Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2018.22108

112 (2018) 161–170
April

Microwave pyrolysis full-scale application on sewage sludge

Jan Ševčík*, Jakub Raček, Petr Hluštík, Petr Hlavínek, Karel Dvořák

Faculty of Civil Engineering, AdMaS Research Centre, Brno University of Technology, Veveří 331/95, 602 00 Brno, Czech Republic, Tel. +420723254976, +420541147728; emails: jansvck@gmail.com (J. Ševčík), racek.j@fce.vutbr.cz (J. Raček), hlustik.p@fce.vutbr.cz (P. Hluštík), hlavinek.p@fce.vutbr.cz (P. Hlavínek), dvorak.k@fce.vutbr.cz (K. Dvořák)

Received 5 November 2017; Accepted 23 February 2018

ABSTRACT

This paper reviews microwave pyrolysis (MP) and then presents a full-scale application of this technology to treat sewage sludge. Disposal of sewage sludge is becoming one of the most important issues in wastewater management in European Union. The use of sludge in agriculture is becoming problematic due to the content of heavy metals (HM) in sludge. Sewage sludge contains valuable resources for further use transformed to pyrolysis output products which are: char (also called biochar), pyrolysis oil and pyrolysis gas (syngas). Sludge pre-treatment and following MP outputs can be influenced by catalysts, eventually other admixtures, its mixing ratios in order of optimization of the depolymerization and microwave processes. The examined output samples were produced using a "full-scale" MP technology with the required pelletization. The input mixtures included dried sewage sludge, dried sludge with a catalyst and dried sludge with more admixtures (catalyst, lignin, hay, sawdust). We roughly quantified depolymerization process in terms of performance and temperature monitoring over time. This research includes a number of analyses: the dry solids content, proportion of organic and mineral components of individual materials, weight and bulk density of the output components in dependence of the course of microwave depolymerization and the preparation of input mixtures. The addition of zeolite similar to ZSM-5 (2.0% wt of dry substance) achieves the best temperature increases mainly with lignin or lignocellulosic admixtures. Chemical analyses monitor the HM content of biochar. As regards biochar, the surface and size of pores were evaluated. The aim of this research step is to show that the MP is a good innovative method to treat sewage sludge.

Keywords: Sewage sludge treatment; Sludge disposal; Microwave pyrolysis; Catalytic depolymerization

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1. Introduction

At present, both legislative and practice need to set the future direction of sewage sludge treatment. Trends across the European Union (EU) are likely to move closer to the current situation in Germany, Austria, Belgium and the Netherlands where the proportion of thermally treated sludge is the highest amongst the EU countries [1]. Although such thermal treatment is often associated with incineration, there are alternative methods such as gasification or pyrolysis (thermochemical decomposition in absence of oxidizing agents) [2,3] producing pyrolysis coal (also referred to as the term biochar, microchar, pyrochar, etc.) which offers attractive applications, for example, in agriculture.

From the global environmental perspective, biochar, also pyrolysis oil and pyrolysis gas (syngas) present a certain solution to circular economy, carbon footprint reduction, heavy metal (HM) fixation and water retention. The European legislative restricts the use of materials for agricultural applications if the limit concentrations of HM are exceeded, thus this application is simply inadmissible as the HM may not be leached from biochar [4]. From a practical point of view, such

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* Corresponding author.

Presented at the 5th International Conference on Sustainable Solid Waste Management (ATHENS 2017), 21–24 June 2017, Athens, Greece.

1944-3994/1944-3986

permanent HM fixation in biochar (depending on many factors, e.g., process temperature) [5,6] appears to be an appropriate solution for the use of sewage sludge for sustainable development with a view of improving the properties of agricultural soil.

HM fixation in biochar is not the only benefit of pyrolysis, when compared with other thermal methods of sludge treatment. Another significant positive feature is the purity of gaseous emissions as opposed to flue gases from mono and co-incineration sludge treatment systems. In such a case, only biochar and liquid pyrolysis condensate (i.e., humidity + oil) are obtained from the original treated input sludge. If an operating unit is installed, the gaseous component is burned in the cogeneration engine whose exhaust system is comparable with car motors, the pyrolysis gas offers itself to be burned directly at the point of origin, for example, in cogeneration units, these are, as a standard, cleaned exhaust emissions [7].

There are numerous scientific studies offering various details on thermal pyrolysis of sewage sludge [8–14]. However, a part of them deals with aspects related to microwave pyrolysis (MP) of sludge [5,15–17], and a minimum of studies concentrate on the "full-scale" solution to the MP of sewage sludge. The major difference between the microwave and standard heated pyrolysis consists in the fact that when using pyrolysis with a standard heat source, this heat is transferred into the material through conventional heat transfer so that all material is heated from the surface [18]. In the case of MP, however, this depends on the structures of material itself, because it is related to its composition (the content of dielectric components, variable at the time of the process), which determines the course of process temperatures depending on the intensity of microwave radiation.

The course of pyrolysis microwave catalytic depolymerization has already been well proven by the technology supplier using other materials (e.g., lignocellulosic biomass) [19]. It is reported that up to 30% of sewage sludge weight can be composed of lipids [15]. The required processes were limited with pulsed microwave radiation and with the aid of catalyst. The proportion of water and oil in the resulting condensate then corresponds to this fact, and energy intensity of such separation of moisture from sludge. The second aspect is that water as a dielectric heats its surroundings, which means that when it is absent a different microwave radiation absorber is desirable as a component of the material to be treated – for example, the so-called "catalyst" or microwave radiation absorbers. By adding the suitable catalyst to the material to be treated, a very efficient structure of material selectivity can be achieved with resulting higher yields of the gaseous and/or liquid components [19,20]. A number of studies and research works highlight the unquestionable potential benefits of pyrolysis technologies for the environment. With the appropriate application of the above knowledge, optimal use of the combination of MP and catalytic depolymerization can be achieved with respect to environmental friendly utilization of sewage sludge in the form of fixing HM in solid carbonaceous residues, the yield of individual output components and their composition.

