

Characteristics of a solid carbonaceous product of microwave pyrolysis/torrefaction of sewage sludge for the use in agriculture and blue-green infrastructure

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ABSTRACT

The aim of this work is to present results of preparation and characterization of the dried municipal sewage sludge and so called solid carbonaceous product, the outcome of its further processing by slow microwave pyrolysis/torrefaction. Characterization intends to determine the use of these products for combustion with energy production, agriculture, and blue-green infrastructure. The tests included several variables influencing pyrolysis such as mixing sewage sludge with additives, pelletization process, pyrolysis residence time, process temperature and parameters such as yield of solid carbonaceous product, yield of pyrolysis oil, yield of pyrolysis gas, content of heavy metals, calorific value, organic carbon, pH, electrical conductivity, and surface area. The results showed that mixing and pelletizing processes improved the feedstock qualitative parameters necessary for the certification as a solid alternative fuel and the subsequent certification as biochar or the soil amendment. For certification of biochar or soil amendment substance, it is necessary to prepare a mixture of raw dried sewage sludge with additives to improve the feedstock qualitative parameters to increase organic matter and to improve other properties such as organic carbon, surface area etc. The results indicate that slow microwave pyrolysis/torrefaction transforms sewage sludge into solid carbonaceous product and represents an eco-friendly way of sewage sludge disposal which belongs to the important strategies of circular economy.

Keywords: Sewage sludge management; Blue-green infrastructure; Microwave pyrolysis/torrefaction; Solid carbonaceous product; Biochar

1. Introduction

In the European Union (EU), current wastewater (WW) management is energy demanding and produces many residues or products that can only partially be used/recycled. This paper aims to advance the WW management system towards the circular economy paradigm [1] and sustainability as targeted in The European Green Deal, one of the Commission priorities for 2019-24 (EC directive 2019) [2]. This research contributes to the EU circular economy

action plan, the bio-economy strategy, and the “Farm-to-Fork” strategy [3], where the main objective is the recovery of nutrients (P, N).

Methods for waste thermal treatment, such as incineration, gasification, hydrothermal carbonization (HTC), pyrolysis, and torrefaction represent acceptable solutions for sewage sludge (SS) disposal [4]. Thus, apart from incineration of SS and producing energy, SS may be transformed into a new product suitable for the use in agriculture or in blue-green infrastructure (BGI).

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The concept of BGI is an environment-friendly method to mitigate some of the environmental issues in urban areas, such as overheating of buildings and the consequent heat effect, flash floods causing sewer system overloading, air pollution from traffic, and thus helping to reduce the energy consumption on air conditioning, to retain the storm water and provide fresh air. The current challenge is the BGI concept which combines blue and green approach for the use of treated WW (gray water, tertiary treated WW from municipal wastewater treatment plants) for green roofs, walls, and parking lots. There is an attractive challenge/possibility for the use of solid carbonaceous product (SCP)/biochar from SS as nutrient carriers, stable carbon, and high specific surface area for water retention in green infrastructure. The BGI concept leads to a reduction of temperature in buildings during summer (green roofs and walls) and reduces the energy needs for cooling buildings, thus improving the microclimate in cities. This concept will capture rainfall and reduce surface runoff into the sewer, nutrients in the biochar (N, P, C, K) will be used in the green infrastructure and the idea of “waste to product” will be implemented. In the case of green parking lots, traffic pollution (petrol, oil) will be reduced/fixed by filtration/adsorption on the SCP/biochar.

This paper explores the potential of using pyrolysis/torrefaction and additives to produce solid carbonaceous product (SCP) which will comply with the strict certification process for application in agriculture or in BGI as a soil amendment substance (SAS).

1.1. Sewage sludge (biosolids)

Strategic management of SS (also called biosolids) is urgent and highly topical issue not only in the EU but also in other countries. The goal is to maximize the reuse of SS as resource in accordance with the Circular Economy Strategy. The 86/278/EEC Sewage Sludge Directive (SSD) [5] was passed more than 30 years ago with the aim encourage SS treatment and to restrict the use of SS in agriculture to prevent harmful impact on soil, vegetation, animals and humans. The EU countries are allowed to specify the conditions when untreated SS can be directly used. There have been several attempts to review and amend the directive. In 2014 the directive was evaluated in Ex-post Evaluation of Certain Waste Stream Directives, Bio Intelligence Service, Final report (2014) [6]. The evaluation has shown that SSD has met the original aims, that is, increase in application of SS in agriculture, and reduction of damages in the environment, namely heavy metals (HMs). On the other hand, the evaluation has identified many issues where the directive does not reflect the needs and practice in SS management, as the qualitative indicators are unilaterally directed. The EC opened a public discussion to a roadmap for SSD revision, comments are now being evaluated. The EC is under the pressure of European Parliament that has committed to reevaluate the SSD by the end of 2021 due to the increasing consumption of pharmaceuticals and their accumulation in SS and consequently in the ground and surface water (COM (2019) 128) [7] to be completed by the end of 2020 and based on the research requested by EC.

The EC plan is to support the reuse of SS in agriculture under safe conditions with regards to the Circular Economy, Green Deal and the Farm-to-Fork Strategy which emphasizes the nutrients recovery (namely P, N) and carbon capture and storage strategy challenge. Further, the draft focuses on contaminants of emerging concern (e.g. organic chemicals such as pharmaceuticals, PAH and PFAS, cosmetics and microplastics), which is a complex task where many stakeholders might conflict as well in the context and the potential impact of the Urban Wastewater Treatment Directive 91/271/EEC [8] which is also being evaluated and drafted in 2022.

The 86/278/EEC Sewage Sludge Directive [5] focuses mainly on heavy metals as the potential toxic substances, but industry has managed to reduce their emission and are not the main contaminant in SS. Therefore, there is a need to focus on the emerging pollutants with severe impact on the health that must be evaluated, namely organic and inorganic chemicals, pharmaceuticals, antimicrobial resistance, antibiotic resistance, microplastics, microbiological analysis considering the regional differences. Contaminants of emerging concern (CEC) include pharmaceuticals and personal care products (PPCPs), some of which may, or are suspected to, act as endocrine disruptors (EDs) [9]. From a total of 564 chemicals suggested by various agencies, published papers or reports, as being suspected EDs, 147 were considered likely to be either persistent in the environment or produced at high enough volumes to be potential risks for public health. Effective technologies for removal of the CECs from WW are not well established/generally adopted or these technologies are too expensive. The CECs might accumulate, either as original compounds or as by-products, in the excess sludge generated by the treatment process [10]. Based on the literature [11,12], the pyrolysis process reduces and/or removes selected CECs.

It is necessary to find a compromise where and when SS might be applied.

Currently, the disposal of SS is predominantly managed by landfilling, incineration and direct agricultural use which is no longer acceptable due to the rising content of HMs and harmful pollutants. Thus, the disposal of the SS has become one of the most important issues in circular economy that is a part of the waste management strategy implemented by the EU.

The landfilling of SS is not supported by the EU and is strictly restricted in several EU countries as SS contains large amount of organic matter, which is decomposed at the landfill sites. In addition, due to anaerobic processes it generates CH_4 that is stronger greenhouse gas than CO_2 . Also, the cost of the land needed for landfill is increasing because of its decreasing availability [1].

The incineration reduces the volume of SS up to 70% and decreases pathogens and toxic organic compounds [13,14]. Generally, dry SS has a calorific value similar to the energy in brown coal [15]. At present, incineration of SS is carried out either directly at wastewater treatment plant (WWTP) as mono-incineration, or as the co-incineration of SS with coal or other wastes, or the combustion of SS in cement kilns [16]. Relatively small number of incinerators of SS is located at WWTPs where they use the energy from waste for the treatment process [1]. As the

ash from the incineration of SS contains higher quantities of HMs, namely Cr, Cu, Ni, Pb, Zn and Fe, and is more toxic than the ash from coal combustion [17], the reuse of the ash of SS is another topic that has to be addressed and it seems that the incineration of SS in cement kilns could solve the problem of ash disposal [1,17,18].

Although SS contains organic matter, nitrogen and phosphorus [19] which can be used as a fertilizer in agriculture or in BGI [1], the hazardous substances limiting the use of SS in agriculture are HMs [20–23], and in the near future, the legislation will implement also the limits for the content of organic pollutants [22] and microplastics [23]. SS is an important strategy source of phosphorus because the natural sources are estimated to be exhausted around 2 300 [24].

The SS alone containing approx. 50% of the inorganic parts needs to be treated to improve the depolymerization process to produce SCP or biochar. Mixing and pelletizing SS with additives seems to be a promising method how to improve both the microwave pyrolysis/torrefaction process and the quality of the output SCP. This paper attempts to answer the question which additives and in what proportions will be optimal to use.

1.2. Solid carbonaceous product certification

To produce certified SCP/biochar from SS, the thermochemical reductive treatment process should be defined together with pretreatment procedures of raw SS (the term biochar is defined in this paper as SCP with certification). 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) [25] and The European Biochar Certificate (EBC) [26]. Selected parameters for biochar certification according to

guidelines IBI [25] and EBC [26] are reported in Table 1, the requirements are divided into biochar of Category A/B (IBI) and biochar EBC-Urban/EBC-Agro (EBC). For biochar of Category A and premium biochar, the limits of selected parameters are stricter. The selected general parameters in Table 1 are divided into toxicant assessment with their maximum thresholds and other parameters.

