products and the pyrolysis oil. For incoming and reflected waves a tuner was installed.

For these experiments, the pelletization process used an extrusion die having 6.4 mm. The pyrolyzed feedstock were approx. 6.4 mm diameter pellets of mixed SS with additives made by pelletizing press. The input weight of feedstock samples was 1.3 kg·batch^{-1}. The feedstock was input to the MT unit in a stainless-steel bowl, the inner diameter was 194 mm, the vessel height was 80 mm and the wall thickness was 3 mm. The height of the feedstock in bowl was approx. 60 mm. The end of the wave tube from the magnetron was 100 mm from the top of the feedstock. During the experiments, the output power of magnetron was 2.7 kW, residence time was 60 minutes, and the temperature during the tests did not exceed 351 °C.

2.2. Sewage sludge samples

The SS composition depends on quality and quantity of the inflow and type of WWTP. The quality and quantity of the inflow strongly influence the chemical composition and physicochemical properties of SS. The SS was contaminated by various HMs originating largely from industrial WW. Thus, SS compositions and characteristics were different for each WWTP.

Raw SS samples

Anaerobically digested and thermally dried SS from two different municipal WWTPs were pyrolyzed.

The WWTP1 has a capacity of around 530 000 population equivalent (PE). WW is predominantly municipal WW originating from households. Only 12-15 % are industrial influents, but generally this WW mostly has the character of municipal WW. The SS was dried using a contact blade paddle dryer at temperature lower than 100 °C. Tested raw dried samples of SS from WWPT1 had dry solids (DS) around 91 % and output fraction from dryer was a powder like material with particle fraction 1-8 mm, see Fig. 2. Random tests revealed that the hygroscopic water content was below 2.0 %.

The WWTP2 has a capacity of around 90 000 PE. WW is a typical municipal WW from households, part of WW came from hotels and restaurants. Several percent of industrial WW originated from the production of mineral water which contains relatively higher concentrations of As. The SS was dried using a belt dryer at the temperature lower than 85 °C. Tested raw dried SS samples from WWTP2 had DS around 90 % and output fraction from the dryer was a noodle of around 25 mm in length and around 5 mm in diameter, see Fig. 2. Random tests revealed that the hydroscopic water content was below 2.0 %.

Fig. 2 Selected dried raw SS (left: powder shape sample of WWTP1, right: noodle shaped sample of WWTP2)

Mixing SS with additives

Our previous research focused on the pretreatment of dried SS prior to the MT, namely on mixing process with additives and pelletizing process of this mixture [24]. The dried SS may require mixing with catalyst and/or organic additives. The catalyst was added and mixed with SS to absorb microwave radiation after evaporation of moisture and to support catalytic cracking of specific hydrocarbons. SS contains low-level of organic matter thus the organic additive was added to increase the ratio of organic matter and surface area in the SCP. Based on our previous research [paper in press 42], catalyst and organic additive can be used to immobilize most of HMs in biochar structure.

Dried SS from WWTP1 was mixed with catalyst: crushed limestone (in the ratio 98:2%, i.e. 98% SS and 2% additive), and organic additives: waste cellulose (95:5%), plastic waste – low density polyethylene (LDPE, 95:5%), wooden sawdust (90:10%), hay (70:30%), and husks (70:30%).

Dried SS from WWTP2 was mixed with catalyst: crushed limestone (98:2%), and organic additives: waste cellulose (95:5%), plastic waste LDPE (95:5%), wooden sawdust (90:10%), wooden dust (90:10%), hay (70:30%), and husks (70:30%).

Selected mixtures of organic additives are show in Fig. 3; this represents the state before the pelletization process.

Fig. 3 Selected mixture of dried raw SS with organic additive (left: SS of WWTP1 with plastic waste LDPE, right: SS of WWTP2 with cellulose)

Pelletized feedstock

The mixtures of dried raw SS with catalysts and organic additives were pelletized by industrial pelletizing press. The extraction matrix was used for SS with 6.4 mm diameter holes. The additive type, ratio SS:ADD (additive), and density before and after pelletization process are reported in Table 2 and Table 3.

Table 2 Feedstock composition of WWTP1 before and after pelletization process

Additive type		**Ratio SS:ADD (%)**	**Sample ID**	**Density (kg·m^{-3})**
Catalyst	Crushed limestone	98:2	MFS1.1 - mixtures FS1.1 - pellets	820 726
Organic additives	Waste cellulose	95:5	MFS1.2 - mixtures FS1.2 - pellets	685 772
	Plastic waste (LDPE)	95:5	MFS1.3 - mixtures FS1.3 - pellets	800 670
	Wooden sawdust	90:10	MFS1.4 - mixtures FS1.4 - pellets	694 775
	Hay	70:30	MFS1.5 - mixtures FS1.5 - pellets	774 710
	Husks	70:30	MFS1.6 - mixtures FS1.6 - pellets	590 736

Notes: SS-sewage sludge, MFS-mixtures of feedstock, FS-feedstock, SCP-solid carbonaceous product, ADD-additive

During the pelletizing process of mixtures from WWTP1, the temperature not exceeded 75 °C. The density of mixtures dried powder shape SS from WWTP1 and additives was 590-820 kg·m^{-3}. After pelletizing process the density was 670-775 kg·m^{-3}.

Table 3 Feedstock composition of WWTP2 before and after pelletization process

Additive type		**Ratio SS:ADD (%)**	**Sample ID**	**Density (kg·m^{-3})**
-	Dried SS	100:0	SS2.1 - input FS2.1 - pellets	318 736
Catalyst	Crushed limestone	98:2	MFS2.2 - mixtures	350

			FS2.2 - pellets	690
Organic additives	Waste cellulose	95:5	MFS2.3 - mixtures	350
			FS2.3 - pellets	742
	Plastic waste (LDPE)	95:5	MFS2.4 - mixtures	340
			FS2.4 - pellets	650
	Wooden sawdust	90:10	MFS2.5 - mixtures	392
			FS2.5 - pellets	764
	Wooden dust	90:10	MFS2.6 - mixtures	374
			FS2.6 - pellets	620
	Hay	70:30	MFS2.7 - mixtures	360
			FS2.7 - pellets	680
	Husks	70:30	MFS2.8 - mixtures	394
			FS2.8 - pellets	644

Notes: SS-sewage sludge, MFS-mixtures of feedstock, FS-feedstock, SCP-solid carbonaceous product, ADD-additive

During the pelletizing process of mixtures from WWTP2, the temperature did not exceed 69 °C. The density of mixtures dried noodle shape SS from WWTP2 and additives was 318-394 $kg \cdot m^{-3}$. After pelletizing process the density was 620-764 $kg \cdot m^{-3}$. Selected pellets of feedstock SS with organic additive and catalyst are show in Fig. 4, this represents the state after the pelletization process.

Fig. 4 Selected pellets of feedstock SS with organic additive and catalyst (left: feedstock of WWTP1 with wooden sawdust, right: feedstock of WWTP2 with crushed limestone)

Solid carbonaceous product after microwave torrefaction

Input weight of feedstock samples was 1.3 $kg \cdot batch^{-1}$ per dose. These pellets of feedstock with additives were pyrolyzed in MT reactor at low pressure 800 hPa, the output power of magnetron was 2.7 kW, residence time was 60 minutes, and temperature during the tests did not exceed 351 °C. Selected pellets of feedstock additives are show in Fig. 5; this represents the state after the MT process.

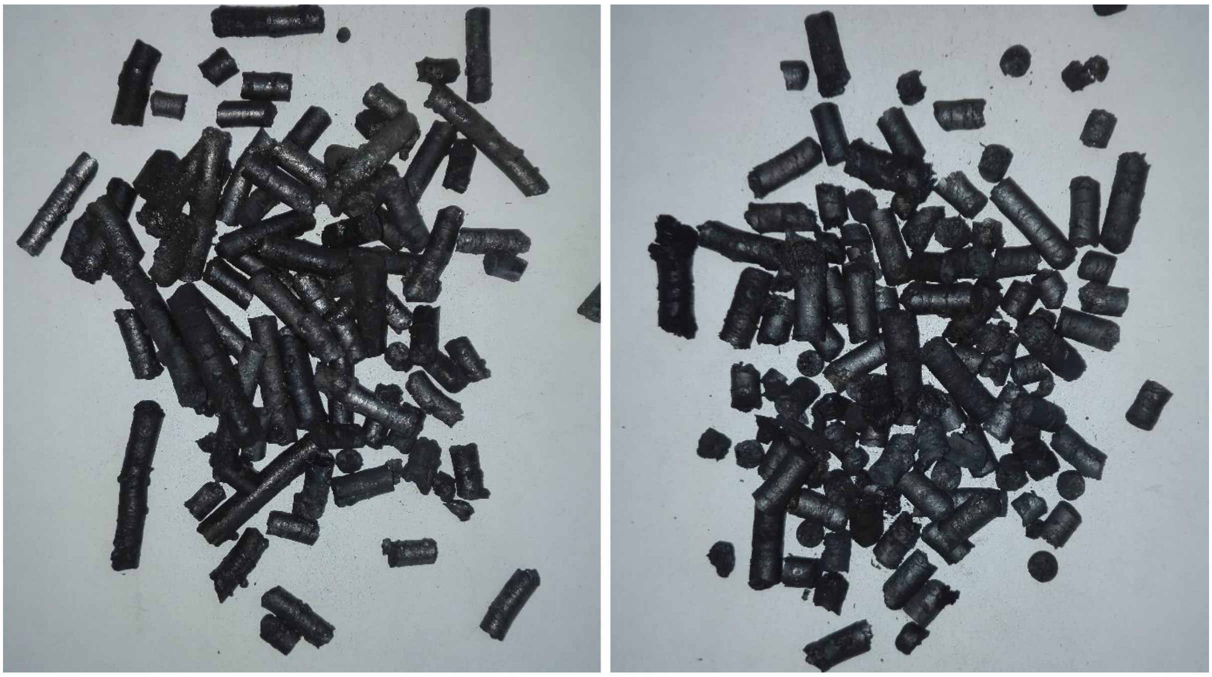

Fig. 5 Selected pellets of solid carbonaceous product (left: SCP of feedstock of WWTP1 with husks, right: SCP of feedstock of WWTP2 with hay)