Such mixture can be optimally penetrated by microwave radiation (in the case of the "full-scale" application with continuous operation a stirred reactor is considered). The choice of tested pellet diameters corresponded to the technological possibilities and recommendations provided by supplier of the pyrolysis reactor. Another advantage of such mixtures for the MP process is the fact that when the pellets are pressed and pass through a hot die of the pelletizing press (e.g., over 80°C), the surface gets smooth and partially "baked". Such an encapsulated pellet thus offers the function of a kind of "micro-reactor" where pressure increases during heating up to the breaking point of the surface. Consequently, simply said, volatile matter molecules are ejected through the sealed surface once the pressure limits have been reached. This is similar to the so-called "pop-corn" effect when heating results in increasing pressure inside the grain up to the limit value [19]. Another considerable benefit of such pelletization is simply handling of biochar which does not create dusty environment and it can also be assumed that potential granulate application in agriculture can be more acceptable.

Capodaglio and Callegari [15] describe similar outputs stating that the gas contains, in particular, H_2, CO, CO_2 and CH_4, the liquid components being mainly various hydrocarbons, organic acids, high molecular weight carbonyl compounds, phenols, aromatic components, aliphatic alcohols, acetic acid and water. The output biochar is composed mainly of solid carbon and ash containing HM. If sludge is treated through pyrolysis processes, the main stated advantage is that HM contained in sludge should be concentrated in the output biochar after the process (this may not apply to Hg and Cd) [15].

Previous research has shown that lignocellulosic biomass without the aid of catalyst was affected by the required processes in a very limited degree. Pre-treatment of sludge using pelletization offers certain advantages already verified on other (e.g., lignocellulosic) materials [21]. By adding the suitable catalyst to the treated material, a very effective material selectivity can be achieved, and thus a higher yield of gaseous or liquid components can be achieved. The sewage sludge was mixed with three types of admixtures in order to absorb microwave radiation and two admixtures approximating the microwave process. Typically, the energy required for these processes is lower than the energy needed for processes without catalytic support [21]. If MP treats directly the dewatered sludge (i.e., about 70% moisture content), it is even stated that without the addition of a microwave radiation the main effect is sludge drying [15]. In our case, zeolite is used as absorber – a catalyst – whose secondary function should appear mainly once the moisture evaporates when the already treated material does not contain enough dielectric substances to heat up its surroundings. In this situation, under optimal conditions, catalytic cracking of hydrocarbons supported by zeolite – catalyzer – occurs [19]. When drying sludge, a certain amount of volatile matter also leaves the system along with moisture. The designation of zeolites as catalysts can be viewed from various perspectives. Catalyst is defined as a substance that facilitates, enables or adjusts the rate of targeted reaction but at the same time it leaves the process unchanged. In principle, zeolite may work but chemically bound water can also play a role, as it leaves at temperatures up to about 250°C. The role of catalyst supporting the cracking of hydrocarbons is also considerable in the optimized process.

The proportion of organic matter not only is related to the sludge management concept of the wastewater treatment plant (WWTP) but also plays a role in further sludge treatment. Organic components are of key importance for microwave depolymerization because during the process pyrolysis oil, gas, etc., are formed, that is, mainly components that do not reach the output biochar. One of the indicators providing information about organic matter content in sludge for this research was "total organic carbon" (TOC), that is, all organic carbon. In the field of sewage treatment, the proportion of organic and mineral substances in sludge is often monitored using the "loss on ignition" (LOI) indicator. AdMaS Research Centre offers the possibility of using portable computer-controlled model (TOC-LCSH/CPH, Shimadzu) TOC analyser with an additional SSM module. The aforesaid LOI can be also used for the purposes of benchmarking with TOC by the output of thermogravimetry (TA Instruments Discovery Q550) which provides information on the moisture content, ash content and combustible components.

This paper analyses the use of MP in combination with input material pelletization and brings outputs referring to energy efficient treatment of mixtures containing selected kinds of admixtures.

2. Materials and methods

The MP unit is installed at AdMaS Research Centre, Faculty of Civil Engineering, Brno University of Technology, the Czech Republic. Therefore, this paper also provides a brief introduction of the particular microwave technology as well as other laboratory equipment.

2.1. Technology

The principle of microwave heating consists in the effects of rapidly changing microwave radiation (electromagnetic field), which leads to the material molecules vibration which basically results in frictions increasing the temperature [18]. The vibrations increase the mean temperature as this increases the internal energy. From the point of view of the reaction to microwave radiation, the materials can be divided into absorbents, conductors and insulators [18]. Dielectric carbon-containing materials have a good ability to absorb and convert it into thermal energy. Such microwave radiation absorbers contain a minimum of charge carriers and when exposed to microwave radiation they transfer only a negligible proportion and absorb most of it and convert it into thermal energy [22]. Pyrolysis of various organic materials can produce three basic output components: biochar, pyrolysis oil (or a similar liquid consisting of oil and water) and gas which leaves the system after vapour condensation.

As the research concerns the treatment of a larger quantity of mixtures in already prepared forms, which could be identical with the case of full-scale installations (pelletization, admixture), the preparation of the sludge and its treatment faced problematic facts which would probably not occur in other cases.