The pyrolysis of non-plant biomasses such as SS, livestock manure, manure containing biogas digestates or bones and slaughterhouse wastes may also produce valuable raw materials that could be used in the interests of the bioeconomy and climate protection [27,28]. It is planned to include these raw materials from mid-2022 in the EBC [26] feedstock list following a key review publication about the product safety and conditions of use.

According to the EBC guideline [26], EBC-Urban provides a strong standard for the use of biochar in tree planting, park maintenance, sidewalk embellishments, ornamental plants, and rainwater drainage and filtration. The main risk of all those uses is ground- and surface water contamination and work safety, which EBC-Urban certification prevents effectively. As the urban use of biochar is not subject to agricultural legislation, some parameters, and their respective limit values were replaced by limit values that are better adapted to the special matrix of biochar. Namely, the EBC-Urban limit value for PAHs is limited to the eight carcinogenic PAHs using the same limit value as for EBC-Feed and EBC-Agro. PAHs are ubiquitous in urban environments (e.g., from tyre abrasion and car exhaust), and urban soil applied biochar which is a strong adsorber of PAHs will act as a net adsorber of those environmental toxins when low biochar PAH-contents are guaranteed (as is the case when EBC-Urban biochar is used).

Other options for certification of SCP of pyrolysis/torrefaction is certification as the soil amendment substance (SAS) as substances without a number of nutrients,

Table 1
Selected parameters for biochar certification according to IBI and EBC guidelines [25,26]

| General parameter | Selected parameter | Guidelines to biochar certification | | | |
|---|---|---|-----------------|---|-------------|
| | | International Biochar Initiative (IBI) [25] | | European Biochar Certificate (EBC) [26] | |
| | | Category A | Category B | EBC-Urban | EBC-Agro |
| Toxicant assessment, maximum allowed thresholds – HMs | As, mg kg ⁻¹ dry wt-mass | 13 | 100 | 13 | 13 |
| | Cd, mg kg ⁻¹ dry wt-mass | 1.4 | 20 | 1.5 | 1.5 |
| | Cr, mg kg ⁻¹ dry wt-mass | 93 | 100 | 90 | 90 |
| | Cu, mg kg ⁻¹ dry wt-mass | 143 | 6,000 | 100 | 100 |
| | Pb, mg kg ⁻¹ dry wt-mass | 121 | 300 | 120 | 120 |
| | Hg, mg kg ⁻¹ dry wt-mass | 1 | 10 ^a | 1 | 1 |
| | Ni, mg kg ⁻¹ dry wt-mass | 47 | 400 | 50 | 50 |
| | Zn, mg kg ⁻¹ dry wt-mass | 416 | 7,400 | 400 | 400 |
| Other parameters | C _{org} , % | ≥60 | ≥30 | | ≥50 |
| | pH | | Declaration | | Declaration |
| | Electrical conductivity, dS m ⁻¹ | | Declaration | | Declaration |
| | S _{BET} , m ² g ⁻¹ | | – | | ≥150 |

C_{org} – organic carbon; ^amethyl mercury 10 mg kg⁻¹; inorganic mercury 40 mg kg⁻¹.

which biologically, chemically or physically affect the soil, improve its state or increase the efficiency of fertilizers.

1.3. Solid carbonaceous product of microwave torrefaction

SCP is a product of thermochemical treatment process. Unlike the thermochemical oxidative treatment processes as combustion in which oxygen is present in stoichiometric or larger amounts, this research focuses on the SCP produced via the thermochemical reductive processes like gasification, hydrothermal carbonization, and namely pyrolysis and torrefaction [29] as they offer wider spectrum of products and further application.

Selected literature describes torrefaction [30–34] as a mild pyrolysis when biomass (including SS) are heated in an inert atmosphere at temperature about 200°C–300°C for residence time 30 min–4 h. Torrefaction produces primarily 60%–80% solids, 20%–40% gases, and a relatively small amount of liquid that can be burned together with gases. The pyrolysis process can further be divided into two categories such as conventional and microwave pyrolysis/torrefaction. In principle, it can be carried out either by using conventional heat transfer via conduction or microwave heating of pyrolyzed material [35].

Based on the type of microwave pyrolysis/torrefaction (MP/T), the dried SS may be mixed with additives [36] as catalysts and/or organic additives improving the process or structure. The catalyst represents the additive with theoretically catalytic effect, thus various types of zeolites may be added and mixed with SS to absorb microwave radiation after evaporation of moisture and to support catalytic cracking of specific hydrocarbons. Generally, the organic additives represented by organic matter, such as wood sawdust, lignin, and hay, are mixed with SS in order to improve 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 [37], 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 MP/T processed output. Thus, SS is mixed with additives and consequently pelletized for MP/T process. The pellets with 6 mm diameter are 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”.

1.4. Aims

Based on the previous SCP review of SS [4], this paper presents preliminary results from a pilot study on SS processing and introduces a characterization of the produced SCP after MP/T process 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, organic carbon (C_{org}), pH, electrical conductivity (EC), and Brunauer–Emmett–Teller (BET) surface area (S_{BET}).

This work investigates the influence of catalyst with focus on temperature and yields of products by MP/T of SS. It is further investigated whether the addition of an organic additive of less than 25%, that is, the recommended maximum dilution recommended by the STRUBIAS Group [38], can achieve biochar certification after pyrolysis of SS.

The overall goal of the paper is to increase the knowledge of the SCP produced from SS via MP/T and the conclusions may serve as the basis for biochar certification.

2. Materials and methods

2.1. Feedstock

2.1.1. Sewage sludge samples

Anaerobically digested and thermally dried SS (SS1 and SS2) from two different municipal WWTPs (WWTP1 and WWTP2) 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, despite the relatively low industrial WW ratio, HMs in SS are at higher concentrations. The SS was dried using a contact blade paddle dryer at temperature lower than 100°C. Tested raw dried samples of SS from WWTP1 had dry solids (DS) around 91% and output fraction from dryer was a powder like material with particle fraction 1–8 mm, 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 percentages of industrial WW originated from the production of mineral water which contains relatively higher concentrations of As. Other HMs are also present in these WW. 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. Random tests revealed that the hygroscopic water content was below 2.0%.

2.2. Pretreatment process

For this paper, the pretreatment of SS samples for MP/T consists of two consequent steps: mixing dried SS with additives and pelletizing this mixture according Fig. 1. SS was mixed in 4 different ratios with the following additives: catalyst or organic additives.

2.3. Mixed samples

As catalyst, crushed limestone was added and mixed with SS to absorb microwave radiation after evaporation of moisture and to support catalytic cracking of specific hydrocarbons. Based on our previous research [35], catalyst and organic additive can be used to immobilize most of HMs in SCP structure.

As shown in Table 2 dried SS from WWTP1 was mixed with one of the selected catalysts: crushed limestone

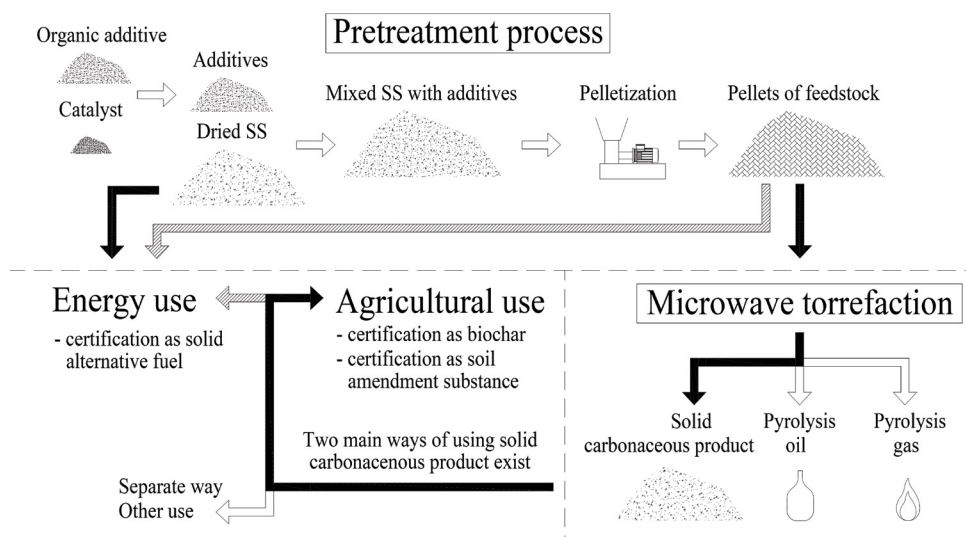


Fig. 1. Scheme of pretreatment and MP/T process, the main direction is indicated by solid arrows.