2.3. Testing

The combustion tests were determined in feedstock and in carbonaceous product. Content of HMs was determined in feedstock and in SCP, and the total HMs content was determined after digestion of samples in *Aqua Regia*. C_{org}, pH, EC, and S_{BET} were carried out to selected samples.

Combustion test

The combustion tests were carried out according to the Czech standard ČSN EN ISO 1716 (7300883). The energy efficiency of samples was measured by semi-automatic device (IKA C 200) under the standard laboratory conditions.

At the first part, the random small doses were determined for combustion tests. The small doses were ground to fine dust by friction dishes. The quantity of fine dust 0.4-0.8 g was prepared for measurement of calorimetric energy and input to calorimetric bomb of the specimen holder. The dose was interfaced with the spark plug circuit using a cotton thread. The entire specimen holder assembly was placed in a calorimetric bomb which was sealed and supplemented with pure oxygen at an internal pressure of 34 bar. The calorimetric bomb was input to a calorimetric heat-insulated container with demineralized water. With constant intensive stirring of water in a calorimetric vessel, the water temperature was monitored for 3 minutes until a constant value was established. Subsequently, a bomb sample was ignited by the ignition circuit, and a calorific value was determined from the temperature change in the calorimetric vessel as a result of the contribution tests of the sample. The results were the average of the three calorific values for each sample.

Determination of HMs

For comparison, primary and secondary samples were measured by two optimization methods. For the optimization of the AMA and AAS methods for determination of selected HMs were used certified reference materials of calibration standard solutions ASTASOL® with concentration of measured metal 1000±0.002 $mg \cdot L^{-1}$ in 5% HNO_3, from Analytika Ltd., Czech Republic (Czech Metrological Institute). All other used chemicals were of analytical reagent grade.

Digestion in *Agua Regia* was performed as follows: 10 grams of the milled sample was transferred to a flask containing 60 mL of *Aqua Regia* ($HCl:HNO_3$ in a ratio 3:1). The sample thus prepared was boiled under reflux for 2 hours. After cooling, the sample was filtered. For analysis, it was diluted with distilled water in a ratio of 1:8. Thermal programs for the determination of selected HMs (As, Cd, Cr, Cu, Pb, and Zn) are reported in Table 4.

Analyses of HMs contents were performed using atomic absorption spectrometer with electrothermal atomization ZEEnit 60 from Analytik Jena (Germany) with Zeeman background correction and selected hollow cathode lamp by Photron (Australia). Optimal measurement parameters and specific temperature program were used for each HM. Other conditions were graphite cuvette with platform, slit width 0.2-0.8 nm, used current was

3-8 mA and injection volume 20 μL. All obtained results are the average of three separate independent determinations, each was measured for atomic absorption spectrometer five times.

Table 4 Thermal programs for the determination of selected HMs: As, Cd, Cr, Cu, Pb, and Zn

Metal	**Wavelength (nm)**	**Drying 1/2/3 (°C)**	**Pyrolysis (°C)**	**Atomization (°C)**	**Cleaning (°C)**
As	193.70	90/100/110	1 000	2 200	2 400
Cd	228.80	90/105/110	500	1 500	2 300
Cr	357.90	90/110/120	1 000	2 100	2 400
Cu	324.80	90/110/130	1 000	1 800	2 300
Pb	283.30	90/100/110	1 100	2 000	2 300
Zn	213.90	90/105/120	600	1 800	2 300

Hg was analysed on atomic spectrometer Advanced Mercury Analyzer AMA 254 (Altec, s. r. o., Czech Republic) at wavelength 253.65 nm under conditions reported in Table 5.

Table 5 Temperature mode of the AMA 254, for the determination of Hg

Process	**Drying (°C)**	**Decomposition (°C)**	**Waiting (s)**
Cleaning	60	120	45
Blank	60	60	45
Calibration	60	120	45
Determination	10	200	50

Determination of C_{org}, pH, EC, and S_{BET}

C_{org} determination was performed by Shimadzu TOC-LCSH/CPH analyzer. The evaluation was performed using the TOC-L Sample Table Editor software. The crushed sample was placed in a container and added to analyzer. The input temperature was 900 °C, the sample was analysed at 5-10 minutes depending on the weight and type of sample. The test was performed 3 times and the average was calculated.

Electric conductivity (EC) was measured on conductometer ECTestr 11+ (Oakton Instruments), and pH values were measured on a Shott pH meter (SI Analytics, GmbH), and calibration was performed on pH 7 buffer. S_{BET} was measured by Quantachrome Nova 3200e gas adsorption and using NovaWin software. Nitrogen was used with the setting: adsorption/desorption 0.050/0.050, time equilibrium adsorption/desorption was 240/240 s, time equilibrium output adsorption/desorption was 480/480 s, temperature was -196 °C. Samples were degassed in a vacuum dryer for 24 hours at 50 °C. S_{BET} was determined at five points using a multi-point BET method. BJT analysis was used for pore size analysis. 24 points were measured for adsorption and 38 points were measured for desorption.

3. Results and discussions

The characterization of the SCP was carried out for combustion energy and agricultural use. The results included these parameters: yield of SCP, yield of pyrolysis oil, yield of pyrolysis gas, calorific value, content of HMs, C_{org}, pH, EC, and S_{BET}.

3.1. Temperature, yields and combustion energy

Feedstock (FS) composition from WWTP1 and SCP composition after MT is reported in Table 6. The crushed limestone as one catalyst was used. Five organic additives were used: waste cellulose, plastic waste LDPE, wooden sawdust, hay, and husks. These selected parameters were measured: moisture, pellet diameter, temperature, yield of SCP, yield of pyrolysis oil, yield of pyrolysis gas, and calorific value.

Table 6 FS composition from WWTP1 and SCP composition after MT: temperature, yields, and energy

Additive type		**Ratio SS:ADD (%)**	**Sample ID**		**Moisture (%)**	**Pellet diameter (mm)**	**Maximum temperature (°C)**	**Yields (%)**			**Calorific value ($MJ \cdot kg^{-1}$)**
								SCP	**Pyrolysis oil**	**Pyrolysis gas**	
Catalyst	Crushed limestone	98:2	FS1.1	FS1.1-1	6.9	6.50	-	-	-	-	12.05
			SCP1.1	SCP1.1-1	2.9	5.78	277	58.2	8.8	33.0	10.26
				SCP1.1-2	2.9	5.70	330	59.5	9.4	31.1	-
				SCP1.1-3	-	5.98	245	62.5	7.8	29.7	-
Organic additives	Waste cellulose	95:5	FS1.2	FS1.2-1	7.1	6.39	-	-	-	-	12.57
			SCP1.2	SCP1.2-1	2.7	5.82	248	59.1	10.8	30.1	10.71
				SCP1.2-2	-	5.45	210	60.2	10.4	29.4	-
				SCP1.2-3	-	5.81	208	62.2	10.2	27.6	-
	Plastic waste (LDPE)	95:5	FS1.3	FS1.3-1	8.9	6.42	-	-	-	-	13.48
			SCP1.3	SCP1.3-1	0.6	5.20	240	62.5	6.8	30.7	11.03
				SCP1.3-2	-	5.40	260	62.7	7.5	29.8	-

				SCP1.3-3	-	5.70	288	66.2	7.0	26.8	-
	Wooden sawdust	90:10	FS1.4	FS1.4-1	3.4	6.49	-	-	-	-	13.30
			SCP1.4	SCP1.4-1	3.2	5.46	260	61.7	8.5	29.8	10.29
				SCP1.4-2	-	5.40	278	55.5	7.2	37.3	10.62
				SCP1.4-3	-	5.46	278	64.0	4.4	31.6	12.09
	Hay	70:30	FS1.5	FS1.5-1	5.7	6.51	-	-	-	-	13.47
			SCP1.5	SCP1.5-1	3.3	5.45	351	46.3	11.3	42.4	9.36
				SCP1.5-2	-	5.61	275	55.8	9.2	35.0	12.54
				SCP1.5-3	-	5.32	271	56.8	15.4	27.8	12.91
	Husks	70:30	FS1.6	FS1.6-1	4.6	6.59	-	-	-	-	13.60
			SCP1.6	SCP1.6-1	3.1	5.40	271	56.9	12.6	30.5	13.78
				SCP1.6-2	-	5.45	222	56.7	12.7	30.6	13.11
				SCP1.6-3	-	5.45	239	60.0	11.0	29.0	9.84

Notes: FS-feedstock, SCP-solid carbonaceous product, ADD-additive

According to Table 6, the moisture in FS was represented ranging from 3.4-8.9 % and after MT the moisture was lower ranging from 0.6-3.3 %.

