Microwave pyrolysis of sewage sludge

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Abstract

The paper deals with the requirements for suitable sewage sludge pre-treatment to enable its processing based on microwave pyrolysis, including the topics of optimal catalysts, admixtures, mixing ratios and optimization of the depolymerization process (performance and temperature monitoring over time). It also includes demonstrations of the differences between results obtained through various pre-treatment methods in order to ensure potential implementation of this system in waste management. These are not results obtained through sludge treatment in a laboratory pyrolyzer. The examined output samples were produced using a "full-scale" technology for which they were prepared with the required granulation. The microwave pyrolysis 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.

The presented article specifies possible input mixture variants and compares them with the final conducted analyzes. The input mixture variants include dried sewage sludge, dried sludge with a catalyst and dried sludge with a catalyst and other admixtures (sawdust, lignin and hay). The proportion of wood or similar material in the mixture can facilitate approximation to the processes of microwave catalytic depolymerization of lignocellulosic biomass. Therefore, comparison with the processes performed on materials with the aforesaid additives is also included. Besides the monitoring of heavy metals, organic components, etc., this research stage covers the determination of a particular direction of further examination associated with the combination of microwave pyrolysis and catalytic depolymerization to be applied in municipal sewage sludge treatment.

This research encompasses a number of input and output media analyzes. The main parameters is 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. Chemical analyzes monitor the heavy metal content, and possibly other secondary indicators of the input mixtures and output biochar. As regards biochar, the surface and size of pores were evaluated. Some of the aforesaid indicators in combination with supporting data were obtained using thermogravimetry, TOC analyzer and gas adsorption. In this case, pyrolysis gas, its characteristics, etc. were not monitored in detail.

1. Introduction

The present question is the future direction of sewage sludge treatment both in legislative and practical terms. Trends across the EU are likely to move closer to the current situation in Germany, Austria, Belgium and the Netherlands where the proportion of thermal sludge treatment is the highest amongst the EU countries (Šumná, 2016) Although such thermal treatment is often associated with incineration, alternative methods such as gasification or pyrolysis are being offered, the product of which being pyrolysis coal (hereunder referred to as biochar) which offers attractive applications e.g. in agriculture. Note: long-term discussions could be held with respect to the term biochar but this is not a subject of this paper. There are a number of other designations such as microchar, pyrochar etc. However, as already mentioned, the term biochar will be used here despite potential controversy. What is also essential is a more global environmental perspective, where biochar, but also pyrolysis oil or gas, present a certain solution to circular economy, carbon footprint reduction, heavy metal fixation (hereunder HM) and water retention. From a certain point of view, the European legislative approach that restricts the use of materials for agricultural applications may seem to be problematic -if the limit concentrations of heavy metals are exceeded, such an application is simply inadmissible. The fact that HM may not be leached from biochar is not taken into account. (Decree of the Ministry of Environment 437/2016 Sb., 2016). From a practical point of view, such permanent HM fixation in biochar appears to be an appropriate solution for the use of sewage sludge for sustainable development with a view to improving the properties of agricultural soil.

Although this is the focal point of this article, HM fixation in biochar is not the only benefit of pyrolysis, which can be offered compared to 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. If an operating unit is installed, the pyrolysis gas is often burned directly at the point of origin. E.g. in cogeneration units (CHP), these are, as a standard, cleaned exhaust emissions. In such a case, only biochar and liquid condensate (i.e., humidity + oil) are obtained from the original treated input sludge, the gaseous component is burned in the cogeneration engine whose exhaust system is comparable to car motors.

There are numerous scientific studies offering various detailed focuses on thermal pyrolysis of sewage sludge. However, fewer scientific outputs deal with aspects related to microwave pyrolysis of sludge, and a minimum of studies are close to concentrating on the "full-scale" solution to the microwave sludge pyrolysis. This paper describes pre-treatment of sludge using granulation, which offers certain advantages already verified on other (e.g. lignocellulosic) materials (Bionic Fuel Knowledge Partners, 2014). 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. In the case of microwave pyrolysis; however, this depends on the material itself. 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 article therefore presents a technology that can be considered, based on a number of supporting data, the best available technology for eco-friendly disposal of sewage sludge or other materials as well as with respect to the use of this technology to ensure heavy metals fixation in biochar.