Two different reactors have been used in the laboratory for this particular research. Both reactors operate in a vacuum mode ensuring essentially anoxic conditions. A vacuum pump was used to extract the air present initially and then vapours during the process while constant vacuum was monitored and controlled in the system. In this vacuum pipe system, coolers were used in both cases to condense vapour. The remaining gaseous component was burned on a gas burner in order to ensure purity of ambient air. The negative pressure was maintained at about 400 hPa below normal atmospheric pressure, thus at about 600 hPa.

One of the reactors was designed for the use of a special 2-L glass flask placed in the centre of the furnace where magnetron emitted radiations from one side, and on the other the microwaves were reflected by a reflector. This reactor has the advantage of separating a laboratory glass system in which the pyrolysis itself takes place from the space in which the magnetron is located.

The second reactor is a single segment (chamber and magnetron) from a large rotating "full-scale" reactor where the magnetron is separated from the chamber in which pyrolysis directly takes place by a special screen. This reactor does not offer such accurate temperature measurement over time and the magnetron output is often constant throughout the process. The temperature trend corresponds to ongoing processes. A larger batch can be fed to this reactor (i.e., 3–10 kg of pelletize).

2.2. Materials

Composition of sewage sludge depends on processes applied at WWTP of its origin. Each individually produced sewage sludge has its own composition and properties, so it is possible to state every single sludge is different. Final properties are influenced by previous digestion steps at WWTP.

In general, it can be assumed that the sewage sludge is a heterogenous mixture of undigested organics (paper, plant residues, oils, etc.), microorganisms, inorganic material and moisture. Undigested organic part of sludge consists of several hydrocarbons such as proteins, peptides, lipids, polysaccharides, phenolics and aliphatic structures containing macromolecules, polycyclic aromatic hydrocarbons, etc. [14]. Sludge treated in AdMaS laboratories was mostly digested, so significant part of organic matter was reduced by digesting at WWTP with biogas production. Its real LOI value is mentioned bellow.

2.2.1. Sludge samples

The main source of sludge for laboratory tests was the WWTP in Brno Modřice, Czech Republic, with a capacity of approximately 531,000 PE (22-d digestion at 35°C), where the drying (Nara paddle dryer) is heated to 100°C with a retention time of about 3 h [23]. The basic characteristics of the individual samples of sludge subject to the microwave technology treatment are as follows:

- dry solids: 91.5%–91.9%, [23]
- LOI: 47.1%–49.0%, [23,24]
- fraction: approximately 1–8 mm (bound finer fractions) [23].

2.2.2. Admixtures

In this research, the sewage sludge was mixed with three types of admixtures in order to absorb microwave radiation after evaporation of the contained moisture (and possible support for catalytic cracking of above mentioned hydrocarbons) and two admixtures approximating the microwave process to lignocellulosic biomass depolymerization (wood sawdust, lignin). The admixtures used are summarized as follows:

- zeolite similar to ZSM-5 with an admixture of other zeolites (faujasite, wassalite, etc.) – synthetic zeolite showing an optimal effect on the process of microwave depolymerization of lignocellulosic biomass, fineness <100 μm,
- zeolite Lehotka BL 200 – zeolite extracted in Slovakia (composition: sanidine, muscovite, kaolinite, etc.), milling fineness 200 μm,
- biochar from previous tests – fraction 0.1–0.5 mm,
- hay,
- sawdust – fraction 0.1–0.5 mm, soft wood,
- lignin – waste from Swedish paper mills.

The preparation of input raw material took place with respect to the desired properties of the output components. The first stage of sludge treatment for MP can be considered as one of the sludge treatment stages at WWTPs producing sludge. An important role is played both by the characteristics of the WW influent to the WWTPs and by the sludge management conception at the treatment plant. Significant factors are the presence or absence of anaerobic stabilization and sludge dryer. When municipal WWTP is the source of sludge for MP, it is advisable to have an installed dryer and thus feed the dried sludge directly to the reactor. The proportion of dry matter in the input material plays an important role in the sludge preparation even during the pyrolysis process itself. It is required to be around 88% (necessary not only for the pelletization but also for the microwave process). Such moisture content facilitates possible pelletization and, besides, during the first step of pyrolysis, the residual moisture content is evaporated from the treated mixture together with a share of the other volatile substances and vapours.

The sludge preparation for laboratory tests consisted of a number of steps. These samples of dried sludge (from tens up to hundreds of kilograms) were blended with admixtures in specified proportions, pelletized, dampened and stored.

Relevant methods [18,25] present and describe relationships for determining the penetration depth of microwave radiation in various materials. However, with regard to the characteristics of the dried sewage sludge, it should be sufficient to make an estimate with regard to comparable materials for which these values are known. Allowing the use of penetration depth in specific materials is appropriate for obtaining homogeneously radiated processed output mixtures. Therefore, the sludge was pelletized into an input mixture (previously tested diameters were mainly 6 and 8 mm) prior to the treatment in the microwave reactor.

2.3. Testing method for indicators

2.3.1. Proportion of output components

Output biochar was weighed directly, the volume of liquid condensed component was measured in a graduated cylinder and consequently, an informative proportion of output gas was determined based on the following simplified relationship:

$$\mathrm{GP} = \frac{\mathrm{ID} - \mathrm{BP} - \mathrm{CV}}{\mathrm{ID}} \times 100(\%) \tag{1}$$

where GP is the share of output gas production (%), ID is the weight of the input dose (g), BP stands for the weight of the produced biochar (g) and CV is the condensate volume (mL). The aforesaid relationship deducts volume from the weight but in this simplified case the bulk density of the condensate of 1,000 kg m^{-3} is considered. Despite the fact that gas yields from the individual experiments were determined in this manner, Table 1 shows the yields of solid, liquid and