The output pellet diameter was reduced from 6.39-6.59 before MT before MT to 5.20-5.98 mm after MT. This is related to weight reduction due to the MT process.

FS with 2% catalyst had maximum temperatures 245-330 °C, FS with 5% waste cellulose had maximum temperatures 208-248 °C, FS with 5% plastic waste LDPE had maximum temperature 240-288 °C, FS with 10% wooden sawdust had maximum temperature 260-278 °C, FS with 30% hay had maximum temperature 271-351 °C, FS with 30% husks had maximum temperature 222-271 °C.

FS with 2% catalyst had 58.2-62.5% SCP yields, 7.8-9.4% pyrolysis oil yields, and 29.7-33.0% pyrolysis gas yields. FS with 5% waste cellulose had 59.1-62.2% SCP yields, 10.2-10.8% pyrolysis oil yields, and 27.6-30.1% pyrolysis gas yields. FS with 5% LDPE had 62.5-66.2% SCP yields, 6.8-7.5% pyrolysis oil yields, and 26.8-30.7% pyrolysis gas yields. FS with 10% wooden sawdust had 55.5-64.0% SCP yields, 4.4-8.5% pyrolysis oil yields, and 29.8-37.3% pyrolysis gas yields. FS with 30% hay had 46.3-56.8% SCP yields, 9.2-15.4% pyrolysis oil yields, and 27.8-42.4% pyrolysis gas yields. FS with 30% husks had 56.7-60.0% SCP yields, 11.0-12.7% pyrolysis oil yields, and 29.0-30.6% pyrolysis gas yields.

FS with 2% catalyst had calorific value 12.05 MJ·kg^{-1} and SCP with 2% catalyst had calorific value lower 10.26 MJ·kg^{-1} than before MT. FS with 5% waste cellulose had calorific value 12.57 MJ·kg^{-1} and SCP had calorific value lower 10.71 MJ·kg^{-1} than before MT. FS with 5% LDPE had calorific value 13.48 MJ·kg^{-1} and SCP had calorific value lower 11.03 MJ·kg^{-1} than before MT. FS with 10% wooden sawdust had calorific value 13.30 MJ·kg^{-1} and SCP had calorific value lower 10.09-10.62 MJ·kg^{-1} than before MT. FS with 30% hay had calorific value 13.47 MJ·kg^{-1} and SCP had calorific value lower 9.36-12.91 MJ·kg^{-1} than before MT. FS with 30% husks had calorific value 13.60 MJ·kg^{-1} and SCP had calorific value lower 9.84, 13.11 MJ·kg^{-1} and higher 13.78 MJ·kg^{-1} than before MT.

SS and FS composition from WWTP2 and SCP composition after MT is reported in Table 7. The raw SS and crushed limestone as one catalyst were used. Six organic additives were used: waste cellulose, LDPE, wooden sawdust, wooden dust, hay, and husks. These selected parameters were measured: moisture, pellet diameter, temperature, yield of SCP, yield of pyrolysis oil, yield of pyrolysis gas, and calorific value.

Table 7 SS, FS composition from WWTP2 and SCP composition after MT: temperature, yields, and energy

Additive type		**Ratio SS:ADD (%)**	**Sample ID**		**Moisture (%)**	**Pellet diameter (mm)**	**Maximum temperature (°C)**	**Yields (%)**			**Calorific value (MJ·kg^{-1})**
								SCP	**Pyrolysis oil**	**Pyrolysis gas**	
-	Dried SS	100:0	SS2.1	SS2.1-1	2.4	6.49	-	-	-	-	13.49
			SCP2.1	SCP2.1-1	2.9	4.45	129	86.6	5.2	8.2	14.30
Catalyst	Crushed limestone	98:2	FS2.2	FS2.2-1	3.7	6.31	-	-	-	-	12.63
			SCP2.2	SCP2.2-1	1.9	5.20	242	65.5	15.6	18.9	11.64
				SCP2.2-2	-	5.00	2445	57.1	10.1	32.8	9.32
				SCP2.2-3	-	5.03	2734	56.2	9.8	34.0	9.68
Organic additives	Waste cellulose	95:5	FS2.3	FS2.3-1	6.5	6.51	-	-	-	-	12.61
			SCP2.3	SCP2.3-1	2.6	5.62	291	60.3	6.4	33.3	9.30
				SCP2.3-2	2.4	5.70	324	57.4	9.6	33.0	10.01
				SCP2.3-3	2.3	5.80	329	56.6	9.8	33.6	9.72
	Plastic waste (LDPE)	95:5	FS2.4	FS2.4-1	5.0	6.50	-	-	-	-	14.68
			SCP2.4	SCP2.4-1	2.5	5.43	310	54.8	5.0	40.2	12.01
				SCP2.4-2	-	5.44	274	56.7	7.5	35.8	-
				SCP2.4-3	-	5.41	250	55.8	6.6	37.6	-
	Wooden sawdust	90:10	FS2.5	FS2.5-1	17.2	6.51	-	-	-	-	13.60
			SCP2.5	SCP2.5-1	2.8	5.80	176	59.6	12.9	27.5	12.69
				SCP2.5-2	3.1	5.75	225	57.7	15.3	27.0	12.56
				SCP2.5-3	3.2	5.20	273	46.6	14.3	39.1	9.46
	Wooden dust	90:10	FS2.6	FS2.6-1	6.9	6.51	-	-	-	-	13.49
			SCP2.6	SCP2.6-1	2.8	5.42	296	45.2	12.5	42.3	10.01
				SCP2.6-2	2.6	5.48	263	46.1	9.5	44.4	11.19
				SCP2.6-3	2.3	4.83	313	62.1	8.3	29.6	-

Hay	70:30	FS2.7	FS2.7-1	3.8	6.54	-	-	-	-	13.49
		SCP2.7	SCP2.7-1	3.5	5.48	278	45.2	15.9	38.9	12.76
			SCP2.7-2	-	5.72	246	64.5	12.3	23.2	11.06
			SCP2.7-3	-	5.48	259	53.2	7.2	39.6	12.66
Husks	70:30	FS2.8	FS2.8-1	6.0	6.49	-	-	-	-	13.89
		SCP2.8	SCP2.8-1	3.4	5.71	281	47.5	9.9	42.6	11.72
			SCP2.8-2	3.5	5.71	276	48.2	7.5	44.3	12.67
			SCP2.8-3	3.6	5.72	268	45.9	11.2	42.9	11.10

Notes: SS-sewage sludge, FS-feedstock, SCP-solid carbonaceous product, ADD-additive

According to Table 7, the moisture in FS was represented ranging from 2.4-17.2 % and after MT the moisture was lower ranging from 1.9-3.6 %.

The output pellet diameter was reduced from 6.31-6.54 to 4.45-5.80 mm after MT This is related to weight reduction due to the MT process.

SS without additives had maximum temperature 129 °C, FS with 2% catalyst had maximum temperatures 242-274 °C, FS with 5% waste cellulose had maximum temperatures 291-329 °C, FS with 5% LDPE had maximum temperature 250-310 °C, FS with 10% wooden sawdust had maximum temperature 176-273 °C, FS with 10% wooden dust had maximum temperature 263-313 °C, FS with 30% hay had maximum temperature 246-278 °C, FS with 30% husks had maximum temperature 268-281 °C.

SS without additives had 86.6% SCP yields, 5.2% pyrolysis oil yields, and 8.2% pyrolysis gas yields. FS with 2% catalyst had 56.2-65.5% SCP yields, 9.8-15.6% pyrolysis oil yields, and 18.9-34.0% pyrolysis gas yields. FS with 5% waste cellulose had 56.6-60.3% SCP yields, 6.4-9.8% pyrolysis oil yields, and 33.0-33.6% pyrolysis gas yields. FS with 5% LDPE had 54.8-56.7% SCP yields, 5.0-7.5% pyrolysis oil yields, and 35.8-40.2% pyrolysis gas yields. FS with 10% wooden sawdust had 46.6-59.6% SCP yields, 5.0-7.5% pyrolysis oil yields, and 35.8-40.2% pyrolysis gas yields. FS with 10% wooden dust had 45.2-62.1% SCP yields, 8.3-12.5% pyrolysis oil yields, and 29.6-44.4% pyrolysis gas yields. FS with 30% hay had 45.2-64.5% SCP yields, 7.2-15.9% pyrolysis oil yields, and 23.2-39.6% pyrolysis gas yields. FS with 30% husks had 45.9-48.2% SCP yields, 7.5-11.2% pyrolysis oil yields, and 42.6-44.3% pyrolysis gas yields.