2. Materials and methods

The course of pyrolysis microwave catalytic depolymerization has already been well proven by the technology supplier using other materials (e.g. lignocellulosic biomass). In such a case, the required processes would be limited without pulsed microwave radiation and without the aid of catalyst. By adding the correct catalyst to the material to be treated, a very efficient material selectivity can be achieved with resulting higher yields of the gaseous and/or liquid components (Bionic Fuel Knowledge Partners, 2014). With the appropriate application of the above knowledge, optimal use of the combination of microwave pyrolysis and catalytic depolymerization can be achieved with respect to environmental friendly utilization of sewage sludge in the form of fixing heavy metals in solid carbonaceous residues, the yield of individual output components and their composition. A number of studies and research works highlight the unquestionable potential benefits of pyrolysis technologies for the environment.

Capodaglio et al. describe similar outputs stating that the gas contains, in particular, H2, CO, CO2 and CH4, 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 heavy metals contained in sludge are concentrated in the output biochar after the process (this may not apply to Hg and Cd) (Capodaglio, 2017).

Previous external research has shown that lignocellulosic biomass without the aid of catalyst was affected by the required processed in a very limited degree. By adding the correct 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. Typically, the energy required for these processes is lower than the energy needed for processes without catalytic support (Bionic Fuel Knowledge Partners, 2014). If microwave pyrolysis 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 (Menédez et al., 2001). 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 (Bionic Fuel Knowledge Partners, 2014). It is assumed that without the addition of a catalyst, it would probably be only mostly about drying but it is a question of how this matter is viewed. 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. It is known that a 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 it is advisable to realize that 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.

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. (Luťcha, 2015) The vibrations themselves mean temperature rising as this increases internal energy. From the point of view of the reaction to microwave radiation, the materials can be divided into absorbents, conductors and insulators (Church, 1993). 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. (Jones et al., 2002) 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.

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 initial air 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 200 hPa below normal atmospheric pressure, thus at about 800 hPa.

One of the reactors was designed for the use of a special 2l 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 (e.g. 3-10 kg of granulate). This is not a research associated with the use of a laboratory pyrolyzer where the usual material batch is in grams or less but it concerns the treatment of a larger quantity of mixtures in already prepared forms, which could be identical with the case of full-scale installations (granulation, admixture). For this reason, the preparation of the sludge and its treatment faced problematic facts which would probably not occur in other cases.

2.2. Materials

Sludge

The main source of sludge for laboratory tests was the WWTP in Brno Modřice, Czech Republic, with a capacity of approx. 531,000 EO (22-day digestion at 35 °C), where the drying (Nara paddle dryer) is heated to 100 °C with a retention time of about 3 hours. (Brněnské vodárny a kanalizace, 2017). The basic characteristics of the individual samples of sludge subject to the microwave technology treatment are as follows:

dry solids	91.5 – 91.9 %
loss on ignitron	47.1 – 49.0 %
fraction	cca 1 – 8 mm (bound finer fractions)

Admixtures

The sewage sludge was mixed with 3 types of admixtures in order to absorb microwave radiation after evaporation of the contained moisture (and possible catalytic reaction support) and 2 admixtures approximating the microwave process to lignocellulosic biomass depolymerization (wood sawdust, lignin). The additives used are summarized as follows:

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

Of course, the preparation of input raw material takes place with respect to the desired properties of the output components. The first stage of sludge treatment for microwave pyrolysis 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 but also by the sludge management conception at the treatment plant. Significant factors are the presence or absence of anaerobic stabilization and sludge drier. Whatever municipal wastewater treatment plant is the source of sludge for microwave pyrolysis 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 for 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 proportion of oil and water in the condensate from exhausted vapours is a factor used in deciding upon the advantages of separating these two components.

The sludge preparation for laboratory tests consists of a number of steps. This requires samples of dried sludge (tens up to hundreds of kilograms), blending with additives in specified proportions, ensuring the pelletization of the prepared mixture, possibly dampening, storage etc.

Available studies (Vollmer, 2004) 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 is 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 a granulated input mixture (previously tested diameters were mainly 6 and 8 mm) prior to the treatment in the microwave reactor. 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 microwave pyrolysis 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 granule 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 (Bionic Fuel Knowledge Partners, 2014). Another considerable benefit of such granulation is the simplicity of handling the produced biochar which does not create dusty environment and it can also be assumed that potential consolidation of layers of agriculturally applied granulate does not proceed as fast as with fine biochar.