Table 2
Feedstock composition before and after pelletization process

| Additive type | Ratio SS:ADD (%) | Sample ID | Density (kg m ³) | |
|-------------------|----------------------------|---------------------|------------------------------|-----|
| – | Mix0 (control): Dried SS | 100:0 | SS WWTP2 – input | 318 |
| | | | FS WWTP2 – pellets | 736 |
| | | | FS WWTP1 – mixtures | 820 |
| Catalyst | Mix1: Crushed limestone | 98:2 | FS WWTP1 – pellets | 726 |
| | | | FS WWTP2 – mixtures | 350 |
| | | | FS WWTP2 – pellets | 690 |
| | Mix2: Waste cellulose | 95:5 | FS WWTP1 – mixtures | 685 |
| | | | FS WWTP1 – pellets | 772 |
| | | | FS WWTP2 – mixtures | 350 |
| Organic additives | Mix3: Plastic waste (LDPE) | 95:5 | FS WWTP2 – pellets | 742 |
| | | | FS WWTP1 – mixtures | 800 |
| | | | FS WWTP1 – pellets | 670 |
| | Mix4: Wooden sawdust | 90:10 | FS WWTP2 – mixtures | 340 |
| | | | FS WWTP2 – pellets | 650 |
| | | | FS WWTP1 – mixtures | 694 |
| Organic additives | Mix5: Wooden dust | 90:10 | FS WWTP1 – pellets | 775 |
| | | | FS WWTP2 – mixtures | 392 |
| | | | FS WWTP2 – pellets | 764 |
| | Mix6: Hay | 70:30 | – | – |
| | | | – | – |
| | | | FS WWTP2 – mixtures | 374 |
| Organic additives | Mix7: Husks | 70:30 | FS WWTP2 – pellets | 620 |
| | | | FS WWTP1 – mixtures | 774 |
| | | | FS WWTP1 – pellets | 710 |
| | | FS WWTP2 – mixtures | 360 | |
| | | FS WWTP2 – pellets | 680 | |
| | | FS WWTP1 – mixtures | 590 | |
| | FS WWTP1 – pellets | 736 | | |
| | FS WWTP2 – mixtures | 394 | | |
| | FS WWTP2 – pellets | 644 | | |

SS – sewage sludge; FS – feedstock; ADD – additive.

(in the ratio 98%:2%, that is, 98% SS and 2% additive) in Mix1, waste cellulose (95%:5%) in Mix2, plastic waste – low density polyethylene (LDPE, 95%:5%) in Mix3, wooden sawdust (90%:10%) in Mix4, hay (70%:30%) in Mix6, and husks (70%:30%) in Mix7. Mix5 was used only for SS from WWTP2.

As shown in Table 2 dried SS from WWTP2 was mixed with one of the selected catalysts: crushed limestone (98%:2%) in Mix1, and organic additives: waste cellulose (95%:5%) in Mix2, plastic waste LDPE (95%:5%) in Mix3, wooden sawdust (90%:10%) in Mix4, wooden dust (90%:10%) in Mix5, hay (70%:30%) in Mix6, and husks (70%:30%) in Mix7.

Selected mixtures of organic additives are shown in Fig. 2; this represents the state before the pelletization process.

One mix was always performed, which was pelletized. Subsequently, three feedstocks were selected from the pelletized samples to perform MP/T.

2.4. Pelletized feedstock

The mixtures of dried raw SS with catalysts and organic additives were pelletized by industrial pelletizing

press. The additive types, ratio SS:ADD (additive), and density before and after pelletization process are reported in Table 2. For these experiments, the pelletization process used an extrusion die having 6.4 mm. The temperature during pelletization was measured on the metal matrix of the pelletizer. The pyrolyzed feedstock were approximately 6.4 mm diameter pellets of mixed SS with additives made by pelletizing press.

Selected pellets of feedstock SS with organic additive and catalyst are shown in Fig. 3, this represents the state after the pelletization process.

2.5. Microwave torrefaction process

MP/T was performed in laboratory, small-scale conditions [39], in a small-scale MP/T unit working under low pressure 80 kPa. Microwave was generated by a magnetron with 3.0 kW input power and with 2.45 GHz. This unit works discontinuously, and the maximum capacity is around 12 kg batch⁻¹ of feedstock. The glass condenser attached to the pyrolyzer was used for the separation of gaseous products and the pyrolysis oil. For incoming

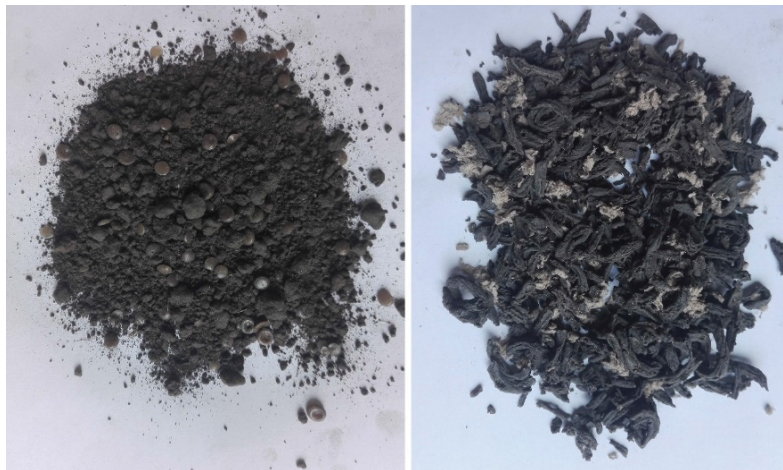


Fig. 2. Selected mixtures of dried raw SS with organic additive (a) Mix3 SS of WWTP1 with plastic waste LDPE and (b) Mix2 SS of WWTP2 with cellulose, before pelletization.



Fig. 3. Selected pellets of feedstock SS with organic additive and catalyst FS1.4 and FS2.2 (a) Mix4 feedstock of WWTP1 with wooden sawdust and (b) Mix1 feedstock of WWTP2 with crushed limestone, after pelletization process.

and reflected waves a tuner was installed. The infrared (IR) thermometer was placed in the center (top surface) of the input feedstock (FS). The scheme of small-scale MP/T unit is illustrated in Fig. 4.

The input weight of feedstock samples was 1,300 g batch⁻¹. The feedstock was placed into the MP/T 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 around 60 mm. The use of stainless-steel material is acceptable with the following advantages: variability of production of different bowl shapes, not brittle and easy maintenance (bowl cleaning). Also the stainless steel as the material of reactor and the bowl for input feedstock load was discussed and recommended by magnetron producer. 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 min, and the temperature did not exceed 351°C.

Selected pellets containing feedstock and additives are shown in Fig. 5; this represents the state after the MP/T process.

2.6. Analytical procedures

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

2.7. Combustion test

The combustion tests were carried out according to the EN ISO 1716 [40]. The energy efficiency of samples was

measured by the semi-automatic device (IKA C 200) under the standard laboratory conditions.

In the first part, the random small doses were determined for combustion tests. The small doses were ground to fine dust by friction dishes. 0.4–0.8 g of fine dust were prepared for calorimetric measurement. 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 min 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 combustion tests of the sample. The results were the average of the three calorific values for each mix.

2.8. Determination of HMs

For comparison, the content of HMs in FS/SS and SCP samples were measured by two optimization methods. For the optimization of the Advanced Mercury Analyzer (AMA) and Atomic Absorption Spectrometer (AAS) methods for determination of selected HMs certified reference materials of calibration standard solutions ASTASOL[®] with concentration of measured metal 1,000 ± 0.002 mg L⁻¹ in 5% HNO₃, from Analytika Ltd., Czech Republic (Czech Metrological Institute), were used. All other used chemicals were of analytical reagent grade.

Extraction in distilled water (water extraction) was performed as follows: 5 g of the milled sample was weighted

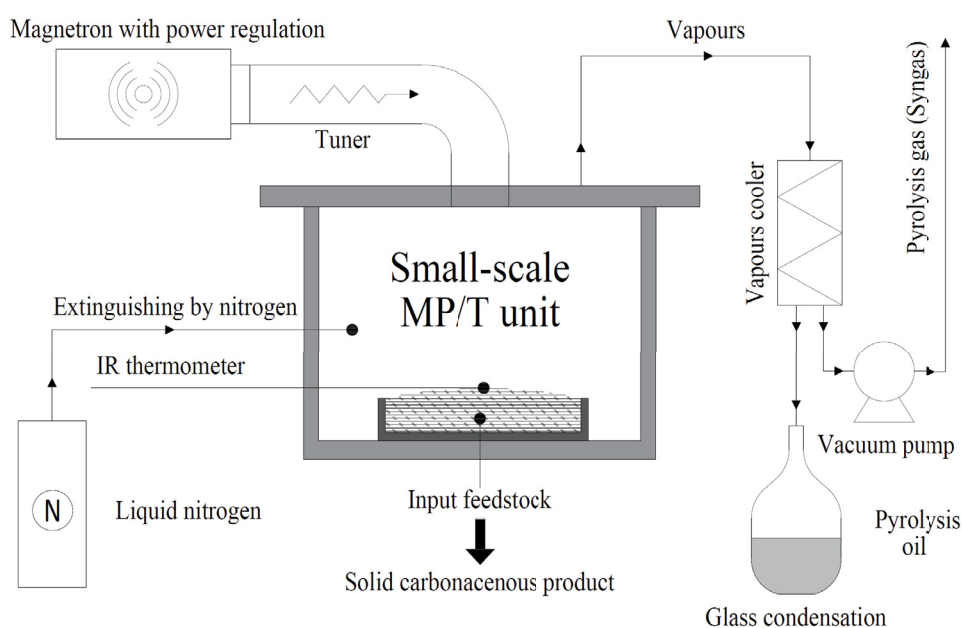


Fig. 4. Scheme of small-scale MP/T unit.