SS without additives had calorific value 13.49 MJ·kg^{-1} and SCP without additives had calorific value higher 14.30 MJ·kg^{-1} than before MT. FS with 2% catalyst had calorific value 12.63 MJ·kg^{-1} and SCP had calorific value lower 9.32-11.64 MJ·kg^{-1} than before MT. FS with 5% waste cellulose had calorific value 12.61 MJ·kg^{-1} and SCP had calorific value lower 9.30-10.01 MJ·kg^{-1} than before MT. FS with 5% LDPE had calorific value 14.68 MJ·kg^{-1} and SCP had calorific value lower 12.01 MJ·kg^{-1} than before MT. FS with 10% wooden sawdust had calorific value 13.60 MJ·kg^{-1} and SCP had calorific value lower 9.46-12.69 MJ·kg^{-1} than before MT. FS with 10% wooden dust had calorific value 13.49 MJ·kg^{-1} and SCP had calorific value lower 10.01-11.19 MJ·kg^{-1} than before MT. FS with 30% hay had calorific value 13.49 MJ·kg^{-1} and SCP had calorific value lower 11.06-12.76 MJ·kg^{-1} than before MT. FS with 30% husks had calorific value 13.89 MJ·kg^{-1} and SCP had calorific value lower 11.10-12.67 MJ·kg^{-1} than before MT.

The graph in Fig. 6 shows temperature during MT process for selected samples from WWTP1 with crushed limestone catalyst (SCP1.1-1, SCP1.1-3), and selected samples from WWTP2 without catalyst (SCP2.1-1) and with crushed limestone catalyst (SCP2.2-1, SCP2.2-3).

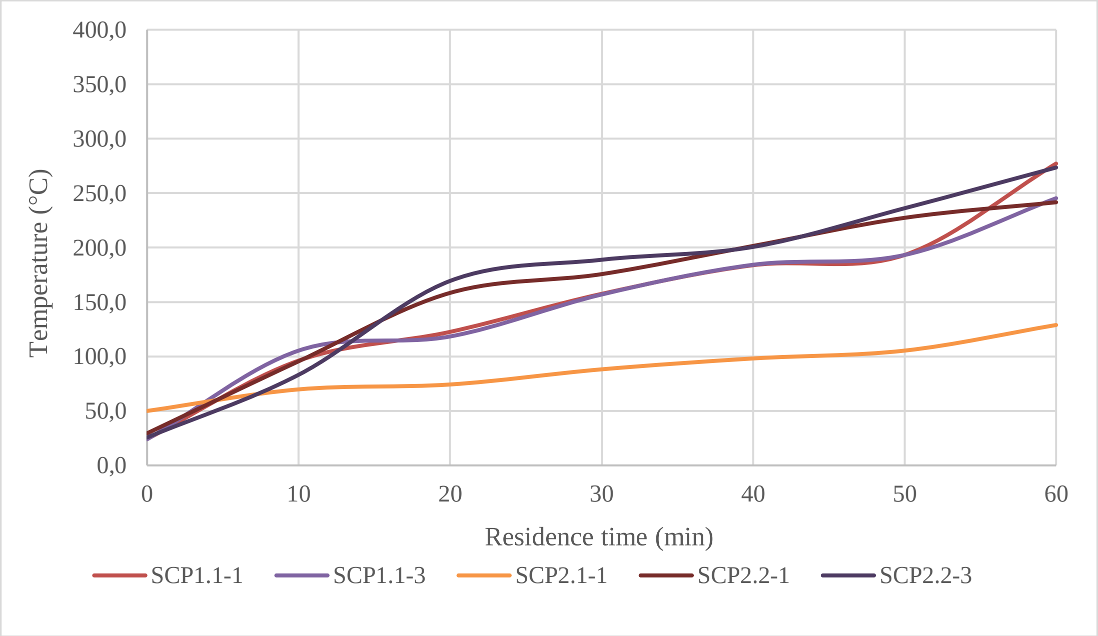

Fig. 6 Temperature during MT process for residence time, selected samples from WWTP1 and WWTP2 without additives and with catalyst

According to Fig. 6 sample from WWTP1 with 2% crushed limestone catalyst (SCP1.1-1, SCP1.1-3) achieved maximum temperature 245 and 277 °C and the course of temperature over time was linearly increasing. Sample from WWTP2 without additives (SCP2.1-1) achieved maximum temperature 130 °C and the course of temperature over time was almost linear and slightly rising. Samples from WWTP2 with 2% crushed limestone catalyst (SCP2.2-1, SCP2.2-3) achieved maximum temperature 242 and 274 °C and the course of temperature over time was linearly increasing.

The graph in Fig. 7 shows temperature during MT process for selected samples from WWTP1 with 5% waste cellulose (SCP1.2-1) and with 5% LDPE (SCP1.3-1), and selected samples from WWTP2 with 5% waste cellulose (SCP2.3-3) and with 5% LDPE (SCP2.4-1).

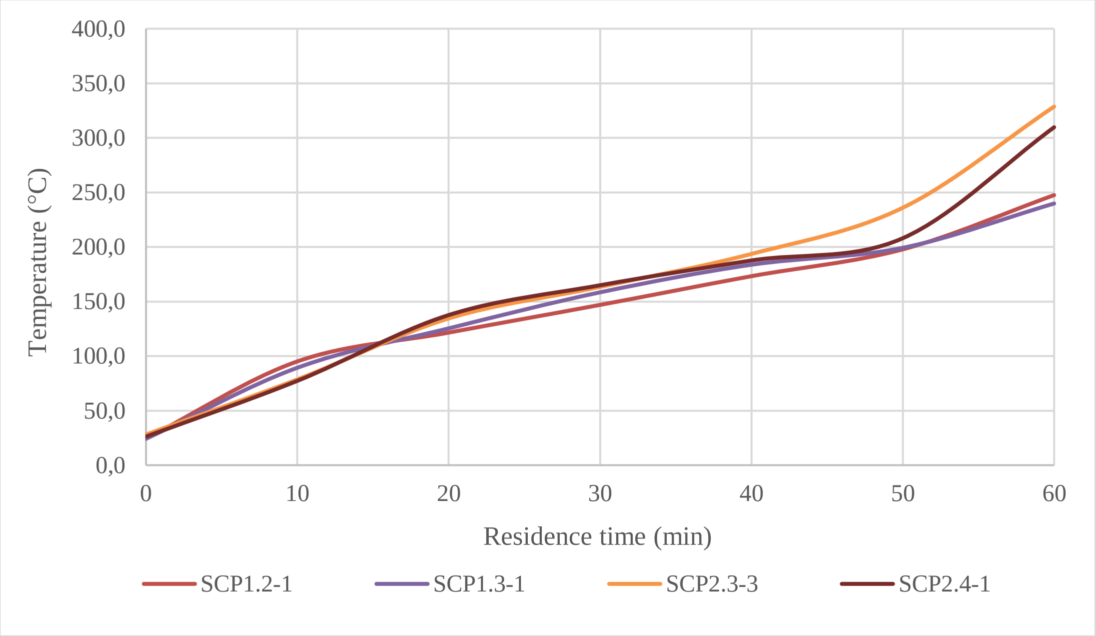

Fig. 7 Temperature during MT process for residence time, selected samples from WWTP1 and WWTP2 with 5% organic additives

According to Fig. 7 samples from WWTP1 with 5% waste cellulose (SCP1.2-1) achieved maximum temperature 248 °C and the course of temperature over time was linearly increasing. While samples from WWTP1 with 5% LDPE (SCP1.3-1) achieved maximum temperature 240 °C and the course of temperature over time was linearly increasing. Samples from WWTP2 with 5% waste cellulose (SCP2.3-3) achieved maximum temperature 329 °C and the course of temperature over time was linearly increasing but except for the final phase that had exponential endings. And samples from WWTP2 with 5% LDPE (SCP2.4-1) achieved maximum temperature 310 °C and the course of temperature over time was linearly increasing but except for the final phase that had exponential endings.

The graph in Fig. 8 shows temperature during MT process for selected samples from WWTP1 with 10% wooden sawdust (SCP1.4-1), and selected samples from WWTP2 with 10% wooden sawdust (SCP2.5-3) and with 10% wooden dust (SCP2.6-1).