2.3. Monitored indicators

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.

$$GP = \frac{ID - BP - CV}{ID} * 100\ (\%) \qquad \text{eq. 1}$$

Where GP is the share of output gas (gas production) (%), ID weight of the input batch (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 1000 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 gaseous components as a percentage. It is reported that up to 30% of sewage sludge weight can be composed of lipids (Capodaglio et al., 2017). 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. Furthermore, it should be noted that the above relationship does not take into account the proportion of dry matter in the input material, which was about 90% for all the input samples. Internally, the individual yields were compared with the indicative yield values relative to higher dry solids content, which confirmed the specific proportions.

Proportion of organic and mineral substances in input and output material

One of the indicators providing indicative information about organic matter content in sludge for this research was "Total Organic Carbon" (TOC) i.e. 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" indicator (VSS/ LOI). AdMaS research centre offers the possibility of using Shimadzu TOC-LCSH/CPH (PC controlled model) TOC analyzer with an additional SSM module. The aforesaid loss on ignition can be replaced for the purposes of benchmarking with TOC by the output of thermogravimetry (TA instrument- Discovery Q550 below) which provides information on the moisture content, ash content and combustible components. The proportion of organic matter may, inter alia, be related to the sludge management concept of the wastewater treatment plant, but it also plays a role in further sludge treatment. Organic components are of key importance for microwave depolymerisation because during the process pyrolysis oil, gas, etc. are formed, i.e. mainly components that do not reach the output biochar.

TOC determination

Using 2 furnaces of the aforesaid analyzer 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

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

(Shimadzu Corp., 2017) eq. 2

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

Determination of loss on ignition:

In principle, loss on ignition is based on the measurement of sample weight before and after ignition (burning out / evaporation of organic matter). In this specific case, the loss ignition values were obtained directly from the WWTP providing sludge samples. However, the determination was made in a way that respects the following relationship No. 3 (eq. 3). This applies both to automatic measuring scales and laboratory manual determination.

$$\mathrm{LOI} = \frac{\mathrm{Min} - \mathrm{Mout}}{\mathrm{Min}} * 100\ (\%)$$

eq. 3

Where LOI is the loss on ignition(%), Min stands for the input sample weight (g) and Mout is the weight of output ignited sample (g). However, it must be noted that data obtained through the thermogravimetric analysis (TA Instruments Discovery Q55O) automatically include output data of the LOI type. TA Instruments Discovery Q55O uses a heating rate of 10°C/min from the laboratory temperature to 1000°C in air flow (flow rate of 60 ml/min). Up to ca. 200°C moisture is taken out, between ca.200 - 600 °C the organic proportion is degraded along with some mineral compounds, and some hydrocarbons at higher temperatures (Ca, Mg).

Dry solids

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 microwave pyrolysis process itself. The water content in the sludge, i.e. 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. The proportion of water and oil in the resulting condensate then corresponds to this fact, without mentioning the details of the energy intensity of such separation of moisture from sludge. The second aspect is that water as a dielectric heats its surroundings, which means that in its absence a different microwave radiation absorber is desirable as a component of the material to be treated – e.g. the so-called “catalyst“ (or only a microwave radiation absorber). 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 Q55O) and from the wastewater treatment plant. However, the data provided by the treatment plants was 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:

$$\mathrm{Dry\ Substance} = \frac{\mathrm{Mdry}}{\mathrm{Mwet}} * 100\ (\%)$$

eq. 4

where Mdry stands for the weight of sample dried up to stabilization (g) and Mwet is the weight of humid input sample (g).

Heavy metals

From the point of view of environmental protection, Cd, Hg, Pb, As, Cr are designated as hazardous, along with, e.g. Ni, which is then defined by the relevant regulations. (Ulbrichová, 2007) 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 (Decree of the Ministry of the Environment 437/2016 Sb., 2016), the second variant is sludge treatment enabling production of fertilizers with CE classification. Within these limits there are some differences:
Organic CE fertilizer must have a Cd concentration below 1.5 mg / kg dry solids, Hg below 1 mg/kg dry solids, Ni below 50 mg/kg dry solids, Pb below 120 mg/kg dry solids (Šumná, 2016).

As regards direct application of sludge to agricultural land, the following HM values must be kept below the limits. The limits are: for As 30 mg/kg dry matter, Cd 5 mg/kg dry matter, Cr 200 mg/kg dry matter, Cu 500 mg/kg dry matter, Hg 4 mg/kg dry matter, Ni 100 mg/Dry matter and Zn 2500 mg/kg dry matter (Decree of the Ministry of Environment 437/2016 Sb., 2016).