Table 1
Description of mixtures and output characteristics

Mixture description (admixtures to sludge before pelletizing, dose related to dry solids)	Sample designation	Biochar yield (%)	Liquid yield (%)	Gas yield (%)	TOC biochar (%)	Organic matter thermogravimetrically (%)
No admixtures	K0.0	61.0	9.6	29.4	27.4	22.8
0.5% zeolite ZSM-5	Z0.5	61.6	13.9	24.5	23.1	30.1
1.0% zeolite ZSM-5	Z1.0	58.9	18.2	22.9	29.3	40.3
2.0% zeolite ZSM-5	Z2.0	56.8	15.8	27.4	24.4	39.5
2.0% zeolite ZSM-5 + ca 2.0% hay	Z2.0 G	62.1	19.3	18.6	33.6	34.4
0.5% zeolite BL200	L0.5	56.7	20.0	23.4	27.1	35.8
1.0% zeolite BL200	L1.0	58.1	13.5	28.4	26.2	35.5
2.0% zeolite BL200	L2.0	53.5	25.2	21.3	27.2	27.5
2.0% zeolite BL200 + ca 2.0% hay	L2.0 G	63.4	19.3	17.4	39.4	44.6
0.5% biochar 0.1–0.5 mm	C0.5	57.0	19.7	23.3	29.4	32.6
1.0% biochar 0.1–0.5 mm	C1.0	63.7	11.5	24.8	23.1	30.5
2.0% biochar 0.1–0.5 mm	C2.0	58.9	20.6	20.5	29.6	35.0
1.0% zeolite ZSM-5 + 30% lignin	Z1.0 LIG30	59.6	21.1	19.3	–	–
1.0% zeolite ZSM-5 + 30% sawdust	Z1.0 SD30	58.5	16.7	24.8	–	–

gaseous components as a percentage. In addition, it consists predominantly of nutrients, organic matter and organic micro-pollutants. If the selected process is optimal, these organic components are almost fully converted into liquid or gaseous state. This indirectly means that the lower the yield of biochar, the better result is achieved. The above relationship does not take into account the proportion of dry matter in the input material, which was about 88% for all the input samples.

For TOC determination, we used two furnaces of the analyser with the optional module, the proportions of total and inorganic carbon were determined on samples weighing around 1 g (for both input and output materials), from which the total organic carbon can subsequently be determined using the relationship below [26]:

$$\mathrm{TOC} = \mathrm{TC} - \mathrm{IC}\ (\%) \tag{2}$$

where TC stands for total carbon in (%), IC is inorganic carbon in (%), and a TOC is the determined total organic carbon.

In principle, LOI is based on the measurement of sample weight before and after ignition (burning out/evaporation of organic matter). In this specific case, the LOI values were obtained directly from the WWTP providing sludge samples. However, the determination was made in a way that respects the following relationship (Eq. (3)). This applies both to automatic measuring scales and laboratory manual determination:

$$\mathrm{LOI} = \frac{M_{\mathrm{in}} - M_{\mathrm{out}}}{M_{\mathrm{in}}} \times 100(\%) \tag{3}$$

where LOI in (%), M_{in} stands for the input sample weight (g) and M_{out} is the weight of output ignited sample (g). However, it must be noted that data obtained through the thermogravimetric analysis (TA Instruments Discovery Q550) automatically include output data of the LOI type. TA Instruments Discovery Q550 uses a heating rate of 10°C/min from the laboratory temperature to 1,000°C in air flow (flow rate of 60 mL/min). Up to 200°C moisture is taken out, between 200°C and 600°C the organic proportion is degraded along with some mineral compounds, and some hydrocarbons at higher temperatures.

2.3.2. Dry solids analysis

The dry solids content in the input and output solid material is a very important indicator both with respect to the calorific value and other properties of the output product and with respect to the process of the MP process itself. The water content in the sludge, that is, in the input mixture in the pyrolysis process, should be kept at an optimally low value. In case of high moisture content, the contained water is evaporated at the first phase of the process. Information on the dry solids content of input and output materials was obtained using drying weights (at temperatures up to 105°C) and thermogravimetry (TA Instruments Discovery Q550) and from the WWTP. However, the data provided by the treatment plants were usually indicative only as the sludge was further treated. More accurate information was provided in the form of laboratory results. Similarly to the determination of the LOI, the determination of the dry solids content is principally based on the monitoring and the comparison of the weights of raw and dried samples (after weight stabilization). Although the drying scales evaluate the proportion of dry solids automatically, the relationship can be described as follows:

$$\mathrm{Dry}_{\mathrm{Sub}} = \frac{M_{\mathrm{dry}}}{M_{\mathrm{wet}}} \times 100(\%) \tag{4}$$

where M_{dry} stands for the weight of sample dried up to stabilization (g) and M_{wet} is the weight of wet input sample (g).

2.3.3. HM analysis

From the point of view of environmental protection, Cd, Hg, Pb, As, Cr are designated as hazardous, along with, for example, Ni, which is then defined by the relevant regulations [27]. From the legislative point of view, two main methods of sewage sludge application in agriculture can be envisaged. One variant is direct application (limited in the future) of stabilized, hygienized sludge, which meets the limits set by the decree [4], the second may be certified biochar production. Probably there will not be any possibility to use sewage sludge without admixtures for production of certified fertilizer.