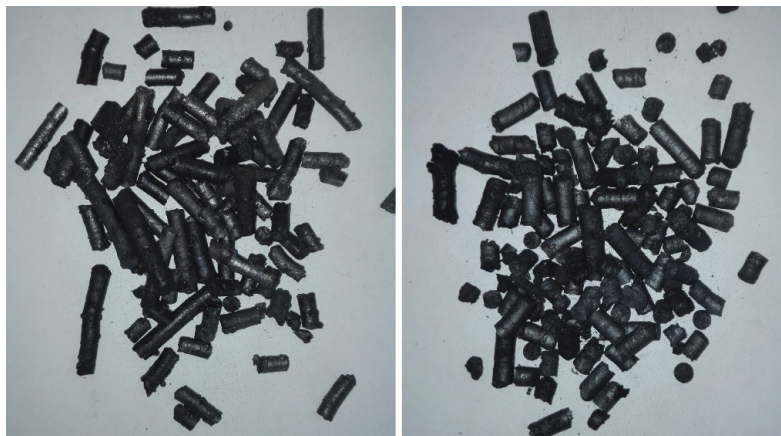


Fig. 5. Selected pellets of solid carbonaceous product (a) Mix7 SCP1.6 of feedstock FS1.6 of WWTP1 with husks and (b) Mix6 SCP2.6 of feedstock of WWTP2 with hay FS2.6 after MP/T.

to the plastic bottle and 50 mL of water (prepare on Milli-Q Ultrapure Water Systems) was added. The mixture was shaken for 24 h and then filtered.

Digestion in Aqua Regia was performed as follows: 10 g of the milled sample was transferred to a flask containing 60 mL of Aqua Regia (HCl:HNO₃ in a ratio 3:1). The sample thus prepared was boiled under reflux for 2 h. After cooling, the sample was filtered. For analysis, it was diluted with distilled water in a ratio of 1:8.

Analyses of HMs contents were performed using atomic absorption spectrometer with electrothermal atomization ZEE nit 60 from Analytik Jena (Germany) with Zeeman background correction and selected hollow cathode lamp by Photron (Australia). Optimal measurement parameters and specific temperature programs, reported in Table 3, were used. 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.

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 4.

2.9. 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 min depending on the weight and type of sample. The test was performed 3 times and the average was calculated. The EC and pH parameters were measured in aqueous extracts. EC was measured on conductometer EC Testr 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 h at 50°C. S_{BET} was determined at five points using a multi-point BET method. Bipolar junction transistor (BJT) analysis was used for pore size analysis. 24 points were measured for adsorption and 38 points were measured for desorption. pH was measured using Titrator Scot TitroLine alpha plus equipped with combined glass electrode WTW Sen Tix 81. In principle, 1 g of biochar was milled in laboratory ball mill (steel), then it was dispersed in 10 mL of deionized water. The suspension constantly stirred for 24 h, filtered and then pH was measured. The reported values are averaged values of three measurements.

3. Results and discussions

The characterization of the SCP was carried out to identify its combustion energy and potential for agricultural use. The results included these parameters: temperature and density of pelletizing process, temperature of MP/T process, 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. Pelletizing, temperature, yields and combustion energy

During the pelletizing process of mixtures from WWTP1, the temperature did not exceed 75°C, and the density was 590–820 kg m⁻³ and after pelletizing process was 670–775 kg m⁻³. During the pelletizing process of the mixtures from WWTP2, the temperature did not exceed 69°C, and the density was 318–394 kg m⁻³, and after pelletizing process the density was 620–764 kg m⁻³. The pelletization temperature is associated with the quality of the pelletized material. The samples from WWTP1 were pelletized with higher temperature accompanied by higher compressive forces on the pelletizer matrix, so the feedstock had a higher density than the samples from WWTP2.

Feedstock (FS) composition from WWTPs and SCP composition after MP/T is reported in Table 5. The raw SS and crushed limestone as one catalyst were used. Six organic additives were used: waste cellulose, LDPE, wooden sawdust,

Table 3
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 |

Table 4
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 |

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.

The output pellet diameter was reduced from 6.3–6.6 to 4.5–5.8 mm after MP/T this is related to weight reduction due to the MP/T process. A reduced pellet diameter of 12%–29% subsequently reduced the volume for transporting biochar for agricultural, BGI or other uses.

As it can be seen, during the same MP/T treatment for 5 min under constant energy load, the SS without additives reached maximum temperature 129°C, FS with 2% catalyst reached maximum temperatures 274°C–330°C, FS with 5% waste cellulose reached maximum temperatures 248°C–329°C, FS with 5% LDPE reached maximum temperature 288°C–310°C, FS with 10% wooden sawdust reached maximum temperature 278°C–273°C, FS with 10% wooden dust reached maximum temperature 313°C, FS with 30% hay reached maximum temperature 278°C–351°C, FS with 30% husks reached maximum temperature 271°C–281°C. An interestingly high temperature was achieved with the addition of 2% crushed limestone catalyst in the Mix1 from WWTP1, in this case a temperature of 330°C was reached. The highest temperature of 351°C was reached when 30% hay was added to the SS from WWTP1, thus the temperature increase is probably related to a higher proportion of organic matter in this Mix6 and has consequences on the yield of SCP and pyrolysis oil.

The average SCP yield was roughly 55% and the highest SCP yield was achieved with raw dried SS from WWTP2 and crushed limestone. The SCP yield decreases as the organic additive ratio increases, the lowest SCP yield of 47.2% was achieved for 30% husks.

The low yield of 5.2% pyrolysis oil was achieved by dried SS from WWTP2, therefore the MP/T process was not

achieved, probably only further drying occurred. Another low yield of 6.4%–7.1% pyrolysis oil was achieved for plastic waste (LDPE), probably plastic waste was inert to microwave irradiation and no hydrocarbon depolymerization occurred. A relatively high yield of 11.8% pyrolysis oil was achieved when 2% crushed limestone was added, so even a small catalyst charge can significantly increase the MP/T process and the associated pyrolysis oil yield.

The low yield of 8.2% pyrolysis gas was achieved by dried SS from WWTP2, therefore the MP/T process was not achieved. A relatively high yield of 28.6%–31.3% pyrolysis gas was achieved when 2% crushed limestone was added. Other pyrolysis gas yields were relatively balanced in the range of 29.1%–43.3%.

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 MP/T, probably MP/T process was not achieved. In summary, the highest calorific value was obtained from 30% hay, 30% husks and 5% plastic waste (LDPE), thus before MP/T. Low calorific value of SCP 10.2–10.3 MJ kg⁻¹ after MP/T process was achieved in 2% crushed limestone, probably significant depolymerization of organic part in this sample was achieved.

The graph in Fig. 6 shows the temperatures during MP/T process for selected samples from WWTP1 with catalyst and organic additives. In particular, the temperature affects the yields of pyrolysis products, partially HMs immobilization and S_{BET}. Residence time is mainly related to the economy of MP/T operation, thus operating costs.

According to Fig. 6 the Mix1 from WWTP1 with 2% crushed limestone catalyst achieved maximum temperature 245°C and the course of temperature over time was linearly increasing. The Mix2 with 5% waste cellulose achieved maximum temperature 208°C and the course of temperature over time was linearly increasing. While Mix3 with 5% LDPE achieved maximum temperature 240°C and the course of temperature over time was linearly increasing. The Mix4 with 10% wooden sawdust achieved maximum temperature 256°C and the course of temperature over time had a relatively rapid exponential increase. The Mix6 with 30% hay achieved maximum temperature 275°C and the course of temperature over time had a relatively rapid exponential increase. And the Mix7 with 30% husks achieved maximum temperature 239°C and the course of temperature over time had a relatively rapid exponential increase.