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 (Ulbrichová, 2007). 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 (Kistler et al., 1987) 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 heavy metals do not escape from the system together with other vapours (Kistler et al., 1987). With respect to the process temperature, one of the more sensitive heavy metals would be mercury, which would completely evaporate (reduction to Hg0 followed by volatility) at about 350 °C, which is a temperature that is theoretically above the pyrolysis process temperature. However, this applies 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 heavy metals 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 heavy metals may be entrained by the vapour stream into a condensation exhaust system (Kistler et al., 1987). 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 (Agrafioti et al., 2013). Other sources (Kistler et al., 1987) indicate 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 hydrox-complexes. However, it is assumed (according to Kistler et al., 1987) that in the low-temperature pyrolysis the pH value of the leachate could be closer to the neutral range than to the said value. On the other hand, it is stated that heavy metals can be mobilized from biochar using acids with organic ligands (Kistler et al., 1987). It is also stated that the behaviour and mobilization capacity of heavy metals is dependent on the chemical form of HM occurrence and that microwave heating is more efficient in HM immobilization (Liu et al., 2016). One of the research outcomes mentions the reaction of HM during the pyrolysis process which can stabilize the HM:

ion HM - > hydroxide HM -> oxide HM (Liu et al., 2016)

In addition, the same source mentions 3 main forms of HM occurrence with a division depending on the bioavailability, i.e. 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 pyrolyses (Liu et al., 2016). This fact is associated with the finding that HM contained in biochar from microwave pyrolysis are fixed better than in biochar produced by standard heating (Liu et al., 2016).

The heavy metal 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:

$$\mathrm{HMfix} = \mathrm{HMar} - \mathrm{HMw}\ (\mathrm{ng/g}) \qquad \text{eq. 5}$$

Where HM_{fix} are heavy metals fixed in biochar (ng/g), HMar stand for heavy in aqua regia leachate in (ng/g) and HMw mean heavy metals from aqueous extracts (ng/g).

Surface and pore analysis

One of the characteristic features of biochar produced by microwave pyrolysis is a greater pore surface area than the one offered by biochar from conventional heating. (Liu et al., 2016).

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:

Analysis gas: Nitrogen, Press tolerance adsorption / desorption: 0,050/0,050 Equilibrium time adsorption / desorption: 240/240 s, Equilibrium time out adsorption / desorption: 480/480 s, Temperature 77,350 K. 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 hours at a temperature of 50°C.

3. RESULTS AND DISCUSSION

Experience from 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 granulate pressed into 6mm pellets. Comparison was made between compressed granulates with 6 and 8 mm pellets and granulates 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-millimeter granulate.

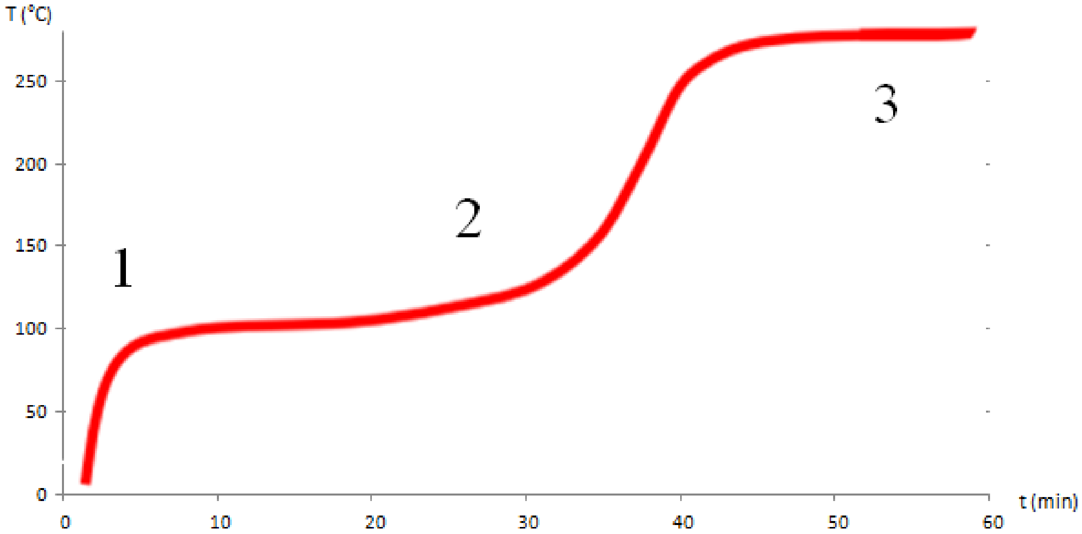

Figure 1 – Typical course of temperatures in time for lignocellulosic biomass (for 6mm pellets, divided into 3 steps) (Bionic Fuel Knowledge Partners, 2014)