This is related to the course of geochemical cycles and HM contained in soil and HM accumulation in soil is dependent on pH of the soil. If the environment is acidic, HM are released more easily, they move better in the soil solution and are more easily acceptable for plants (part of them is re-released by the plants, some of them are accumulated in organisms or subsequently in animal organs). Such HM mobility endangers ground water [27]. What causes a problem is the indirectly mentioned fact that HM, the concentration of which in sludge is just below the limit, will probably be above the limit in many cases due to the fixation in output biochar because they remain contained in the solid component but the volume and weight of the solid component will be reduced after the process. However, the statement of higher HM concentration in biochar need not apply universally. It is subject to a number of factors. An important role is played by the temperature of pyrolysis process [5,6] and the retention time. However, the concentration of HM is also affected by the related efficiency of microwave depolymerization. Due to the process temperature of pyrolysis, which is, in this case, most often below 250°C (low-temperature pyrolysis), it could in theory be ensured that HM do not escape from the system together with other vapours [6]. With respect to the process temperature, one of the more sensitive HM would be mercury, which would completely evaporate (reduction to Hg^0 followed by volatility) at about 350°C, which is a temperature that is theoretically above the pyrolysis process temperature. However, this applies mostly to pure mercury. If it is present in molecules of other substances, its physical properties are different. As regards chromium, nickel, copper, zinc and lead, it has been demonstrated that these elements remain fairly safely fixed in biochar in sulphides, hydroxides, etc., at process temperatures of up to 750°C in chemical terms. A special case is cadmium found in sludge in carbonates and sulphides (sulphides in digested sludge) that remains in biochar at process temperatures of up to 505°C but leave the system at 750°C along with vapours. The release at process temperatures between these values is dependent on the retention time. As mentioned above, at our process temperatures there is a presumption in this respect that there should be no risk of HM escape from the system or this risk should be at least substantially limited. HM should thus remain mostly fixed in biochar. However, a practical problem is that particles containing HM may be entrained by the vapour stream into a condensation exhaust system [6]. However, the assumption is that such escape plays a minimal role. A question offered for further investigation is the role of vacuum in such a process. Expert articles provide information stating that HM leachates from the biochar depend on pH and the pore structure and surface area of the pores [10]. The same study by Agrafioti et al. [10] indicates that the process temperature of pyrolysis and the pH value of the leachate from biochar is directly proportional. At the same time, however, the solubility of metals is dependent on pH. At extreme values over 12, Zn, Pb, Cr and Al can be dissolved through the formation of hydroxy complexes. However, it is assumed (according to [10]) that in the low-temperature pyrolysis the pH value of the leachate could be closer to the neutral range than to the said value. It is also stated that the behaviour and mobilization capacity of HM is dependent on the chemical form of HM occurrence and that microwave heating is more efficient in HM immobilization [5]. One of the research outcomes mentions the reaction of HM during the pyrolysis process which can stabilize the HM:

$$\text{Ion HM} -> \text{hydroxide HM} -> \text{oxide HM} \qquad (5)$$

In addition, the same source mentions three main forms of HM occurrence with a division depending on the bioavailability, that is, the ability of plants to absorb these HM. For plants, the best available HM are those that are bound to carbonates. Another form of HM is bound to iron or manganese oxides that are also bioavailable but more stable than carbonate HM while exhibiting some instability in contact with biosphere or living organisms. The most stable are crystalline HM but it is reported that they can be converted to unstable fractions and released only at high temperature pyrolysis [5]. This fact is associated with the finding that HM contained in biochar from MP are fixed better than in biochar produced by standard heating [5].

The HM content in biochar was determined using leachate. The total HM concentration in the biochar was determined using aqua regia leachate and, simply said, bioavailable HMs were determined by using an aqueous leachate. For informative evaluation, we could then apply a relationship which gives a certain idea of the HM content detected in the biochar:

$$HM_{fix} = HM_{ar} - HM_{w}\ (ng/g) \qquad (6)$$

where HM_{fix} are HM fixed in biochar (ng/g), HM_{ar} stand for HM_{in} aqua regia leachate (ng/g) and HM_{w} mean HM from aqueous extracts (ng/g).

2.3.4. Surface and pore analysis

One of the characteristic features of biochar produced by MP is a greater pore surface area than the one offered by biochar from conventional heating [19].

The surface area of the biochar pores was measured using gas adsorption in Quantachrome Nova 3200e using NovaWin software and based on following process analysis characteristics:

Adsorbate gas: nitrogen, temperature: 77.350 K, press tolerance adsorption/desorption: 0,050/0,050 Pa, equilibrium time adsorption/desorption: 240/240 s, equilibrium time out adsorption/desorption: 480/480 s. For the specific surface analysis five points were measured and assessed using multi-point BET method.

For the pore size, the analytics method BJH was used. For the adsorption 24 points and for desorption 38 points were measured. All the samples were carefully degassed in a vacuum dryer for at least 24 h at a temperature of 50°C.

3. Results and discussion

3.1. Sewage sludge and lignocellulosic differences in biomass processes

Not only with respect to experience of the previous research (as mentioned above) with regard to a number of objectives (handling, penetration depth, visual evaluation of biochar, liquid yield, etc.) but also with respect to feasibility in the laboratory and in practice pointed out that the most suitable input mixture is pelletize pressed into 6 mm pellets. Comparison was made between compressed pellets with 6 and 8 mm pellets and pellets from belt and solar dryers. Given the assumption that the smaller the pellet diameter, the better the radiability and given the aforesaid findings from the previous research, the submitted results are related to experiments carried out on a 6-mm pelletize.

Fig. 1 describes three main steps of the process initially optimized for lignocellulosic biomass.

Zone 1: rapid heating of dielectric materials from about 80°C, escape of vapours and a share of volatile substances from pellets accompanied by the formation of nano-channels, potential lignocellulosic biomass still intact.

Zone 2: after evaporation of moisture, zeolite as a radiation absorber heats up its surroundings, destruction of cellulosic chains, moderate zeolite-assisted cracking with low evaporation of hydrocarbons, formation of carbonaceous centers.