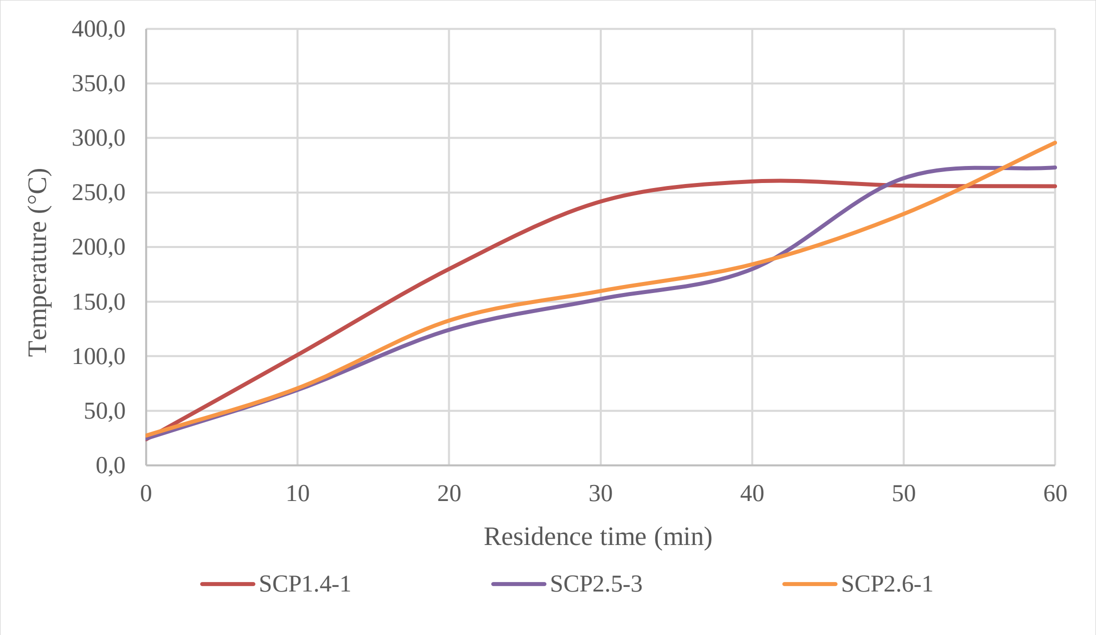

Fig. 8 Temperature during MT process for residence time, selected samples from WWTP1 and WWTP2 with 10% organic additives

According to Fig. 8 samples from WWTP1 with 10% wooden sawdust (SCP1.4-1) achieved maximum temperature 256 °C and the course of temperature over time had a relatively rapid exponential increase. Samples from WWTP2 with 10% wooden sawdust (SCP2.5-3) achieved maximum temperature 273 °C and the course of temperature over time was linearly increasing but except for the final phase that time had a relatively rapid exponential increase. And samples from WWTP2 with 10% wooden dust (SCP2.6-1) achieved maximum temperature 296 °C and the course of temperature over time was linearly increasing but except for the final phase that had exponential endings.

The graph in Fig. 9 shows temperature during MT process for selected samples from WWTP1 with 30% hay (SCP1.5-2) and with 30% husks (SCP1.6-3), and selected samples from WWTP2 with 30% hay (SCP2.7-1) and with 30% husks (SCP2.8-1).

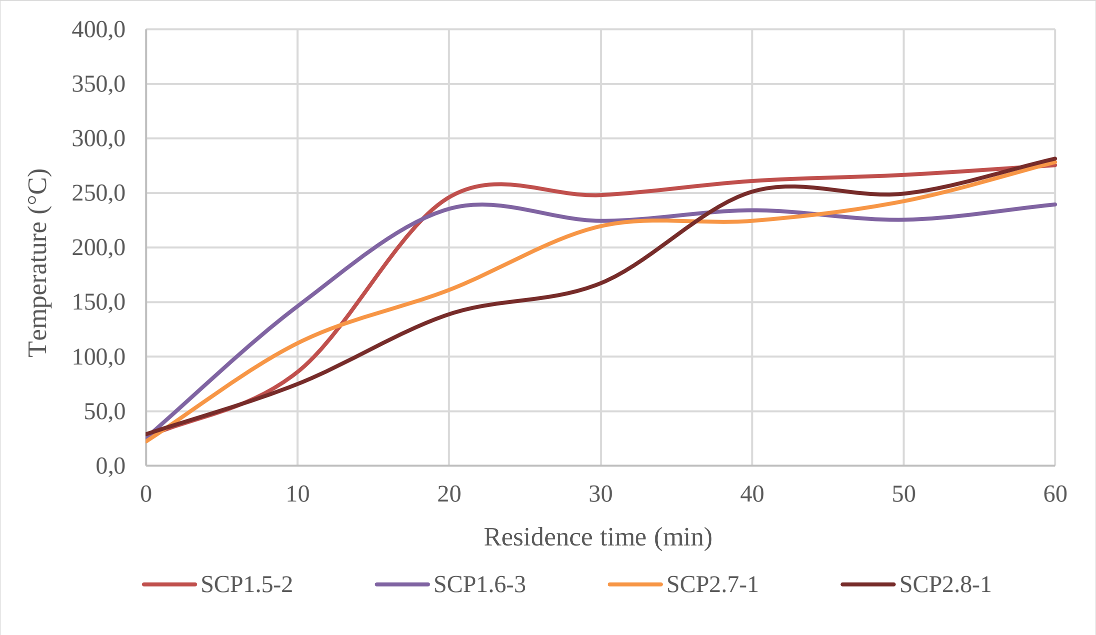

Fig. 9 Temperature during MT process for residence time, selected samples from WWTP1 and WWTP2 with 30% organic additives

According to Fig. 9 samples from WWTP1 with 30% hay (SCP1.5-2) achieved maximum temperature 275 °C and the course of temperature over time had a relatively rapid exponential increase. And samples from WWTP1 with

30% husks (SCP1.6-3) achieved maximum temperature 239 °C and the course of temperature over time had a relatively rapid exponential increase. Samples from WWTP2 with 30% hay (SCP2.7-1) achieved maximum temperature 278 °C and the course of temperature over time had a relatively rapid exponential increase. And samples from WWTP2 with 30% husks (SCP2.8-1) achieved maximum temperature 281 °C and the course of temperature over time had a relatively rapid exponential increase.

3.2. Content of HMs, C_{org}, pH, EC, and S_{BET}

FS composition from WWTP1 and SCP composition after MT is reported in Table 8. The crushed limestone as one catalyst was used. Five organic additives were used: waste cellulose, LDPE, wooden sawdust, hay, and husks. These selected parameters were measured: HMs (Cu, Pb, Cd, As, Ni, Cr, Hg, Zn), C_{org}, pH, EC, and S_{BET}.

Table 8 FS composition from WWTP1 and SCP composition after MT: HMs, C_{org}, pH, EC, and S_{BET}

Additive type		**Sample ID**	**Selected agricultural parameters**											
			HMs ($mg \cdot kg^{-1}$ DS)								**C_{org} (%)**	**pH (-)**	**EC ($\mu S \cdot cm^{-1}$)**	**S_{BET} ($m^2 \cdot g^{-1}$)**
			Cu	**Pb**	**Cd**	**As**	**Ni**	**Cr**	**Hg**	**Zn**				
Catalyst	Crushed limestone	FS1.1-1	384.92	29.81	3.01	5.28	24.04	268.34	50.25	3074.22	31.86	6.729	2480	-
		SCP1.1-1	639.98	43.44	3.45	11.81	35.89	372.75	1.32	3344.24	24.81	7.165	328	-
		SCP1.1-2	665.00	67.29	4.60	36.12	40.58	488.62	0.93	3273.48	-	7.040	535	-
		SCP1.1-3	379.36	58.62	4.72	14.77	36.74	336.30	3.34	3328.23	-	7.053	461	-
Organic additives	Waste cellulose	FS1.2-1	356.86	38.62	3.56	7.06	28.23	705.39	65.75	3030.88	31.29	6.625	2111	-
		SCP1.2-1	454.34	43.38	3.09	17.82	41.92	446.95	2.75	3977.99	34.46	7.331	534	-
		SCP1.2-2	557.03	40.96	4.02	45.72	42.47	378.75	2.28	3773.81	-	7.159	447	-
		SCP1.2-3	821.53	41.73	3.14	17.47	37.92	371.90	1.58	3987.01	-	7.153	354	-
	Plastic waste (LDPE)	FS1.3-1	451.07	35.45	3.55	14.48	25.31	300.38	60.28	4482.65	23.46	6.654	2040	-
		SCP1.3-1	628.20	40.75	2.94	31.51	41.20	406.30	1.08	2971.68	25.27	7.320	611	-
		SCP1.3-2	546.67	40.81	4.20	34.33	38.53	348.32	1.61	4817.75	-	-	-	-
		SCP1.3-3	652.02	42.50	4.04	18.84	39.25	403.95	1.28	3659.73	-	6.890	330	-
	Wooden sawdust	FS1.4-1	514.23	39.12	2.70	3.81	28.98	514.23	76.53	517.81	33.62	8.758	2041	-
		SCP1.4-1	659.10	52.56	2.47	5.22	48.54	659.10	6.49	594.45	26.93	7.991	765	-
		SCP1.4-2	718.61	55.51	3.06	5.65	50.18	718.61	3.90	612.82	-	7.560	602	-
		SCP1.4-3	622.10	47.69	4.64	3.85	34.99	622.10	17.41	492.07	-	6.555	453	-
	Hay	FS1.5-1	75.07	23.47	0.28	1.27	8.49	61.06	27.60	370.56	34.87	8.972	1952	1.078
		SCP1.5-1	164.93	32.79	2.13	20.86	23.84	96.52	0.65	661.87	33.19	8.232	1297	10.098
		SCP1.5-2	134.65	33.41	2.10	20.11	15.07	85.02	1.52	642.06	31.35	8.510	1127	6.394
		SCP1.5-3	98.11	27.20	1.07	0.85	15.82	92.11	2.41	595.67	29.85	8.614	1104	7.886
	Husks	FS1.6-1	108.31	22.12	0.57	1.07	7.55	65.84	32.16	447.28	33.92	5.495	2032	1.295
		SCP1.6-1	162.71	37.16	1.42	1.86	21.32	95.60	6.74	790.71	31.22	6.745	641	5.347
		SCP1.6-2	151.29	33.61	2.31	27.45	19.10	91.51	4.69	658.03	30.08	7.015	514	5.033
		SCP1.6-3	146.29	33.64	0.90	7.28	30.12	55.82	1.16	725.94	33.89	-	-	-