Figure 1 above describes 3 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

Zone 3: achieving pyrolysis oil evaporation temperature, intensive formation of carbon centres supporting cracking, plasma el. discharges, intensive cracking due to zeolite and carbon centers, vapour treatment at the point of origin (e.g. decarboxylation) prior to escape from pellets (Bionic Fuel Knowledge Partners, 2014). These zones were also present in the same order when treating sewage sludge. The main difference was the retention time (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.

It has been examined whether it is suitable to add an additive 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 (Figure 2 below) indicate the effectiveness of ZSM-5 zeolite support in samples labelled Z2.0 and Z1.0 with possible extensions (i.e. 2 and 1% concentrations with potential additives) for microwave heating. The table below (Table 1) describes both the sample marking and some of the principal collected data. Thanks to the legend, information from Figure 2 can be read.

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 additives	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 % zeoliteZSM-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 % zeol. 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
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	-	-

Biochar and condensate yields from the mixture with a 30% lignin admixture (shown in Table 1), which are 4085 g and 1445 mL, respectively, percentually related to the weight of the input dose, i.e. 59.6% biochar and 21.1% condensate provide the most interesting results of all these 3 mixtures with 1% ZSM-5. This finding confirms the fact that zeolite ZSM-5 is optimized for lignocellulosic biomass and, at the same time, just like the temperature of the sample Z1.0 LIG30 (Figure 2), it points to the fact that it might be interesting to treat sewage sludge together with lignin.