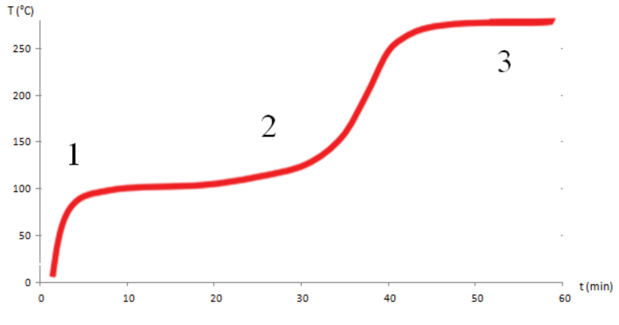

Fig. 1. Typical course of temperatures in time for lignocellulosic biomass (for 6 mm pellets, divided into three steps) [19].

Zone 3: achieving pyrolysis oil evaporation temperature, intensive formation of carbon centres supporting cracking, plasma electrical discharges, intensive cracking due to zeolite and carbon centers, vapour treatment at the point of origin (e.g., decarboxylation) prior to escape from pellets [19,21].

Note: These zones were also present in the same order when treating sewage sludge. Another study by Yu et al. [17] showed similar temperature steps during the process even with much more lower input dry substance, The main differences were the retention times, temperatures (for sludge it is several times higher) and also during the 3rd process zone when, in the case of sewage sludge, the catalytic reaction (mainly cracking) was usually still insufficiently optimized using the ideal catalyst. That means there can be an expectation of similarity in graph curve shape for most of microwave-treated biomass kinds with differences caused mainly by treated material different compositions and other process parameters. Main role of composition can be connected to differences of benchmarked sludge and lignocellulosic biomass which are different molecular composition, different inorganic substance content, moisture content, etc.

It has been examined whether it is suitable to add an admixture to the input mixture to provide some catalytic support for pyrolysis reactions, with the main anticipated effect of being microwave radiation absorption. Results shown in the graph (Fig. 2) indicate the effectiveness of ZSM-5 similar zeolite support in samples labelled Z2.0 and Z1.0 with possible extensions (i.e., 2% and 1 % concentrations with potential admixtures) for microwave heating. Table 1 describes both the sample marking and some of the principal collected data.

Biochar and condensate yields from the mixture with a 30% lignin admixture (shown in Table 1), which are 4,085 g and 1,445 mL, respectively, percentually related to the weight of the input dose, that is, 59.6% biochar and 21.1% condensate provide the most interesting results of all these three mixtures with 1% ZSM-5 like zeolite. This finding confirms

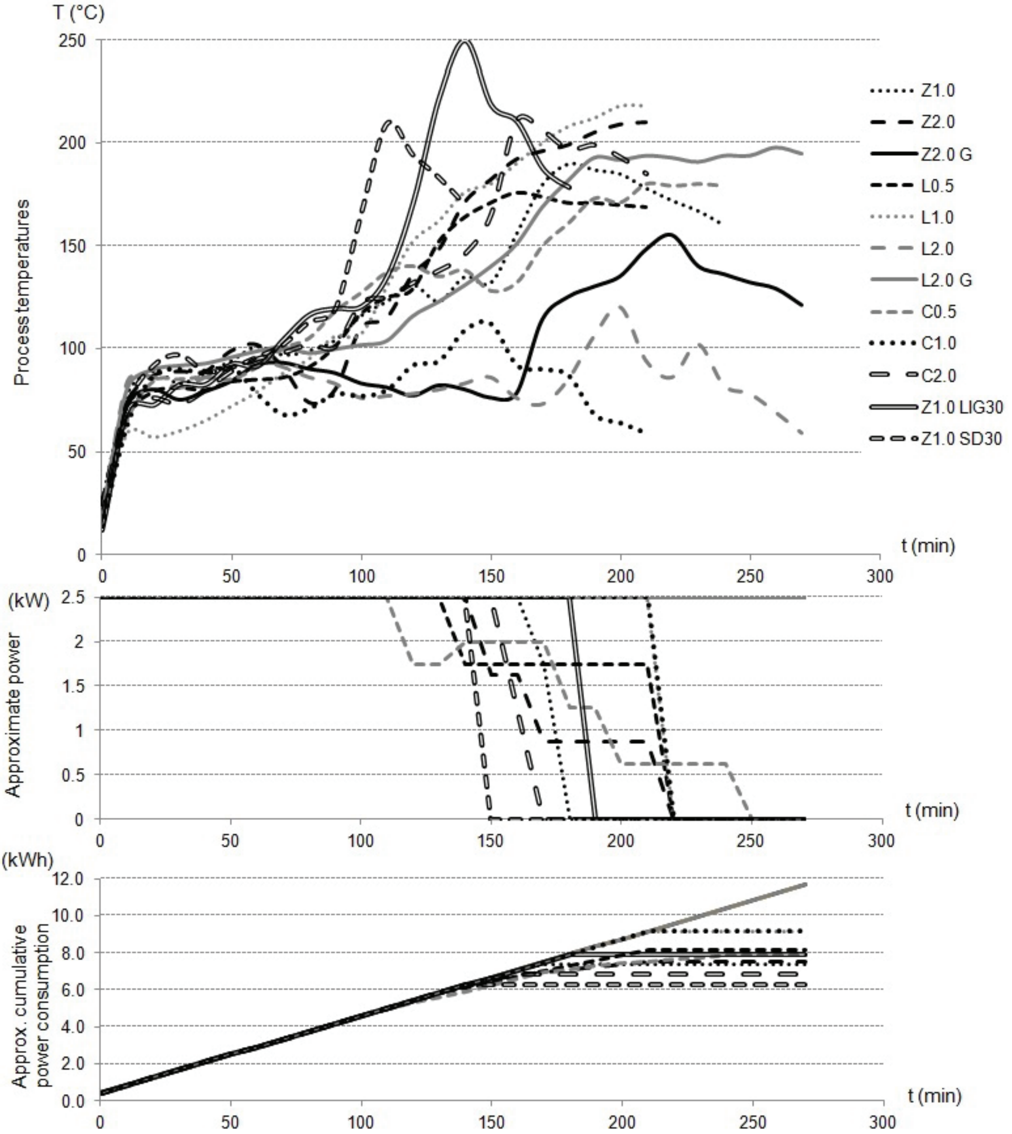

Fig. 2. Temperature over time (power included) – 6 mm pellet processing.