Table 5
 FS and SCP composition after MP/T: 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 |
| – | 100:0 | SS WWTP2 | 2.4 | 6.5 | – | – | – | 13.5 | |
| | | SCP WWTP2 | 2.9 | 4.5 | 129 | 86.6 | 5.2 | 8.2 | 14.3 |
| Catalyst | 98:2 | FS WWTP1 | 6.9 | 6.5 | – | – | – | – | 12.1 |
| | | SCP WWTP1 | 3.1 | 5.8 | 330 | 60.1 | 8.7 | 31.3 | 10.3 |
| | | FS WWTP2 | 3.7 | 6.3 | – | – | – | – | 12.6 |
| | | SCP WWTP2 | 2.1 | 5.1 | 274 | 59.6 | 11.8 | 28.6 | 10.2 |
| | | FS WWTP1 | 7.1 | 6.4 | – | – | – | – | 12.6 |
| | | SCP WWTP1 | 2.9 | 5.7 | 248 | 60.5 | 10.5 | 29.0 | 10.7 |
| Waste cellulose | 95:5 | FS WWTP2 | 6.5 | 6.5 | – | – | – | – | 12.6 |
| | | SCP WWTP2 | 2.4 | 5.7 | 329 | 58.1 | 8.6 | 33.3 | 9.7 |
| | | FS WWTP1 | 8.9 | 6.4 | – | – | – | – | 13.5 |
| | | SCP WWTP1 | 2.0 | 5.4 | 288 | 63.8 | 7.1 | 29.1 | 11.0 |
| | | FS WWTP2 | 5.0 | 6.5 | – | – | – | – | 14.7 |
| | | SCP WWTP2 | 2.5 | 5.4 | 310 | 55.8 | 6.4 | 37.9 | 12.0 |
| Wooden saw-dust | 90:10 | FS WWTP1 | 3.4 | 6.5 | – | – | – | – | 13.3 |
| | | SCP WWTP1 | 2.8 | 5.4 | 278 | 60.4 | 6.7 | 32.9 | 11.0 |
| | | FS WWTP2 | 17.2 | 6.5 | – | – | – | – | 13.6 |
| | | SCP WWTP2 | 3.0 | 5.6 | 273 | 54.6 | 14.2 | 31.2 | 11.6 |
| | | FS WWTP1 | – | – | – | – | – | – | – |
| | | SCP WWTP1 | – | – | – | – | – | – | – |
| Wooden dust | 90:10 | FS WWTP2 | 6.9 | 6.5 | – | – | – | – | 13.5 |
| | | SCP WWTP2 | 2.6 | 5.2 | 313 | 51.1 | 10.1 | 38.8 | 10.6 |
| | | FS WWTP1 | 5.7 | 6.5 | – | – | – | – | 13.5 |
| | | SCP WWTP1 | 3.4 | 5.5 | 351 | 53.0 | 12.0 | 35.1 | 11.6 |
| | | FS WWTP2 | 3.8 | 6.5 | – | – | – | – | 13.5 |
| | | SCP WWTP2 | 2.5 | 5.6 | 278 | 54.3 | 11.8 | 33.9 | 12.2 |
| Hay | 70:30 | FS WWTP1 | 4.6 | 6.6 | – | – | – | – | 13.6 |
| | | SCP WWTP1 | 3.2 | 5.4 | 271 | 57.9 | 12.1 | 30.0 | 12.2 |
| | | FS WWTP2 | 6.0 | 6.5 | – | – | – | – | 13.9 |
| | | SCP WWTP2 | 3.5 | 5.7 | 281 | 47.2 | 9.5 | 43.3 | 11.8 |
| | | FS WWTP1 | – | – | – | – | – | – | – |
| | | SCP WWTP1 | – | – | – | – | – | – | – |

FS – feedstock; SCP – solid carbonaceous product; ADD – additive; – not measured.

The curves were compared, and the resulting findings is that a 30% additive addition had a different effect on temperature increase. The Mix7 with 30% husks has a significant increase in temperature. If HMs are immobilized and S_{BET} increases with a significant temperature rise, it would be possible to shorten residence time from 60 to 20 min and thus save input energy.

Fig. 7 shows the temperatures during MP/T process for selected samples from WWTP2 without additives, thus only dried SS, and samples with catalyst and organic additives. In particular, the temperature affects the yields of pyrolysis

products, partially HMs immobilization and S_{BET} . It is important to note that the relatively short residence time of 60 min was suggested in the previous research [36], in which the duration of pyrolysis was tested.

According to Fig. 7, the Mix0 (control) from WWTP2 without additives achieved maximum temperature 130°C and the course of temperature over time was almost linear and slightly rising. The Mix1 with 2% crushed limestone catalyst achieved maximum temperature 242°C and the course of temperature over time was linearly increasing. The Mix2 with 5% waste cellulose achieved maximum

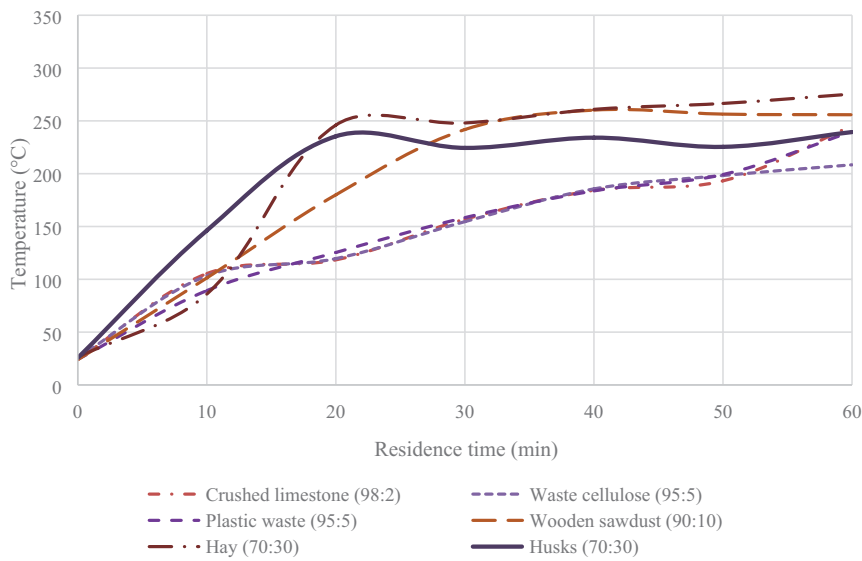


Fig. 6. Temperatures during MP/T process for residence time, selected samples from WWTP1 with crushed limestone (98:2), waste cellulose (95:5), plastic waste (95:5), wooden sawdust (90:10), hay (70:30), and husks (70:30).

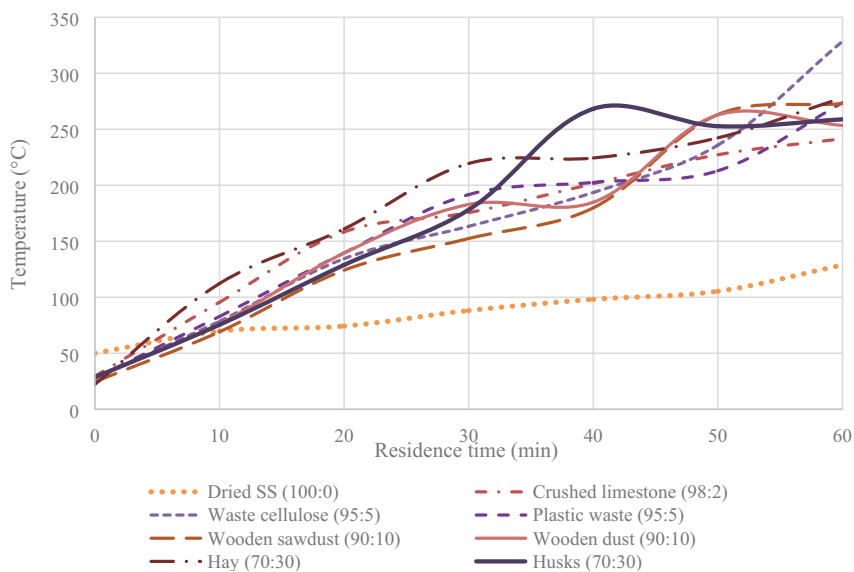


Fig. 7. Temperatures during MP/T process for residence time, selected mixes from WWTP2 without additive: dried SS (100:0), with crushed limestone (98:2), waste cellulose (95:5), plastic waste (95:5), wooden sawdust (90:10), wooden dust (90:10), hay (70:30), and husks (70:30).

temperature 329°C and the course of temperature over time was linearly increasing but except for the final phase that had exponential endings. And the Mix3 with 5% plastic waste achieved maximum temperature 274°C and the course of temperature over time was linearly increasing but except for the final phase that had exponential endings. And in the final phase there was a steeper increase in temperature. The Mix4 with 10% wooden sawdust 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 Mix5 with 10% wooden dust achieved maximum temperature 253°C and the course of temperature over time was linearly increasing but except for the final phase that had exponential endings. The Mix6 with 30% hay achieved maximum temperature 278°C and the course of temperature over time had a relatively rapid exponential increase. And the Mix7 with 30% husks achieved maximum temperature 259°C and the course of temperature over time had a relatively rapid exponential increase.

The curves were compared and have shown that a 2% catalyst addition had a similar effect on temperature linear increase. A significant difference in the temperature reached is in the catalyst which increases the temperature and improves the MP/T process.

30% organic additive addition had a different effect on temperature increase. The Mix7 with 30% husks has a significant increase in temperature.

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

FS composition from WWTPs and SCP composition after MP/T is reported in Table 6. The crushed limestone was used as a catalyst. 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} .

As can be seen in Table 6, the dried SS from WWTP2, and the corresponding SCP without additive had a significantly higher content of Cu, Pb, Zn after MP/T, in contrast to Pb, Cd, As, whose content did not show significant difference after MP/T, while Ni, Cr, and Hg content was lower after MP/T as the HMs sublimed into the pyrolysis oil/gas. SCP with 2% crushed limestone catalyst had Cu, Pb, Ni, Zn content predominantly higher than before MP/T, and Cd content did not show significant difference after MP/T, and As, Cr content from WWTP2 is lower after MP/T, and Hg content from WWTPs is lower after MP/T. SCP with 5% waste cellulose had Cu, Pb, Ni, Zn content predominantly higher than before MP/T, and Cr content from WWTP2 did not show significant difference after MP/T, and As content from WWTP2 is lower after MP/T, and Cr content from WWTP1 is lower after MP/T, and Cd, Hg content from WWTPs is lower after MP/T. SCP with 5% LDPE had Cu, Pb, As, Ni, Cr, Zn predominantly higher than before MP/T, and Cd content is not significantly different after MP/T, and Hg content is lower after MP/T. SCP with 10% wooden sawdust had Pb, Ni, Zn predominantly higher than before MP/T, and Cd, As, and Cr (from WWTP1) content did not show significant difference after MP/T, and Cu, Cr content from WWTP2 is lower after MP/T and Hg content is lower after MP/T. SCP

from WWTP2 with 10% wooden dust had Cu, Ni, Cr, Zn predominantly higher than before MP/T, and Pb, As content did not show significant difference after MP/T, and Cd, Hg content is lower after MP/T. SCP with 30% hay and SCP with 30% husks showed predominantly higher content of Cu, Pb, Ni, Cr, Zn before MP/T, and Cd, As content from WWTP2 is lower after MP/T and Hg content is lower after MP/T.

