Biochar is a highly porous solid substance, made of different biomass by pyrolysis. Conditions of pyrolysis as well materials used in it can substantially affect biochar properties. Samples with sufficient amount of stable carbon can be added into soil to be sequestered; high sorption surface of biochar could characterize it as a soil additive, able to immobilize risk elements in soil. Soil contamination by risk elements is a serious problem needs to be solved. There are available remediation methods, using plants to remove these elements from soil. Biomass produced during remediation has limited application and biochar production could be one option. Plants for our experiments were grown on contaminated soil of Příbram area. For the experiment they were used: meadow grass, wood mixture of poplar and willows twigs and finally maize. Biomass of these plants was used to prepare biochar. The effect of the type of biomass and the final temperature of pyrolysis on specific surface area and yield of biochar was studied in our experiments. Both temperature and plant material affected properties of biochar. While the final temperature increased, the specific surface area increased and the yield of biochar decreased. The highest surface area was found at biochar from wood mixture and the lowest one from meadow grass.

Biochar properties from different materials of plant origin

Kateřina Břendová*a, Pavel Tlustoš*a, Jiřina Száková*a, Jan Habart*a

Keywords: biochar, soil, heavy metals, slow pyrolysis, biomass.

Introduction

The reuse of harvested plant biomass previously used for remediation of contaminated soils by risk elements is under detailed investigation by several authors. One possibility how to process harvested material is to pyrolyse it to get energy fuels (oil, gas) and char- biochar, which could be used as a soil amendment for phytostabilisation of highly contaminated soils.

Generally, biochar is a carbon–rich, highly porous material, which can be prepared from various types of biomass (wood, agriculture residues, leaves etc.). The biochar production is based on thermal decomposition of raw materials under limited or no supply of oxygen. The process is called pyrolysis. The products of the pyrolysis are bio-oil and bio-gas and finally char. These products could be used as fuels. Here we should describe the terminology: the differences between the words char, charcoal and biochar. Char is the most general term and expresses the product of pyrolysis or natural fires, whether from biomass or other materials. Charcoal is prepared by pyrolysis of animal manure or plant biomass and the product is primarily used for heating. Another author reported that charcoal is surprisingly used in French cuisine. Its use in health care is well known. The production of biochar corresponds to charcoal one though the purpose of using is the soil application.

The biochar application to soil is known since long. In 1929 John Morley in The National Greenkeeper notes the positives of charcoal application into soil and described the improvement of soil porosity. There were also described soils in Amazonia, where burnt biomass and other organic matters led to creation of very fertile soil.

The interest of biochar research has been widely spread recently primarily due to its ability to sequester carbon to soil. Its ability to improve the soil properties causing improvement of crop production was observed. It was also found, that biochar is stable because of aromatic arrangement structure supports slow decomposition in soil, because microorganisms can use such compounds only with difficulty. Finally many interests in biochar are due to its ability to sorb undesirable contaminants of organic and inorganic origin, as pesticides or even heavy metals. Various authors support the hypothesis restriction of mobility of risk elements. It was observed significant reduction of acceptable cadmium and copper and increasing pH values after biochar application within 1-2 months in the incubation experiment. The properties of biochar affect its retention ability as well as the characteristic of retained element. The higher specific surface area of diary- manure derived biochar can positively increased the cadmium retention, but it was also observed greater heavy metal retention capacity of the lower pyrolysis temperature at cottonseed hull biochar. So it was suggested that the biochar for specific soil amendment should be selected on the bases of the biochar characteristics, soil property, and the requested function.