the fact that zeolite similar to ZSM-5 is optimal for lignocellulosic biomass and, at the same time, just like the temperature of the sample Z1.0 LIG30 (Fig. 2), it points to the fact that it might be interesting to treat sewage sludge together with lignin.

It can be seen that Fig. 2 confirms a rapid increase in temperature in the first 10 min for all input mixture variants by heating the moisture content and zeolite or biochar. The graphical representation corresponds to a similar process temperature curve that is reported for lignocellulosic biomass (Fig. 1) [19,21]. In most samples, moisture evaporated within 60–80 min of magnetron power at 83%, which equals 2.5 kW. Approximately half of the samples reacted to the same power by such an increase in the temperature in the second phase of the process that the magnetron power had to be limited. For example, zeolite similar to ZSM-5 (Z2.0) even generated such heat at a concentration of 2.0% of the dry solids weight of the input mixture that the reactor power had to be reduced twice to ensure operating safety. First to 65% and then to 35%. In Fig. 2, these power reductions were manifested as a drop in the so-called "heating-rate", – downstream the highlighted points (140 and 160 min at 171°C and 192°C, respectively) the connecting line does not continue clearly with such a steep increase. The observed temperature increases in the second phase are most likely related to the creation of carbon centres that are formed and heat their surroundings [19,21]. Nevertheless, it has been shown that the addition of zeolite similar to ZSM-5 achieves the best temperature increases. The question arises whether this is mainly due to its dielectric properties or the catalytic support of depolymerization. It can be assumed that hydrocarbon molecules in the sewage sludge are of a different size than in lignin. However, laboratory experiments show that the aforementioned assumption of drying only without the addition of a catalyst cannot be confirmed. It may also be argued that this statement has been partially refuted. A test of a pelletize without any admixtures showed a distinct production of pyrolysis oil, which was, however, approximately half compared with other samples with admixtures. Thus, the pyrolysis oil produced without the addition of catalyst does not probably come only from volatile substances removed together with moisture during drying but it is a product of depolymerization reactions that are effected by the admixture either as radiation absorber and heating support and/or partly as a catalyst for hydrocarbon cracking. The factor contributing to the production of pyrolysis oil is certainly the vacuum kept in the system, because vacuum enables conversion of some substances to volatile substances where this would not occur under atmospheric pressure. Questions related to the effects of radiation absorbers, catalytic support as well as pressure ratios are offered as a topic for further investigation as the collected data do not provide exact information about the effect rate of these factors. Special cases are represented by two samples consisting of sludge, 1% ZSM-5 (based on dry solids) and either 30% sawdust (sample Z1.0 SD30) or 30% lignin (sample Z1.0 LIG30). Faster increase in process temperatures based on experiments with these samples shows that lignocellulosic biomass-type admixtures facilitate catalytic treatment of the prepared mixture using ZSM-5 like zeolite. As regards Z1.0 LIG30, a relatively strong exothermic reaction even occurred in the second phase and to ensure operating safety it was, therefore, necessary to disconnect the magnetron, but even to start filling the system with nitrogen in order to dampen these reactions and thereby reduce the temperature.

3.2. Biochar characteristics

As regards HM, aqua regia leachates and aqueous extract were observed and the values were evaluated according to Eq. (6) to determine the quantity of HM in biochar. The results were attractive as a relatively high fixation was achieved. Therefore, bio-unavailability and insolubility of HM can be expected in practice. Zn, Cd, Pb, Cu, As and Cr metals were monitored. Depending on individual metals and samples, fixation of 81% up to almost 100% of HM in biochar was achieved. The 100% value is based on the fact that the concentration in the aqueous extract was below the level of possible detection (measurability). These figures are the average values of the 12 sample leachates (suspicious input data excluded) for each HM.

The most interesting and widely used information from thermogravimetry include the proportion of organic matter (considered at up to 550°C) and the moisture rate which entails further considerations. The share of organic matter in all input samples was around 50%, which, with a small deviation, confirms the data obtained from the WWTP when dried sludge is extracted. Similarly, large variations could be observed for TOC in input pellets. Its value was around 29%. To assess the porosity of biochar, it is advisable to take into account the content of organic matter in which most pores are likely to be present. The TOC results, which ranged between 23.1% and 39.4% for biochar compared with the proportion of organic matter determined by thermogravimetry (22.8%–44.6%) offer the possibility of deepening the considerations of the proportion of organic matter related to other results. Interestingly, in the K0.0 sample, the TOC was even higher by 4.6% than the value of organic matter obtained by thermogravimetry (Table 1). This value seems to be quite rare and strange and it leads to a consideration of a measurement error, etc. If we compare the TOC: organic matter content, most of the observed biochar is around 0.8, with higher values approaching the limit of 1.0 meaning a more intense charring of the resulting material.