Notes: FS-feedstock, SCP-solid carbonaceous product, HMs-heavy metals, EC-electrical conductivity, S_{BET}-surface area

According to Table 8, SS from WWTP1, SCP with 2% crushed limestone catalyst showed predominantly higher content of Cu, Pb, As, Ni, Cr, Zn than before MT, while Cd content was not significantly different after MT, and Hg content is lower after MT. FS with 5% waste cellulose and FS with 5% LDPE showed predominantly higher content of Cu, Pb, As, Ni, Cr, Zn before MT, and Cd content was not significantly different after MT, and Hg content is lower after MT. FS with 10% wooden sawdust showed predominantly higher content of Cu, Pb, As, Ni, Cr, Zn before MT, and Cd content has not significantly changed after MT, while the Hg content is lower after MT. FS and SCP with 10% wooden sawdust showed lower content of As, and Zn than FS with 2% crushed limestone catalyst, 5% waste cellulose, and 5% LDPE. FS with 30% hay and FS with 30% husks showed predominantly higher content of Cu, Pb, Cd, As, Ni, Cr, Zn before MT, and Hg content is lower after MT. FS and SCP with 30% hay and with 30% husks has lower content all HMs than FS with 2% crushed limestone catalyst, 5% waste cellulose, 5% LDPE, and 10% wooden sawdust.

FS had C_{org} in range of 23.46-34.87 %, and higher values were achieved when added 30% hay or 30% husks. SCP had C_{org} lower after MT in range of 24.81-33.89 %.

FS had pH in range of 5.495-8.972, and higher values were achieved when added 10% wooden sawdust and 30% hay. SCP with 2% catalyst, 5% waste cellulose, 5% plastic waste, and 30% husks had pH higher after MT in range of 6.745-7.331. SCP with 10% wooden sawdust and 30% hay had pH lower after MT in range of 6.555-8.232.

FS had EC in range of 1952-2480 $\mu S \cdot cm^{-1}$ and SCP had EC lower after MT in range of 354-1297 $\mu S \cdot cm^{-1}$.

FS with 30% hay and 30% husks had S_{BET} in range of 1.078-1.295 $m^2 \cdot g^{-1}$ and SCP had S_{BET} higher after MT in range of 5.347-10.098 $m^2 \cdot g^{-1}$.

SS and FS composition from WWTP2 and SCP composition after MT is reported in Table 9. The crushed limestone as one catalyst was used. Five organic additives were used: waste cellulose, LDPE, wooden sawdust, hay, and husks. These selected parameters were measured: HMs (Cu, Pb, Cd, As, Ni, Cr, Hg, Zn), C_{org}, pH, EC, and S_{BET}.

Table 9 SS, FS composition from WWTP2 and SCP composition after MT: HMs, C_{org}, pH, EC, and S_{BET}

Additive type		Sample ID	Selected agricultural parameters											
			HMs (mg·kg^{-1} DS)								C_{org} (%)	pH (-)	EC (µS·cm^{-1})	S_{BET} (m^2·g^{-1})
			Cu	Pb	Cd	As	Ni	Cr	Hg	Zn				
-	Dried SS	SS2.1-1	75.70	18.03	0.48	4.44	8.89	23.84	32.89	322.88	32.59	9.005	3150	-
		SCP2.1-1	81.88	21.01	0.78	4.62	8.72	18.79	13.15	411.37	35.18	9.039	1929	-
Catalyst	Crushed limestone	FS2.2-1	115.07	27.88	0.28	13.55	15.22	97.11	24.10	1014.82	33.15	7.381	4950	-
		SCP2.2-1	152.88	38.99	1.04	9.13	24.35	60.15	1.07	3359.02	32.51	7.587	388	-
		SCP2.2-2	178.95	45.67	0.98	8.37	22.70	65.34	1.34	4969.69	-	7.677	277	-
		SCP2.2-3	177.59	51.20	0.24	11.55	22.24	66.94	1.41	1204.01	-	7.661	365	-
Organic additives	Waste cellulose	FS2.3-1	104.65	28.92	0.21	9.49	16.64	66.93	21.60	528.55	31.46	7.272	4050	-
		SCP2.3-1	195.65	43.06	0.18	7.35	26.86	104.34	2.10	3678.79	36.64	7.665	450	-
		SCP2.3-2	187.97	46.18	0.22	10.15	36.55	59.63	1.97	4370.48	-	7.704	273	-
		SCP2.3-3	176.78	53.53	0.18	7.66	24.89	65.81	2.00	3143.11	-	7.150	138	-
	Plastic waste (LDPE)	FS2.4-1	165.09	36.00	4.10	35.42	13.44	42.24	27.37	2510.46	38.71	7.498	5370	-
		SCP2.4-1	311.96	47.04	4.66	50.81	20.29	74.89	0.74	2444.03	33.95	7.546	226	-
		SCP2.4-2	270.65	64.40	5.80	176.26	21.66	68.59	0.92	1871.87	-	7.477	244	-
		SCP2.4-3	216.90	35.78	5.68	50.30	18.89	63.23	0.90	2428.39	-	6.990	458	-
	Wooden sawdust	FS2.5-1	110.50	30.96	0.23	10.44	16.43	79.37	20.73	1531.54	33.59	7.701	4620	-
		SCP2.5-1	61.95	45.69	4.41	16.85	19.41	61.95	3.82	422.19	32.19	8.012	656	-
		SCP2.5-2	151.69	38.23	0.24	11.53	20.87	59.11	2.34	3704.63	-	7.820	480	-
		SCP2.5-3	111.59	36.91	0.22	10.20	23.93	55.54	2.97	4664.46	-	7.707	348	-
	Wooden dust	FS2.6-1	103.19	31.60	0.22	9.88	15.26	48.51	27.02	473.35	35.00	7.347	4570	-
		SCP2.6-1	167.94	28.68	0.24	11.01	27.01	65.90	1.95	3320.61	33.69	7.632	308	-
		SCP2.6-2	180.92	36.80	0.23	10.51	25.13	70.38	1.74	419.71	-	7.598	351	-
		SCP2.6-3	172.52	34.87	0.24	11.23	23.26	53.44	1.46	842.90	-	7.875	526	-
	Hay	FS2.7-1	140.58	25.73	2.83	21.94	12.44	33.50	13.09	2217.69	37.65	5.490	1965	-
		SCP2.7-1	126.53	24.79	0.17	6.96	20.26	60.71	5.07	620.18	33.29	7.262	1960	-
		SCP2.7-2	266.89	53.19	2.49	13.05	26.09	266.89	2.62	424.91	-	7.955	795	-
		SCP2.7-3	60.01	39.99	3.57	11.47	18.40	60.01	2.79	410.60	-	8.160	843	-
	Husks	FS2.8-1	88.13	25.58	0.28	13.85	12.42	28.57	24.59	407.42	33.59	6.530	5050	-
		SCP2.8-1	145.43	20.55	0.75	9.08	21.71	51.48	0.80	2577.99	33.97	7.405	423	-
		SCP2.8-2	162.44	33.53	0.13	4.33	31.53	51.85	0.63	437.93	-	7.520	332	-
		SCP2.8-3	155.44	33.32	0.15	5.40	24.25	53.81	0.77	151.95	-	7.535	371	-

Notes: SS-sewage sludge, FS-feedstock, SCP-solid carbonaceous product, HMs-heavy metals, EC-electrical conductivity, S_{BET}-surface area

As can be seen in Table 9, SS from WWTP2, SCP without additive had Cu, Pb, Zn content predominantly higher than before MT, and Pb, Cd, As, Ni content did not show significant difference after MT, and Hg content is lower after MT. SCP with 2% crushed limestone catalyst had Cu, Pb, Cd, Ni, Zn content predominantly higher than before MT, and As, Cr, Hg content is lower after MT. FS with 5% waste cellulose and FS with 5% LDPE had Cu, Pb, As, Ni, Cr, Zn predominantly higher than before MT, and Cd content is not significantly different after MT, and Hg content is lower after MT. FS with 10% wooden sawdust and 10% wooden dust had Cu, Pb, Ni, Zn predominantly higher than before MT, and Cd, As, Cr content did not show significant difference after MT, and Hg content is lower after MT. FS and SCP with 10% wooden sawdust and 10% wooden dust has lower content Cu and Zn than FS with 2% crushed limestone catalyst, 5% waste cellulose, and 5% LDPE. FS with 30% hay and FS with 30% husks had predominantly higher content of Cu, Pb, Ni, Cr, than before MT, and Cd, Zn content has not significantly difference after MT, and As, Hg content is lower after MT. FS and SCP with 30% hay and with 30% husks has lower content all HMs than FS with 2% crushed limestone catalyst, 5% waste cellulose, 5% LDPE, 10% wooden sawdust and 10% wooden dust.