Summarizing for HMs, SCP with 30% hay and with 30% husks has lower content of all HMs than FS with 2% crushed limestone catalyst, 5% waste cellulose, 5% LDPE, and 10% wooden sawdust. This is related to the dilution of SS with an organic additive without HMs content.

FS had C_{org} in range of 23.5%–38.7%, and higher values were achieved when added 30% hay or 30% husks. SCP had C_{org} lower after MP/T in range of 24.8%–36.6%. Higher values of C_{org} were determined in samples from WWTP2, thus it relates to the quality of the FS before MP/T process.

FS from WWTP1 had pH in range of 5.50–8.97, and higher values were achieved when added 10% wooden sawdust and 30% hay. SCP from WWTP1 with 2% catalyst, 5% waste cellulose, 5% plastic waste, and 30% husks had pH higher after MP/T in range of 6.75–7.33. SCP from WWTP1 with 10% wooden sawdust and 30% hay had pH lower after MP/T in range of 6.56–8.23. FS from WWTP2 had pH in range of 5.49–9.01, and higher values were achieved without additives. SCP from WWTP2 had higher value after MP/T in range of 6.99–9.04. Dried SS from WWTP2 without additives represents alkaline area.

FS from WWTP1 had EC in range of 1,952–2,480 $\mu\text{S cm}^{-1}$ and SCP had EC lower after MP/T in range of 354–1,297 $\mu\text{S cm}^{-1}$. FS had EC from WWTP2 in range of 1,965–5,370 $\mu\text{S cm}^{-1}$ and SCP had EC lower after MP/T in range of 244–1,960 $\mu\text{S cm}^{-1}$.

FS from WWTP1 with 30% hay and 30% husks had S_{BET} in range of 1.1–1.3 $\text{m}^2 \text{g}^{-1}$ and SCP had S_{BET} higher after MP/T in range of 5.2–9.7 $\text{m}^2 \text{g}^{-1}$. SCP from WWTP2 with 5% waste cellulose, with 30% hay and 30% husks had S_{BET} 3.3, 1.5, and 3.2 $\text{m}^2 \text{g}^{-1}$. If HMs are immobilized and S_{BET} increases with a significant temperature rise, it would be possible to shorten residence time from 60 min to 20 min and thus save input energy in our future experiments.

The total content of HMs in SCP expressed in % of the SS/FS from WWTPs is reported in Table 7. The total HMs content in SS, FS, and produced SCP was determined by extraction using Aqua Regia. The calculation of the values in Table 7 is performed in % based on the weight of the input batch of SS/FS before MP/T process and of the output batch of SCP after MP/T process.

According to Table 7, the evaluation of each HM alone represents the reduction/immobilization of HMs, assuming the total HM content to the total weight before/after MP/T process. Reduction/immobilization of HMs in Aqua Regia was not achieved with dry sludge without additive. Conversely, the total content of HMs after MP/T for the organic additives hay 30% was achieved in 72.9% of the sample WWTP1 and 53.9% for the sample from WWTP2. Thus, according to the acid leaches in Aqua Regia, the reduction/immobilization of HMs was 27.1% for the sample from WWTP1, and 46.1% for the sample from WWTP2.

Table 8 describes the total HMs content by extraction in Aqua Regia in FS from WWTP2 and in SCP after MP/T

Table 6
FS and SCP composition after MP/T: HMs, C_{org}, pH, EC, and S_{BET}

| Additive type | Sample ID | 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 | 76 | 18 | 0.5 | 4.4 | 8.9 | 24 | 32.9 | 323 | 32.6 | 9.01 | 3,150 | - | | |
| | SCP WWTP2 | 82 | 21 | 0.8 | 4.6 | 8.7 | 19 | 13.2 | 411 | 35.2 | 9.04 | 1,929 | - | | |
| Catalyst | FS WWTP1 | 385 | 30 | 3.0 | 5.3 | 24.0 | 268 | 50.2 | 3,074 | 31.9 | 6.73 | 2,480 | - | | |
| | SCP WWTP1 | 561 | 56 | 4.3 | 20.9 | 37.7 | 399 | 1.9 | 3,315 | 24.8 | 7.09 | 441 | - | | |
| | FS WWTP2 | 115 | 28 | 0.3 | 13.6 | 15.2 | 97 | 24.1 | 1,015 | 33.2 | 7.38 | 4,950 | - | | |
| | SCP WWTP2 | 170 | 45 | 0.8 | 9.7 | 23.1 | 64 | 1.3 | 3,178 | 32.5 | 7.64 | 343 | - | | |
| | FS WWTP1 | 357 | 39 | 3.6 | 7.1 | 28.2 | 705 | 65.8 | 3,031 | 31.3 | 6.63 | 2,111 | - | | |
| | SCP WWTP1 | 611 | 42 | 3.4 | 27.0 | 40.8 | 399 | 2.2 | 3,913 | 34.5 | 7.21 | 445 | 8.0 | | |
| Waste cellulose | FS WWTP2 | 105 | 29 | 0.2 | 9.5 | 16.6 | 67 | 21.6 | 529 | 31.5 | 7.27 | 4,050 | - | | |
| | SCP WWTP2 | 187 | 48 | 0.2 | 8.4 | 29.4 | 77 | 2.0 | 3,731 | 36.6 | 7.51 | 287 | 3.3 | | |
| | FS WWTP1 | 451 | 35 | 3.5 | 14.5 | 25.3 | 300 | 60.3 | 4,483 | 23.5 | 6.65 | 2,040 | - | | |
| | SCP WWTP1 | 609 | 41 | 3.7 | 28.2 | 39.7 | 386 | 1.3 | 3,816 | 25.3 | 7.11 | 471 | - | | |
| Plastic waste (LDPE) | FS WWTP2 | 165 | 36 | 4.1 | 35.4 | 13.4 | 42 | 27.4 | 2,511 | 38.7 | 7.50 | 5,370 | - | | |
| | SCP WWTP2 | 267 | 49 | 5.4 | 92.5 | 20.3 | 69 | 0.9 | 2,248 | 34.0 | 7.34 | 309 | - | | |
| | FS WWTP1 | 514 | 39 | 2.7 | 3.8 | 29.0 | 514 | 76.5 | 518 | 33.6 | 8.76 | 2,041 | - | | |
| Wooden sawdust | SCP WWTP1 | 667 | 52 | 3.4 | 4.9 | 44.6 | 667 | 9.3 | 566 | 26.9 | 7.37 | 607 | 9.7 | | |
| | FS WWTP2 | 111 | 31 | 0.2 | 10.4 | 16.4 | 79 | 20.7 | 1,532 | 33.6 | 7.70 | 4,620 | - | | |
| Organic additives | SCP WWTP2 | 108 | 40 | 1.6 | 12.9 | 21.4 | 59 | 3.0 | 2,930 | 32.2 | 7.85 | 495 | - | | |
| | FS WWTP1 | - | - | - | - | - | - | - | - | - | - | - | - | | |
| | SCP WWTP1 | - | - | - | - | - | - | - | - | - | - | - | - | | |
| | FS WWTP2 | 103 | 32 | 0.2 | 9.9 | 15.3 | 49 | 27.0 | 473 | 35.0 | 7.35 | 4,570 | - | | |
| Hay | SCP WWTP2 | 174 | 33 | 0.2 | 10.9 | 25.1 | 63 | 1.7 | 1,528 | 33.7 | 7.70 | 395 | - | | |
| | FS WWTP1 | 75 | 24 | 0.3 | 1.3 | 8.5 | 61 | 27.6 | 371 | 34.9 | 8.97 | 1,952 | 1.1 | | |
| | SCP WWTP1 | 133 | 31 | 1.8 | 13.9 | 18.2 | 91 | 1.5 | 633 | 31.5 | 8.45 | 1,176 | 8.1 | | |
| | FS WWTP2 | 141 | 26 | 2.8 | 21.9 | 12.4 | 34 | 13.1 | 2,218 | 37.7 | 5.49 | 1,965 | - | | |
| Husks | SCP WWTP2 | 151 | 39 | 2.1 | 10.5 | 21.6 | 129 | 3.5 | 485 | 33.3 | 7.79 | 1,199 | 1.5 | | |
| | FS WWTP1 | 108 | 22 | 0.6 | 1.1 | 7.5 | 66 | 32.2 | 447 | 33.9 | 5.50 | 2,032 | 1.3 | | |
| | SCP WWTP1 | 153 | 35 | 1.5 | 12.2 | 23.5 | 81 | 4.2 | 725 | 31.7 | 6.88 | 578 | 5.2 | | |
| | FS WWTP2 | 88 | 26 | 0.3 | 13.9 | 12.4 | 29 | 24.6 | 407 | 33.6 | 6.53 | 5,050 | - | | |
| SCP WWTP2 | 154 | 29 | 0.3 | 6.3 | 25.8 | 52 | 0.7 | 1,056 | 34.0 | 7.49 | 375 | 3.2 | | | |

FS – feedstock; SCP – solid carbonaceous product; HMs – heavy metals; EC – Electrical conductivity; S_{BET} – surface area; – not measured.