It is known that pyrolytic condition and the feedstock biomass can influence the final products of this process. On the basis of pyrolytic condition; there are several types of pyrolysis processes. These are namely fast pyrolysis, slow pyrolysis (also called carbonization) and gasification. The three already meant final products (char, gas and liquid oil) arise in different ratio according to chosen type of pyrolysis. Reaction mechanisms of biomass pyrolysis are complex processes, but can be defined in three main steps. In the first step, there is a loss of moisture and some volatile
substances. In the second step the primary char is formed. Fast reaction is followed by a slower and involves other chemical reactions to form secondary char.\textsuperscript{18} Thus the highest yields of char are produced during slow pyrolysis. Lower temperatures, slow heating rate and long residence time favor the formation of char.\textsuperscript{3} During the slow pyrolysis the portion of products is: 35\% of the char, 35\% gas and 30\% pyrolysis liquid. The final temperature is around 500°C. The retention time of the vapor in the reactor at a slow pyrolysis is of the order of minutes (5-30 minutes). Vapors don’t leak as quickly as during fast pyrolysis, and thus components of the gas phase may further react to form char and liquid.\textsuperscript{19}

In recent studies authors reported that the study of biochar properties is very important to understand its ability to sequester heavy metals into soil\textsuperscript{11} and as Lehmann and Joseph (2009) reported, further research of changes of availability of heavy metals in biochars is not available.\textsuperscript{4} But as Trakal et al. (2011) found, the contaminated biochar has similar effect on sorption risk elements in soil as uncontaminated one.\textsuperscript{3} Up to our knowledge studies describing sorption biochar capacity with relation to source material and temperature of pyrolyses are missing for contaminated feedstock biomass.

The aim of our work was to prepare biochar from different types of plant materials harvested at contaminated sites under different pyrolysis temperatures and to determine main characteristic of biochar mainly element composition and sorption capacity to get immobilization agent for further studies of heavily damaged contaminated sites.

**Experimental**

Plants that grew on the contaminated soil were used as raw materials for the biochar preparation. Specifically, it was whole plants of maize (\textit{Zea mays}), a mixture of fast-growing trees of the family \textit{Salicaceae} of the genera \textit{Salix} and \textit{Populus} and meadow grass harvested in the area of long-term contaminated with cadmium, lead and zinc. This area belongs to the most polluted in the Czech Republic.\textsuperscript{20} The contamination of this area is caused primarily by anthropogenic activity, but also because of original subsoil. Natural contamination is the result of the composition of parent rock, where it is found in high contents of heavy metals: like cadmium, lead and zinc. Anthropogenic contamination of this area was caused by two major sources: atmospheric fallouts of metal works and flood water contaminated by waste from the mills in nearby areas.\textsuperscript{21}

The plant material was first dried to the optimum moisture content of 15\%. Biomass was ground and homogenized. It was subsequently made into pellets with a diameter of 6 mm.

Pyrolytic process was carried out in a muffle furnace under flow of inert gas (nitrogen) 1 m\textsuperscript{3} h\textsuperscript{-1}, at atmospheric pressure and retention time of 30 minutes. The process followed under three different temperatures of 450, 500 and 550 °C.

Surface areas were measured by nitrogen adsorption isotherms at 77 K using ASAP 2050 (Micrometrics Instrument Corporation, USA) surface area analyzer. Specific surface areas were detected by layered adsorption isotherm BET model.\textsuperscript{22}

For each raw feedstock and biochar sample, a single estimate analysis was carried out using FlashEA 1112th from Thermo Scientific Company. The principle of the determination of these elements is based on the momentary combustion of the sample in a stream of oxygen at high temperatures. Gas products of combustion (nitrogen, carbon dioxide, sulfur dioxide and water) are then separated on chromatographic packed column and analyzed by thermal conductivity detector. The oxygen content is determined by difference. These results were used to calculate atomic H/C, O/C and N/C ratios.

**Results and Discussion**

**The elemental composition of feedstock biomass and biochar**

Table 1. describes the elemental composition of feedstock biomass. It was found that grass biomass had higher ash content, it is because the grass takes up higher amount of nutrients during their growing period.\textsuperscript{21} The lowest content of nitrogen was found at wood biomass that was compared by Vassilev et al.’s review;\textsuperscript{24} where it is reported that the nitrogen content is higher at wood biomass in general. The content of nitrogen corresponds to the content of sulfur, the lower values of sulfur where found in wood biomass too. The hydrogen content in biomass was ranging about to 6% according to earlier work and similar values were found at our plant materials also.\textsuperscript{24}