FS had C_{org} in range of 31.46-38.71 %, and higher values were achieved when added 30% hay or 30% husks. SCP had C_{org} lower after MT in range of 32.19-36.64 %.

FS had pH in range of 5.490-9.005, and higher values were achieved without additives. SCP was higher value after MT in range of 6.990-9.039. Dried SS without additives represent alkaline area.

FS had EC in range of 1965-5370 µS·cm^{-1} and SCP had EC lower after MT in range of 244-1960 µS·cm^{-1}.

The graph in Fig. 10 shows HMs content after MT process for selected samples from WWTP1 with crushed limestone catalyst (SCP1.1-1, SCP1.1-2, SCP1.1-3), and selected samples from WWTP2 without catalyst (SCP2.1-1) and with crushed limestone catalyst (SCP2.2-1, SCP2.2-3).

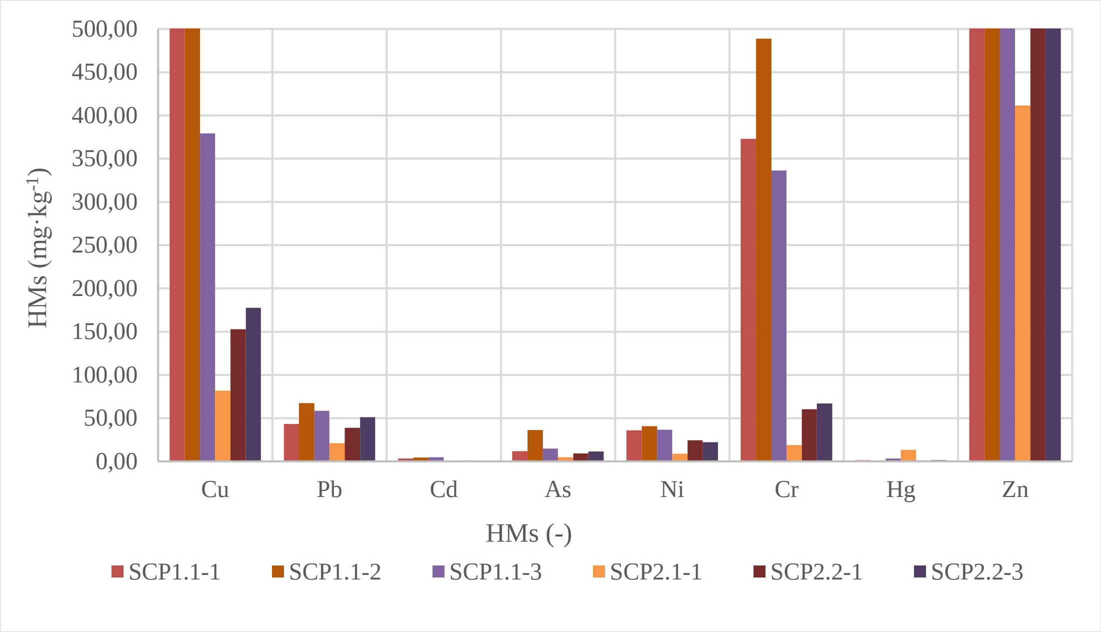

Fig. 10 HMs content after MT for selected samples from WWTP1 and WWTP2 without additives and with catalyst

According to Fig. 10 samples from WWTP1 had higher total HMs content than samples from WWTP2, this is related to the higher input HMs content in SS from WWTP1.

Fig. 11 shows HMs content after MT process for selected samples from WWTP1 with 5% waste cellulose (SCP1.2-1, SCP1.2-2) and with 5% LDPE (SCP1.3-1), and selected samples from WWTP2 with 5% waste cellulose (SCP2.3-3) and with 5% LDPE (SCP2.4-1, SCP2.4-2).

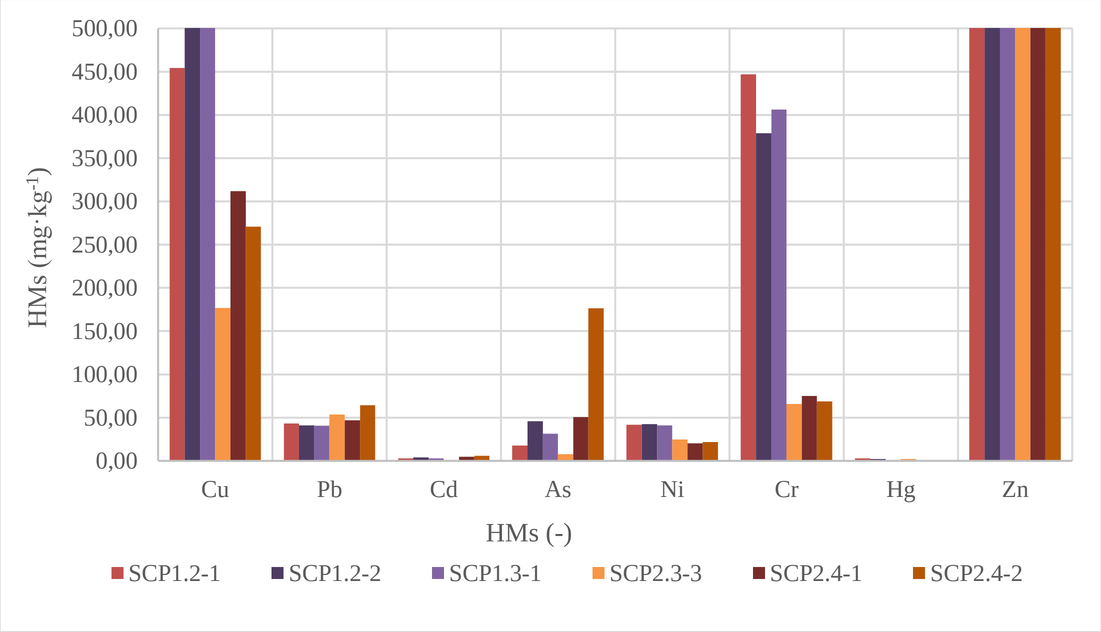

Fig. 11 HMs content after MT for selected samples from WWTP1 and WWTP2 with 5% organic additives

According to Fig. 11 samples from WWTP1 had higher total HMs content than samples from WWTP2, this is related to the higher input HMs content in SS from WWTP1.

Fig. 12 shows HMs content after MT process for selected samples from WWTP1 with 10% wooden sawdust (SCP1.4-1, SCP1.4-2, SCP1.4-3), and selected samples from WWTP2 with 10% wooden sawdust (SCP2.5-3) and with 10% wooden dust (SCP2.6-1, SCP2.6-3).

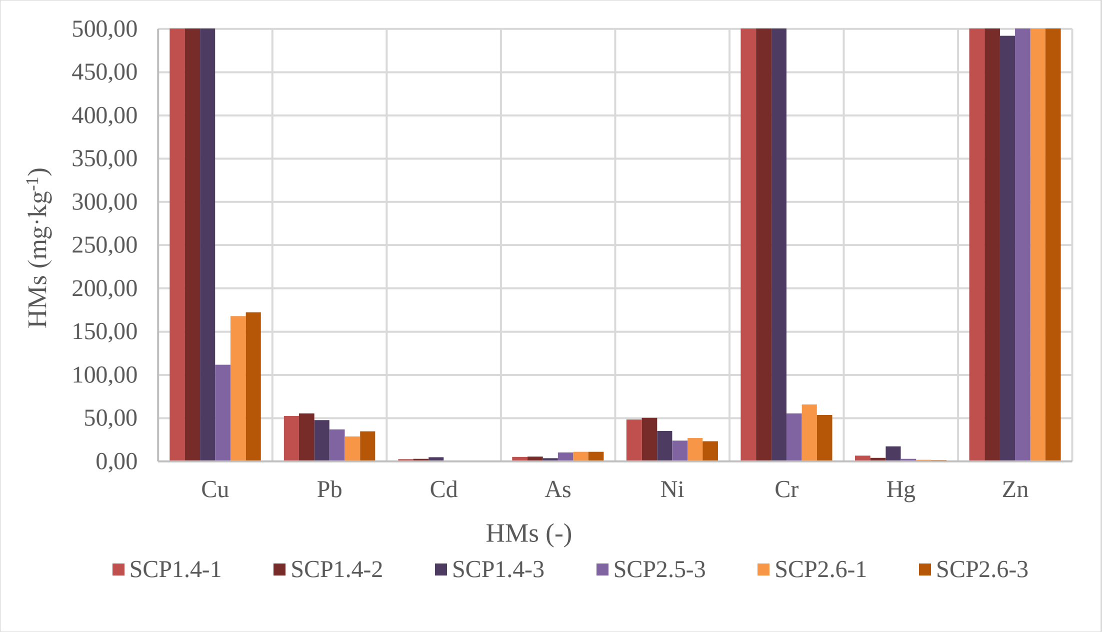

Fig. 12 HMs content after MT for selected samples from WWTP1 and WWTP2 with 10% organic additives

According to Fig. 12 samples from WWTP1 had higher total HMs content than samples from WWTP2, this is related to the higher input HMs content in SS from WWTP1.