Table 7
Total content of HMs in SCP expressed in % of the FS

| Additive type | | | Extraction in Aqua Regia | | | | | | | | |
|-------------------|----------------------|-------|--------------------------|-------|-------|-------|-------|------|------|-------|---------|
| | | | HMs (%) | | | | | | | | Average |
| | | | Cu | Pb | Cd | As | Ni | Cr | Hg | Zn | |
| – | Dried SS | WWTP2 | 93.6 | 100.9 | 140.7 | 90.1 | 84.9 | 68.2 | 34.6 | 110.3 | 90.4 |
| | | WWTP1 | 87.1 | 114.0 | 85.2 | 152.5 | 94.3 | 89.2 | 2.3 | 64.8 | 86.2 |
| Catalyst | Crushed limestone | WWTP2 | 87.5 | 96.1 | 49.9 | 42.4 | 90.7 | 39.2 | 3.1 | 66.6 | 59.4 |
| | | WWTP1 | 104.1 | 65.8 | 58.0 | 151.4 | 87.2 | 34.2 | 2.0 | 78.1 | 72.6 |
| | Waste cellulose | WWTP2 | 103.8 | 95.4 | 53.4 | 51.3 | 102.7 | 66.9 | 5.4 | 100.0 | 72.4 |
| | | WWTP1 | 86.2 | 74.5 | 67.1 | 123.6 | 99.9 | 82.1 | 1.4 | 54.3 | 73.6 |
| Organic additives | Plastic waste (LDPE) | WWTP2 | 89.9 | 76.2 | 73.3 | 78.9 | 84.2 | 90.9 | 1.7 | 49.9 | 68.1 |
| | | WWTP1 | 78.0 | 79.9 | 76.5 | 77.2 | 92.2 | 78.0 | 7.5 | 65.8 | 69.4 |
| | Wooden sawdust | WWTP2 | 53.2 | 71.6 | 53.9 | 68.5 | 70.5 | 40.7 | 8.1 | 99.3 | 58.2 |
| | | WWTP1 | 86.0 | 54.4 | 54.9 | 56.6 | 83.5 | 65.5 | 3.2 | 75.7 | 60.0 |
| | Hay | WWTP2 | 92.0 | 70.0 | 100.0 | 37.8 | 111.6 | 78.9 | 3.0 | 90.2 | 72.9 |
| | | WWTP1 | 62.0 | 86.5 | 42.2 | 26.8 | 95.8 | 92.4 | 13.9 | 11.6 | 53.9 |
| Husks | WWTP1 | 82.1 | 91.2 | 119.7 | 104.5 | 144.1 | 71.4 | 7.6 | 93.9 | 89.3 | |
| | WWTP2 | 82.8 | 53.7 | 58.1 | 21.4 | 98.4 | 86.6 | 1.4 | 34.5 | 54.6 | |

HMs – heavy metals.

based on the total weight per batch (mg batch weight⁻¹) and Table 9 describes the total HMs content by extraction in water.

Table 8 shows the organic additive hay at 70:30, and the total content of 8 HMs in the FS is 3,208 mg and the total HMs content in the SCP (average of 3 values) is 544 mg for the acid extract in Aqua Regia. Table 9 shows the hay, the total content of 8 HMs in the FS is 7.02 mg and the total HMs content in the SCP is 0.69 mg for the acid extract in water.

A graphical representation of the total HMs content in Aqua Regia and in water extracts for the FS/SCP sample from WWTP2 with hay at a ratio of 70:30, before and after MP/T is shown in Fig. 8. In this case, all 8 HMs were reduced/immobilized to 83.0% for the Aqua Regia extract and 90.2% for the water extract.

3.3. Summarizing discussion

In this research, we present properties of several types of SCP produced via MP/T 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 in the following combinations. MP/T temperature and yields of MP/T products were compared especially for crushed limestone as a catalyst and in particular also for 30% organic additives. Mixing with additives was performed up to 30%, thus around the recommended maximum value of 25% according to the STRUBIAS group [38].

3.4. Temperature, yields and energy use

The output pellet diameter with additives after MP/T was reduced volume ranging 12%–29% and reduced weight ranging 35%–55% than input pellet diameter before MP/T, and this volume and weight reduction have a positive impact on SCP transport for agricultural or other uses. Thus, the pelletization process thickens the SS, thus increasing

Table 8
HMs content in FS hay from WWTP2 and HMs content in SCP after MP/T, extraction in Aqua Regia

| Additive type | Ratio SS:ADD (%) | Batch weight before/after MP/T (mg) | Sample ID | Extraction in Aqua Regia | | | | | | | | Total HMs (mg) |
|---------------|------------------|-------------------------------------|-----------|--------------------------------------|------|-----|------|------|------|------|---------|----------------|
| | | | | HMs (mg batch weight ⁻¹) | | | | | | | | |
| | | | | Cu | Pb | Cd | As | Ni | Cr | Hg | Zn | |
| Hay | 70:30 | 1,300 | FS WWTP2 | 182.8 | 33.5 | 3.7 | 28.5 | 16.2 | 43.5 | 17.0 | 2,883.0 | 3,208 |
| | | 587 | SCP | 74.3 | 14.6 | 0.1 | 4.1 | 11.9 | 35.6 | 3.0 | 364.0 | 507.6 |
| | | 839 | WWTP2 | 223.9 | 44.6 | 2.1 | 10.9 | 21.9 | 43.5 | 2.2 | 356.5 | 705.7 |
| | | 691 | WWTP2 | 41.5 | 27.6 | 2.5 | 7.9 | 12.7 | 41.5 | 1.9 | 283.7 | 419.3 |

Table 9
HMs content in FS hay from WWTP2 and HMs content in SCP after MP/T, extraction in water

| Additive type | Ratio SS:ADD (%) | Batch weight before/after MP/T (mg) | Sample ID | Extraction in water | | | | | | | | | |
|---------------|------------------|-------------------------------------|-----------|--------------------------------------|-------|-------|-------|-------|-------|-------|-------|----------------|------|
| | | | | HMs (mg batch weight ⁻¹) | | | | | | | | Total HMs (mg) | |
| | | | | Cu | Pb | Cd | As | Ni | Cr | Hg | Zn | | |
| Hay | 70:30 | 1,300 | FS WWTP2 | 1.394 | 0.025 | 0.001 | 0.138 | 2.785 | 0.313 | 1.394 | 0.967 | 7.016 | 7.02 |
| | | 587 | SCP WWTP2 | 0.245 | 0.001 | 0.001 | 0.088 | 0.436 | 0.118 | 0.014 | 0.640 | 1.543 | |
| | | 839 | | 0.005 | 0.001 | 0.001 | 0.001 | 0.019 | 0.005 | 0.112 | 0.060 | 0.204 | 0.69 |
| | | 691 | | 0.008 | 0.002 | 0.001 | 0.001 | 0.021 | 0.008 | 0.067 | 0.216 | 0.324 | |

its density and improving the conditions for reducing the storage volume requirements and subsequent transport. The drying process followed by FS pelletizing with a dry matter content above 90% also appears to be a suitable technology for stable storage without further microbiological contamination. Thus, the FS can be stored for extended periods of time, for example, in closed containers.

Relatively high temperature and high pyrolysis oil yield was achieved with FS with 2% crushed limestone catalyst. The addition of catalyst supports the MP/T process including depolymerizing the organic matter in the SS. For further research, the combination of two additives, organic additive and catalyst, should be performed. In particular, the temperature affects the yields of pyrolysis products, partially HMs immobilization and S_{BET} . In the case the HMs are immobilized and S_{BET} increases with a significant temperature rise, it would imply the possibility to shorten residence time from 60 to 20 min and thus save the input energy.

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 MP/T 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 MP/T. Thus, for energy recovery, solution will treat the SS in the form of FS, without pyrolysis.

The Mix1 with 2% crushed limestone catalyst achieved maximum temperature 330°C and the course of temperature over time was linearly increasing. Crushed limestone as an inexpensive catalyst, will be useful for raising the temperature to HMs immobilization, increase S_{BET} or increase the yield of pyrolysis oil. Thus, crushed limestone can be

used as a substitute for the expensive zeolite catalyst used in previous research [36] or relatively expensive granular activated carbon [41].

The Mix2 with 5% waste cellulose and 5% LDPE 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.

The Mix4 with 10% wooden sawdust achieved maximum temperature 278°C and the course of temperature over time had a relatively rapid exponential increase. While the Mix5 with 10% wooden dust achieved maximum temperature 313°C and the course of temperature over time was linearly increasing but except for the final phase that had exponential endings.

The Mix6/Mix7 with 30% hay and 30% husks achieved maximum temperature 351°C and the course of temperature over time had a relatively rapid exponential increase, thus the temperature increase is probably related to a higher proportion of organic matter in this sample. And comparing the results in the graphs of Figs. 6 and 7 for 30% of the organic additive we can see a different temperature rise course at two different SS. SS from WWTP1 with 30% hay and with 30% husks has a much more pronounced and steeper temperature increase than the same organic additives for SS from WWTP2. Thus, the composition of the SS itself has a significant effect on the temperature course during the MP/T process and the temperature has influence on yields of products.