<table>
<thead>
<tr>
<th>Type of plant material</th>
<th>Elemental composition (% w/w)*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>Wood mixture**</td>
<td>50.43</td>
</tr>
<tr>
<td>Maize</td>
<td>48.15</td>
</tr>
<tr>
<td>Meadow grass</td>
<td>48.99</td>
</tr>
</tbody>
</table>

*moisture and ash free values, **wood mixture of poplar and willow

Table 2. Trace elements and ash content in feedstock biomass

<table>
<thead>
<tr>
<th>Type of plant material</th>
<th>The content of trace elements (ppm)</th>
<th>Ash (%, w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cd</td>
<td>Zn</td>
</tr>
<tr>
<td>Wood mixture*</td>
<td>14.77±2.58</td>
<td>176.9±39.4</td>
</tr>
<tr>
<td>Maize</td>
<td>1.74±0.17</td>
<td>35.8±4.70</td>
</tr>
<tr>
<td>Meadow grass</td>
<td>0.76±0.31</td>
<td>33.1±11.2</td>
</tr>
</tbody>
</table>

*wood mixture of poplar and willow

The evaluation of all three types of feedstock biomass showed that the highest content of all observed risk elements showed a mixture of willow and poplar wood. However the uptake of risk elements into tissues of maize plants and meadow grass is similar, maize tissues contained significantly more cadmium compared to meadow grass. The zinc content was lower in the meadow grass, but statistically insignificant, as well as the content of lead (Table 2).
The elemental analysis was done at all type of biochars. The content of carbon was lower at biomass of maize and meadow grass. It was found that the carbon content in biochar prepared from woody biomass at lower temperatures (450 °C) is higher than biochar prepared from maize straw at a higher temperature (600 °C). So the carbon yield from herbaceous materials occurs lower than from wood materials. It was also reported similar results of ash content of feedstock biomass, as was shown in Table 1, the herbaceous materials have higher ash contents resulted in lower carbon yield.

In general in the studies of various authors, it was reported that the content of carbon increased with increasing temperature. Our results showed the opposite trend (Table 3). This is most probably caused by imperfect pyrolysis condition. It seems that only limited oxygen conditions are insufficient and the strict controlled conditions are required for biochar preparation.

The nitrogen is conserved by 41% in wood biochar and by 80% in biochar from maize, prepared at 500 °C. Gaskin et al. (2008) reported 3.4% of N in biochar from poultry litter and the higher conservation of nitrogen in biochar from pine (89%) than in poultry litter (24%) at temperature ranged from 400–500 °C, and on the basis of these values suggest biochars as fertilizers. No sulphur was found in prepared biochar, most probably it was escaped during pyrolysis.

Table 3. The elemental composition of biochars from different plant materials, prepared at three different temperatures

<table>
<thead>
<tr>
<th>Type of biochar **</th>
<th>Elemental composition (% w/w)*</th>
<th>Ash (%) w/w</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
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<tr>
<td>Wood mixture**</td>
<td>63.84</td>
<td>2.35</td>
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<tr>
<td>450</td>
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<tr>
<td>500</td>
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<tr>
<td>550</td>
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<td></td>
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<tr>
<td>Maize</td>
<td>63.84</td>
<td>2.21</td>
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<td>500</td>
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<tr>
<td>550</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Meadow grass</td>
<td>62.83</td>
<td>1.97</td>
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<tr>
<td>450</td>
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*moisture and ash free values. **wood mixture of poplar and willow

Table 4. Atomic ratios of prepared biochars

<table>
<thead>
<tr>
<th>Type of biochar</th>
<th>Temperature, °C</th>
<th>C:N</th>
<th>O:C</th>
<th>H:C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood mixture*</td>
<td>54.34</td>
<td>0.32</td>
<td>0.32</td>
<td>0.04</td>
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<tr>
<td>500</td>
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<tr>
<td>Maize</td>
<td>57.51</td>
<td>0.30</td>
<td>0.30</td>
<td>0.03</td>
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<td>500</td>
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<tr>
<td>Meadow grass</td>
<td>62.21</td>
<td>0.31</td>
<td>0.31</td>
<td>0.03</td>
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<td>450</td>
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<td>24.69</td>
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<td>33.36</td>
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The specific surface area and yield of biochars