For the purpose of this evaluation, we performed a surface analysis of biochar on particular pelletizes for the very first time. Therefore, for the time being, its output data were more appropriate for informative purposes. For the BET surface analysis, we selected eight samples from the tested mixtures with two samples taken intentionally from output biochar Z1.0 (sludge + 1.0% zeolite ZSM-5) to measure the specific surface. The data obtained gave rise to a number of considerations. A remarkable finding was that the visually poorly pyrolyzed product Z1.0 had a double specific surface area than the product Z1.0, which appeared to be better pyrolyzed. Incompletely pyrolyzed unsightly pellets, which were also partially sticky, gave the impression that they probably contained liquid aromatic hydrocarbons, potentially tar, etc. The presence of an overwhelming majority of pores in the organic matter only is considered (based on the thermogravimetrically determined organic fraction). If the porosity is related only to the organic proportion in the material, two times higher values would be achieved compared with the initially measured values corresponding to the proportion of organic matter. Thus, such values are the limit values below which, in theory, the specific pore surface is exclusively made up of organic matter in the material. However, the surface characterization of such biochar should be a subject of a special. In the above-mentioned two samples of Z1.0, pore distribution was assessed using the BJH method. In both cases, pores from a diameter of 1.8 nm were present in the measurable area of the volume. After 24 steps up to the pore size of 24 nm they were comparatively distributed but with a surface area that was twice as large. However, some samples probably included micropores of less than 1 nm.

3.3. General discussion

Given the time-consuming nature of the research, only a few variants of admixtures have been tested. The data obtained in some cases do not match the assumption and this brings the question of whether this can be related to any discrepancy, caused, for example, by the heterogeneity of the sample being examined. For a detailed understanding of the process and its further optimization it will be necessary to include evaluation of the effects of pressure conditions during the process, as the pressure is rare due to the combination of expected overpressure in the pellet and vacuum in the chamber itself.

Treatment of mixture of sewage sludge, lignin (for example, in concentration 30% wt dry substance, which was tested) and ZSM-5 like zeolite (in concentration of 1.0% wt dry subst.) seems to be energy attractive, because of its significantly higher process temperatures when comparing with other mixtures. Thus, this would result in the disposal of two continuously generated types of waste at the same time. Treatment without lignin admixture was found out that from the group of all proven admixtures ZSM-5 like zeolite seems to be the most usable admixture to support microwave heating at a concentration of 2.0% wt dry substance.

The results show that 6 mm diameter pellets showed best suitability for the MP process due to its solid character causing non-problematic travel through the reactor. Other advantage of the 6 mm pellets is its correspondence to penetration depth causing complete pellet irradiation. Given the fact that the smaller the pellets, the better the radiation. These 6 mm pellets are the smallest acceptable size processable by the pelletizing press that can be considered. Important is also non-problematic throughput of the material through the reactor, what can be ensured when using pelletizer. In case of this reason could be promising also sludge dried with dryer providing direct pellet output.

HM content in sludge and biochar provided interesting results. Reached percentage level of HM fixation was approximately 81% up to 100% depending on individual HM and sample. It is important to consider these data as tentative results and this topic needs to benchmark all obtained data in details and provide a kind of verification. Next important parameter of biochar which is the pore surface needs to be upgraded with another MP process optimization.

4. Conclusions

This applied research has explored and evaluated the MP of sewage sludge focusing on pre-treatment using pelletization, several variants of admixtures for microwave depolymerization support and HM fixation in biochar, based on a number of supporting data, the article, therefore, presents the technology that can be considered, one of the best suitable technology for eco-friendly disposal of sewage sludge or other organic materials as well as with respect to the use of this technology to enhance bioavailable HM balances in material.

Treatment of mixture of sewage sludge, lignin and proper zeolite seems to be an attractive solution, because of recycling of two kinds of wastes together, producing interesting outputs. Results from this research stage confirm suitability of zeolite similar to ZSM-5 for lignocellulosic biomass catalytic depolymerization as a part of process when treating mentioned mixture. This idea will be tested in further research work. Treatment without lignin admixture was found out that from the group of all proven admixtures ZSM-5 like zeolite seems to be usable admixture to support microwave heating, because of its microwave heating support, but not direct influence to sewage sludge catalytic cracking. The other catalysts or admixtures do not show such heating efficiency after the first step of MP of sewage sludge – evaporation of moisture.

Fixing of HM in biochar has been confirmed for this technology by using leachate and can be considered as a topic for further detailed research, which is planned for following years.

The main findings, beneficial for the practical application, are not only the attractiveness of pelletizing the input mixture with regard to the characteristics of the output biochar but also the gaseous and liquid components. As regards this research, it is beneficial to understand the fact that the aforementioned process cannot be optimized in a comprehensive way but to modify the characteristic properties of one of the output components with the change of the characteristics of the other components being a secondary effect, with the main possibility of such optimization being, in this case, the determination of appropriate admixtures.

The products of pyrolysis can find different types of use. As regards liquid and gaseous components, it is possible to predict their use as a certain ecologically recovered fuel. Solid biochar can be used in a wide spectrum of applications such as agriculture, landscape water management, waste water treatment, etc. The pyrolysis process and the preparation of input materials must be further optimized for the specific purpose of utilizing the particular output component.

This finding results in another focus of the future research which should aim at the integration of optimal catalytic depolymerization into MP of sewage sludge in order to optimize the yield of pyrolysis oil with respect to the priority – HM fixation in biochar and thus it should give rise to a full-fledged microwave catalytic pyrolysis of this inevitably produced waste which may become a valuable resource material.

Acknowledgement

This paper has been worked out under the project No. LO1408 “AdMaS UP – Advanced Materials, Structures and Technologies”, supported by Ministry of Education, Youth and Sports under the “National Sustainability Programme I”.

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