The average SCP yield was roughly 55% and the highest SCP yield was achieved with raw dried SS from WWTP2 and crushed limestone. The SCP yield decreases as the organic additive ratio increases, the lowest SCP yield of 47.2% was achieved for 30% husks. SCP yield is an

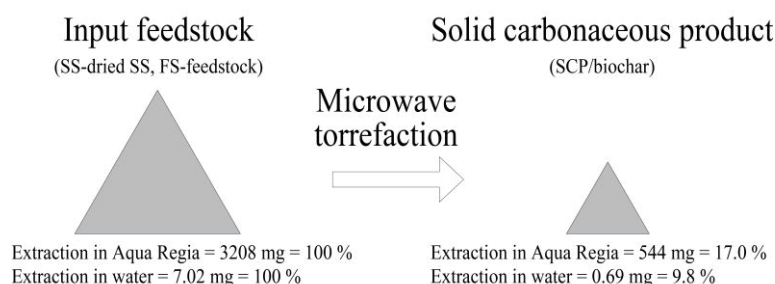


Fig. 8. Illustration of reduction/immobilization of the total content of 8 HMs for the FS with 30% hay (WWTP2) converted to the total content of HMs by extraction in Aqua Regia and extraction in water.

important indicator for storage and subsequent transport to agricultural and non-agricultural uses. The previous pelletization process improves the shape stability of the SCP so that it is possible to store and subsequently transport and use the SCP in agriculture with a minimum amount of small hazardous flying particulate matter, such as powder dried SS. On the contrary, the disadvantage of pelletizing of SS is energy demanding treatment process.

The low yield of 5.2% pyrolysis oil was achieved by dried SS from WWTP2, therefore we assume that process was not achieved, probably only further drying occurred. Another low yield of 6.4%–7.1% pyrolysis oil was achieved for plastic waste (LDPE), thus probably plastic waste was inert to microwave irradiation and no hydrocarbon depolymerization occurred. A relatively high yield of 11.8% pyrolysis oil was achieved when 2% crushed limestone was added, so even a small catalyst charge can significantly increase the MP/T process and the associated pyrolysis oil yield.

The low yield of 8.2% pyrolysis gas was achieved by dried SS from WWTP2, therefore the MP/T process was not achieved. A relatively high yield of 28.6%–31.3% pyrolysis gas was achieved when 2% crushed limestone was added. Other pyrolysis gas yields were relatively balanced in the range of 29.1%–43.3%.

FS with 5% LDPE and 30% organic additives had high calorific value. Thus, mixing and pelletizing process improve the FS qualitative energy parameters and this FS mix can be recommended for the certification as solid alternative fuel. Although based on the comparison of calorific value, it appears economically disadvantageous to MP/T process with the input energy required for magnetrons. Thus, the energy recovery of the SS will preferably be carried out in the form of raw dried SS or dried SS with an organic additive (FS). In view of future stricter legislation in the EU, based on the model of Germany [42] or Austria [43], for the extraction of phosphorus from SS from WWTPs bigger than 50,000 PE, it will be preferable to incinerate raw dried SS. The small incineration device of SS with the possibility of pelletizing with organic additives for the production of electric energy and thermal energy by cogeneration seems to be acceptable for smaller WWTPs. The energy obtained in this way could be used for the operation of selected facilities at the WWTP, especially for the operation of the SS drier.

3.5. Agricultural and other use

Mixing and pelletizing process improved the FS qualitative parameters monitored for the certification as biochar or the SAS. For certification as biochar or SAS, 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. Summarizing the HMs content, SCP with 30% hay and with 30% husks has lower content of all HMs than FS with 2% crushed limestone catalyst, 5% waste cellulose, 5% LDPE, and 10% wooden sawdust. This is related to the dilution of SS with an organic additive without HMs content and can be justified by a better C_{org} composition and thus enabling certification according

to the IBI [25] or EBC [26] guidelines. 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 such as HMs and C_{org} . FS had C_{org} in range of 23.46%–38.71%, and higher values were achieved when added 30% hay or 30% husks. SCP had C_{org} lower after MP/T in range of 24.81%–36.64%. Higher values of C_{org} were determined in samples from WWTP2, thus it relates to the quality of the FS before MP/T process which can be compensated by larger amount of additives in order to attain the certification quality according to guidelines of IBI [25] or EBC [26]. MP/T with pelletizing equipment might be primarily implemented on existing WWTPs or collection areas, where is a sufficient amount of source of SS and especially the organic additives.

HMs measurements revealed a significant heterogeneity of the HMs in SS. The part of HMs volatilized out of batch reactor of MP/T via the vapours to pyrolysis oil and pyrolysis gas. Several HMs tests have shown difference between initial and resulting content of a particular metal, namely Hg. It can be assumed that, under MP/T conditions, Hg was desorbed/vaporized and transported to pyrolysis gas and/or pyrolysis oil. Potential Hg evaporation was partially expected due to low boiling point 356.7°C for pure Hg [44] and due to not-well-understood influence of vacuum.

Reduction/immobilization of HMs in Aqua Regia was not achieved with dry sludge without additive. Thus, it can be seen that MP/T of SS with 30% hay or 30% husks has a potential to immobilize/reduce the content of HMs from SS into SCP. The highest HMs reduction/immobilization was achieved with the addition of 30% hay. The immobilization of HMs can be supported by a combination with a catalyst to increase the temperature in the future. Conversely, the total content of HMs after MP/T for the organic additives hay 30% was achieved in 72.9% of the sample WWTP1 and 53.9% for the sample from WWTP2. Thus, according to the acid leaches in Aqua Regia, the reduction/immobilization of HMs was 27.1% for the sample from WWTP1, and 46.1% for the sample from WWTP2. Some HMs (Hg) are likely to have passed fumes into pyrolysis oil or pyrolysis gas. Alternatively, these HMs were fixed/immobilized into the carbon microstructure in the SCP. This experience has been verified in the form of water extract. For example, in FS with 30% hay, all 8 HMs were reduced/immobilized to 83.0% for the Aqua Regia extract and 90.2% for the water extract.

FS from WWTP1 with 30% hay and 30% husks had S_{BET} in range of 1.078–1.295 $m^2 g^{-1}$ and SCP had S_{BET} higher after MP/T in range of 5.190–9.684 $m^2 g^{-1}$. SCP from WWTP2 with 5% waste cellulose, with 30% hay and 30% husks had S_{BET} 3.329, 1.516, and 3.147 $m^2 g^{-1}$. Thus, SCP with high S_{BET} could be useful as absorbent material to capture water in the soil or, for example, in the system of green roofs/walls as part of a green urban infrastructure. SCP from sewage sludge for non-agricultural use may be acceptable for green roofs, walls, football pitches, golf courses, green areas in cities, etc. Based on the significant stability of carbon in the SCP, this technical utilization appears to be an attractive

solution for carbon capture storage. Physical or chemical S_{BET} improvement is a separate research challenge for the future research. The next step should be to increase the quality parameters N, P, and K, as this activation of SCP could create an interesting fertilizer for non-agricultural use. And this SCP could be used as filtration material to treat WW thus to absorb HMs, organic and inorganic pollutants.

Based on current knowledge of MP/T of SS [10–12], selected CECs will probably be converted or removed into less hazardous substances by pyrolysis under microwave radiation and elevated temperatures. More detailed MP/T product determination is the subject of further research.

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 MP/T 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 or BGI. The second way represents a research challenge which was handled in this research via MP/T producing SCP. The main conclusions of the research are:

- The treatment of raw SS without additives using MP/T to the maximal temperature of 129°C represents only drying and not torrefaction.
- Pelletization process of SS with additives and MP/T process seem to be an attractive optimization technology for the transformation of SS into SCP from the point of view of reduced energy consumption and HMs fixation in the structure of SCP. In addition to mixing the SS with the additive, the quality of the input dried SS will affect the compliance with the selected biochar certification parameters. In the case of non-certification of biochar, it is possible to assume technical utilization of solid carbon product for non-agricultural use, thus blue-green infrastructure.
- The total HMs content in SS, FS, and produced SCP was determined by extraction using Aqua Regia. Nevertheless, our research was focused on soluble fraction (bioavailable, potentially harmful fraction) which is determined by extraction using deionized water. Therefore, the next research will be focused on BCR sequential extraction method, which can bring more detailed information on the forms 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.
- In this work, SS from two municipal WWTPs with the inflow of industrial WW with HMs was tested. Thus, these tested selected SS are not ideal for the production of quality SCP for agricultural or BGI use and for biochar certification. It seems more attractive to install MP/T on a small or medium scale WWTP without the inflow of industrial WW and without high HMs content. Consequently, such FS will be more attractive to the mixing, pelletizing and MP/T process to produce SCP for commercial use. Mixing with a limestone crushed

catalyst in a low 2% ratio as a suitable additive or mixing with a 30% organic additive to increase the temperature. The rapid increase in temperature has a positive effect on the immobilization of heavy metals and S_{BET} , so the addition of these two different additives to improve the quality of biochar is required and shorter residence times save operating costs. Thus, we can say that mixing and pelletizing process with catalyst and organic additives seems to improve the FS qualitative parameters which may lead to the future certification of SCP as biochar or the SAS.

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