Although some of the previous results of biochars analyses are different from literature the results of specific surface area and yields of prepared biochars corresponded well with literature. It was found that feedstock biomass influences the physical properties of prepared biochar. The biochar from wood mixture showed the highest values of specific surface area (to 369 m² g⁻¹), while the lowest values were observed at biochar from meadow grass (Figure 1). These results correspond to the other authors who showed the specific surface biochar prepared from wood which was higher than biochar from grass biomass. The strong positive correlation was observed between pyrolysis temperature and specific surface area of prepared biochars from all types of biomass

The final temperature also affects the physical properties of biochar. For all types of biomass with increasing pyrolysis temperature, the values of specific surface area increased as in other studies also. Lignin compared to cellulose dehydrated more difficult and created more of residual char: up to 45%, which implies that the yield of char depends on the amount of lignin in biomass - a higher content of lignin leads to the higher yield of char, which is confirmed by various studies. Raverdeen et al. reported that the cellulose/lignin ratio influences the yield of char, the highest char yields was achieved within ratio 1:3. The lowest yield was observed at biochar biomass of maize. The highest values of yield showed a biochar from meadow grass: up to 28% (w/w) (Figure 2). This may be due to results of higher ash content of feedstock and also higher presence of SiO₂ at 

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Biochar properties from different materials of plant origin

Section B-Research Paper

grasses as Vassilev et al. reported. Other authors claim that the char yield of a lignocellulosic material cannot be predicted by a simple model that sums the yields of the substrate’s cellulose, hemicellulose, and lignin components, because the char yield is strongly dependent on the vapor-phase conditions presented in the pyrolytic reactor.34

Authors indicate with increasing final temperature, the yield decreases, while increased biochar bio-oil and gas production. In their study there was an assumption that the yields of char are high at low temperatures, because the input biomass doesn’t completely transform into char.35 In our experiment, the yield biochar generally decreased with increasing temperature for all types of biomass. The positive linear correlation was detected between pyrolysis temperature and biochar yields.

Basically, at low temperatures of 200-300 °C under slow heating rate (<50 °C / min), the thermal process is called torrification. Gas portion escapes from biomass primarily and up to 90% of solids remains. The balance of torrification products of willow biomass is: 87% of solid product and 8% of water, 3% of gases (CO, CO₂) and 3% of organic matter escaped.36

Figure 1. The influence of pyrolysis temperature of prepared biochar on specific surface area

Biomass losses can happen through depolymerisation of hemicellulosic folder. Final product of torrification is completely dried out and the air moisture is not received into the material as in raw one. Thanks to these properties, the torrification is considered as a preparatory process for subsequent use of biomass for energy purposes.36 It was said, grass biomass has higher content of ash. There can be higher contents of silicates in contrast to wood biomass, thus the yield of biochar from grass biomass was shown higher than that of wood one.25

Conclusion

This study reported, that the composition of feedstock material and pyrolysis condition highly influence the final product, in our case it is biochar.

The production of the char - biochar, which will be used as a soil additive, has to fulfil certain parameters. It is necessary to prepare a material with sufficient specific surface area, allowing sufficient adsorption of undesirable ions or molecules.

Figure 2. The influence of pyrolysis temperature on biochar yields

From a practical point of view, the biomass mixtures of willow and poplar, pyrolyzed at temperatures from 500 °C appears as suitable to prepare char, which shows high specific surface area. Presence of heavy metals in feedstock has not affected parameters of biochar, but the content of ash played more important role in it.

Next step of our experiments is to analyse the produced biochar and found out the amount of risk elements there. Then the research will continue with batch sorption and desorption experiment, where the availability of risk elements in biochars will be observed as well as its sorption ability of prepared biochar at contaminated and uncontaminated soils.

Acknowledgement

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