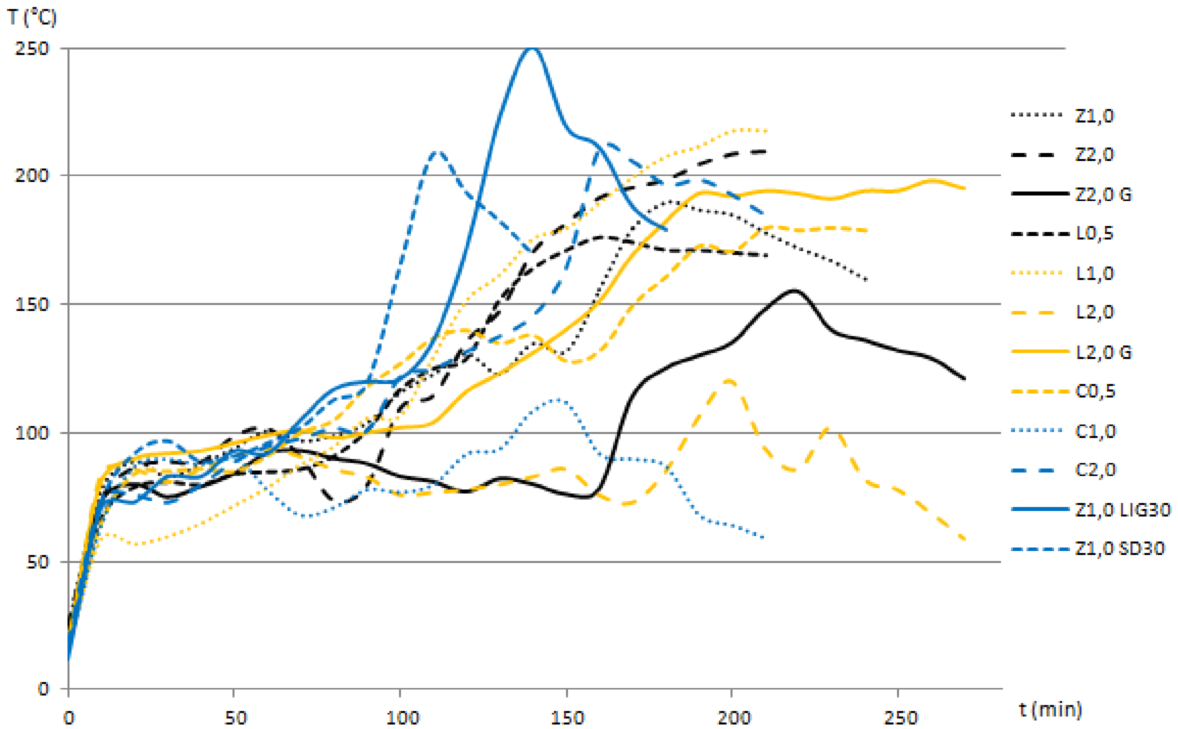

Figure 2 – Temperature over time – 6mm pellet processing

It can be seen that the above Figure 2 confirms a rapid increase in temperature in the first 10 minutes 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 (Figure 1 above) (Bionic Fuel Knowledge Partners, 2014). In most samples, moisture evaporated within 60 – 80 minutes of magnetron power at 83 %, which equals ca.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. E.g. zeolite 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 Figure 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 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 (Bionic Fuel Knowledge Partners, 2014). Nevertheless, it has been shown that the addition of zeolite 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 granulate without any additives showed a distinct production of pyrolysis oil, which was; however, approximately half compared to other samples with additives. 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 additive 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 2 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 additives facilitate catalytic treatment of the prepared mixture using ZSM-5 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. As regards heavy metals, aqua regia leachates and aqueous extract were observed and the values were evaluated according to eq. 5 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. The HMfix values are expressed as a percentage of the HM concentration in the granulate prior to processing in the microwave oven. Zn, Cd, Pb, Cu, As and Cr metals were monitored. Depending on individual metals, 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 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 granulates. 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- 39.4% for biochar compared to the proportion of organic matter determined by thermogravimetry (22.8 to 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 unique and strange and it leads to a consideration of a measurement error, etc. If we compare the TOC: Org. matter content, most of the observed biochars are 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 granulates for the very first time. Therefore, for the time being, its output data was more appropriate for informative purposes. For the BET surface analysis we selected 8 samples from the tested mixtures with 2 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 granules, which were also partially sticky, gave the impression that they probably contained liquid aromatic hydrocarbons, and potentially tar, etc. 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 to three times higher values would be achieved compared to 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, full-blown paper. In the above-mentioned 2 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.

4. CONCLUSIONS

Further research into microwave pyrolysis was based on a selected method of preparing the input mixture in the form of granules of 6 mm in diameter, which showed most suitable compatibility with the microwave reactor system also in other materials and on a long-term basis both is in terms of optimal radiation, in terms of handling with the mixture, and also in terms of penetration through a larger rotating reactor. Given the fact that the smaller the granules, the better the radiation, these 6 mm granules are the smallest acceptable size processable by the pelletizing press that can be considered. Furthermore, it has been shown that out of the tested variants, the zeolite ZSM-5 at a concentration of 2.0% seems to be the most suitable additive for heating this particular sludge. The other catalysts do not show such heating efficiency after the first step of pyrolysis - evaporation of moisture.

Given the time-consuming nature of the research, only a few variants of additives (absorbers/catalysts / sawdust/hay/lignin) have been tested. However, further research will focus on determining the most suitable catalyst (probably zeolite) for microwave depolymerization of sewage sludge in order to optimize the yield of pyrolysis oil (or gas) with respect to the priority - the fixation of bio-unavailable HM in biochar, which has been confirmed for this technology by using leachate

Various 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, wastewater treatment, etc. The pyrolysis process and the preparation of input materials must be optimized for the specific purpose of utilizing the particular output component. The main findings beneficial for the practical application are 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 can not be optimized in a comprehensive way, but only in order 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 additives. This finding results in another focus of the future research which should aim at the integration of optimal catalytic depolymerization into microwave pyrolysis of sewage sludge and thus it should give rise to a full-fledged microwave catalytic depolymerization of this inevitably produced waste, which is often referred to as a valuable material. The data obtained in some cases seem to be paradoxical and this brings the question of whether this can be related to any discrepancy, error or the like, 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 unique due to the combination of overpressure in the pellet and vacuum in the chamber itself. In addition, according to the temperature and biochar and condensate yield, it seems attractive to combine the treatment of sewage sludge with lignin. Thus, this would result in the disposal of two continuously generated types of waste at the same time and so this idea is being offered and will be tested in further research work.

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