Graph in Fig. 13 shows HMs content after MT process for selected samples from WWTP1 with 30% hay (SCP1.5-1, SCP1.5-2) and with 30% husks (SCP1.6-3), and selected samples from WWTP2 with 30% hay (SCP2.7-3) and with 30% husks (SCP2.8-2, SCP2.8-3).

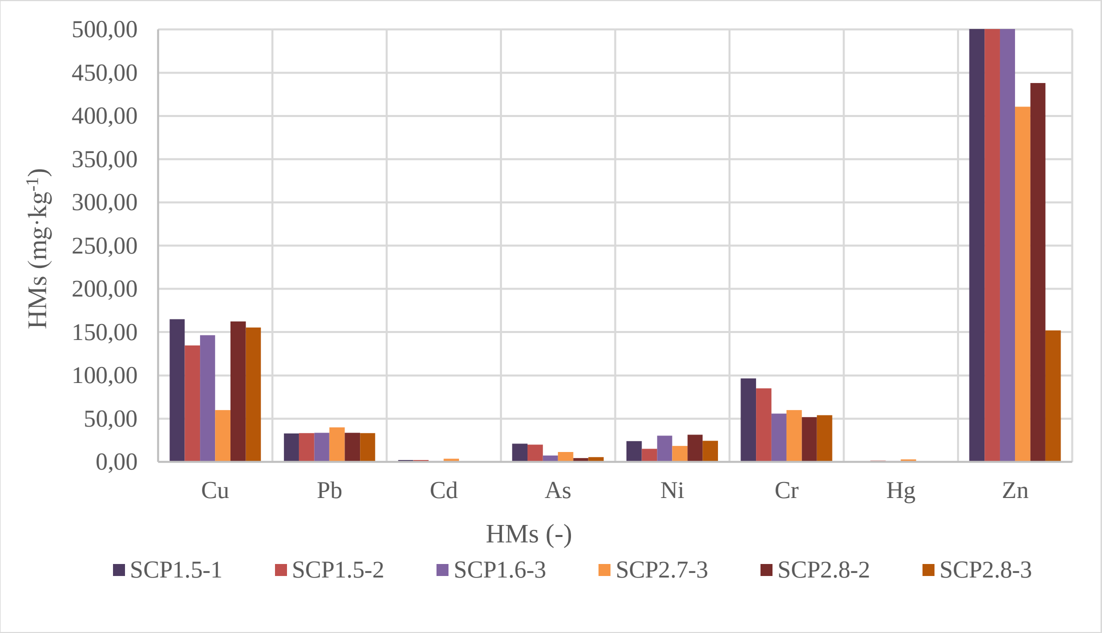

Fig. 13 HMs content after MT for selected samples from WWTP1 and WWTP2 with 30% organic additives

According to Fig. 10 samples from WWTP1 had slightly higher total HMs content than samples from WWTP2, this is related to the higher input HMs content in SS from WWTP1. Generally, HMs content is lower with 30% organic additives.

3.4. Summarizing discussion

In this research, we present a characterization of SCP produced via MT process of SS. We used dried SS from two WWTPs, in the form of dried SS from a contact blade paddle dryer and dust particles and dried SS from a conventional belt dryer in the shape of noodles. SS was mixed in different ratios with the catalyst and organic additives. As follows from the results, the FS and SCP can find energy or agricultural use.

Temperature, yields and energy use

The output pellet diameter with additives after MT was reduced volume ranging 10-20% and reduced weight ranging 35-55% than input pellet diameter before MT, and this volume and weight reduction have a positive impact on SCP/biochar transport for further use.

Relatively high temperature and high pyrolysis oil yield was achieved with FS with 2% crushed limestone catalyst. The addition of catalyst supports the MT process including depolymerizing the organic matter in the SS. For further research, the combination of two additives, organic additive and catalyst, should be performed.

Samples from WWTP2 without additives achieved temperature lower than 129 °C and the course of temperature over time was almost linear and slightly rising. In this case probably not complete MT process was performed. Only further drying of the SS was performed, the bound water was evaporated from the sample, and thus the calorific value was higher after MT.

Samples with 2% crushed limestone catalyst achieved maximum temperature 242-330°C and the course of temperature over time was linearly increasing.

Samples with 5% waste cellulose and 5% LDPE achieved maximum temperature 208-329 °C and the course of temperature over time was linearly increasing but except for the final phase that had exponential endings.

Samples with 10% wooden sawdust achieved maximum temperature 176-313 °C and the course of temperature over time had a relatively rapid exponential increase. While the samples with 10% wooden dust achieved maximum temperature 296 °C and the course of temperature over time was linearly increasing but except for the final phase that had exponential endings.

Samples with 30% hay and 30% husks achieved maximum temperature 222-351 °C and the course of temperature over time had a relatively rapid exponential increase.

High level of pyrolysis oil yield was achieved with 30% organic additives: hay and husks. Low level of pyrolysis oil yield was achieved with 5% LDPE, thus plastic additive is inert to MT decomposition.

FS with 5% LDPE and 30% organic additives had high calorific value. Thus, mixing and pelletizing process improve the FS qualitative energy parameters and FS can be implemented for the certification as solid alternative fuel.

Agricultural use

Mixing and pelletizing process improved the FS qualitative parameters monitored for the certification as biochar or the soil amendment substances. For certification as biochar or soil amendment substances, it is necessary to prepare mix of raw dried SS with additives to improve the FS qualitative parameters to increase organic matter or to improve other properties such as : HMs (Cu, Pb, Cd, As, Ni, Cr, Hg, Zn) content, C_{org}, pH, EC, and S_{BET}.

The limiting hazardous substances of SS for agricultural are especially HMs. The samples from WWTP1 had higher total HMs content than samples from WWTP2, this is related to the higher input HMs content in SS from WWTP1, and HMs content is lower with 30% organic additives. According IBI guidelines biochar category B, SCP with 30% organic additives complies with the limits of the selected parameters: HMs and C_{org}.

HMs measurements revealed a significant heterogeneity of the HMs in SS. The part of HMs volatized out of batch reactor of MT via the vapours to pyrolysis oil and pyrolysis gas. Number of HMs tests have shown difference between initial and resulting content of a particular metal, namely Hg. It can be assumed that, under MT conditions, Hg was desorbed/vaporized and transported to pyrolysis gas and/or pyrolysis oil. Potential Hg evaporation was partially expected due to low melting point 356.95 °C reasons mentioned by Kistler [43] and due to not-well-understood influence of vacuum.

The total HMs content in SS, FS, and produced SCP was determined by extraction using *Aqua Regia*. Especially, our research is focused on soluble fraction (bioavailable, potentially harmful fraction) which is determined by extraction using deionized water. The next research will be focused on BCR sequential extraction method, which can prove more detailed information on the form of HMs in SCP. Furthermore, the attention will be given to addition of other types of biomass to investigate the influence of organic matter on the HMs fixation.

Mixing and pelletizing process improve the FS qualitative parameters for the certification of biochar or the soil amendment substances.

4. Conclusions

In the EU, circular economy strategy of WW treatment postulates a search for new ways of reusing SS. Thermal treatment, such as incineration, gasification, HTC, pyrolysis, and MT represent acceptable solutions of SS disposal. Two different ways exist, the first one is incineration of SS for energy generation and the second one is SS transformation into a new product for other use, especially for agriculture. The second way represents a research challenge which was handled via MT producing biochar/SCP. Pelletization process with adding additives and MT seem to be an attractive optimization technology for the transformation of SS into biochar/SCP from the point of view of reduced energy consumption and HMs fixation in the structure of SCP/biochar. If we want to use SCP in agriculture, it is necessary to define its characteristics and compare it with guidelines certification process for the application in agriculture as a soil amendment. The new knowledge of the SCP/biochar of SS after MT may lead to future certification as biochar.

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