Mass yield of biochar from hydrothermal carbonization of sucrose

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Abstract

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In this article, the effect of increasing dry matter content and reaction time of hydrothermal carbonization on mass yield of biochar was studied. Carbonization took place in batch experiments in a pressure vessel. Results have confirmed the assumption that the mass yield of biochar would increase with growing dry matter content in the initial solution and also with reaction time at reaction temperature of 200°C. It was found that components of the liquid product that remain in the biochar have a measurable impact on its mass yield. Mixing of the reactor proved to have a considerable effect on the mass yield as well. Biochar produced in absence of mixing had higher pore volume and higher yield. This was evident even after subtracting the equivalent liquid phase dry matter in the biochar after drying.

Keywords: HTC; wet torrefaction; reaction time; mixing; process liquid

Constantly increasing global demand for sugar makes it a very dynamically developing commodity. In the period between 1966 and 2012 world production of sugar has increased from 66 mil. to more than 172 mil. t (Smutka et al. 2014). In the Czech Republic the main crop for sugar production is sugar beet. According to Spagnuolo et al. (1997) 1 t of sugar beet serves to produce approximately 250 kg of spent sugar beet slices. With 2.9 mil. t of sugar processed annually in the Czech Republic it comes to 730 thousand tonnes of spent sugar beet slices (Mužík et al. 2012).

From a chemistry point of view, table sugar is the saccharide sucrose. Sucrose is a disaccharide composed of monosaccharides glucose and fructose. Its empirical chemical formula is $C_{12}H_{22}O_{11}$.

One option of utilization sugar industry by-products or wastes containing sucrose might be hydro-thermal carbonization. Hydrothermal carbonization (HTC) is a type of pyrolytic treatment of organic material (Funke, Ziegler 2010). The basic requirement is immersing the substrate in water. The mixture is heated in a closed volume, so temperature rises as well as pressure. Process temperature is usually in the range of 180–300°C. Pressure corresponds approximately to the pressure of saturated water vapour i.e. approximately 1–9 MPa (Tekin et al. 2014). Organic substances first disintegrate and decompose, and afterwards polymerize into the final products. The reaction is overall slightly exothermic (Funke, Ziegler 2010). The product of interest is the solid biochar, sometimes called hydrochar. HTC biochar has higher carbon content in its dry matter than the initial substrate and therefore higher heating value (Malaťák, Dlabaja 2015). At the same time water is released

from the substrate so the biochar can be more easily dewatered. For these reasons the ideal material for hydrothermal carbonization is considered plant biomass with high moisture content where high heating value can be achieved without the need for expensive drying (Funke, Ziegler 2011). The resultant biochar can be used energetically or as a material possibly after further treatment as a soil amendment, adsorbent etc. (Titirici, Antonietti 2010).

The article is based on the hypothesis that the mass yield of biochar increases with increasing content of sucrose in initial mixture and with carbonization time. To confirm or refute this hypothesis it is necessary to experimentally determine the mass yield while varying these process parameters. In this paper, the final form of the reaction products is observed and the influence of matter dissolved in final process liquid is considered. The impact of mixing the reaction was also studied.

MATERIAL AND METHODS

The material used for this article was sucrose in analytical grade (Lach-Ner, s.r.o., Neratovice, Czech Republic). Citric acid (Lach-Ner) was used for adjusting the pH of the solution anhydrous. It was added in an amount sufficient to acidify the solution to pH 3. Contribution of this acid to the mass of biochar was not expected because in earlier experiments citric acid itself did not produce any biochar in hydrothermal conditions. Lynam et al. (2011) added acetic acid, which lowered the mass yield of biochar, however only with much larger quantities. The chemicals were dissolved in distilled water in all experiments.

Specified amount of sucrose was always first dissolved in a quantity of distilled water (200 g for most experiments). The purpose was to achieve the same filling of the reactor each time and thus eliminate the influence of its difference on results. All weights were measured on laboratory scales (A&D GF-3000; A&D Weighing, San Jose, USA) with an accuracy of 0.01 g. Solution pH was measured (Thermo Scientific Orion Star 111; Thermo Fisher Scientific, Waltham, USA) and when necessary it was lowered by citric acid to reach pH 3.

Hydrothermal carbonization of the sample was performed in a laboratory reactor Berghof BR-300 (Berghof GmbH, Eningen, Germany) with an internal volume of 400 ml. Because it is necessary to allow for

the expansion of the solution the reactor was filled always to 2/3 of its volume. Inert atmosphere was not introduced. The reactor is a stainless steel pressure vessel. During the carbonization process biochar becomes deposited on all submerged surfaces of reactor. Thanks to this, the material of the reactor is not expected to have an effect on biochar mass yield.

The reactor was placed on an electric heater with a magnetic stirrer (Heidolph MR Hei Standard; Heidolph Instruments GmbH & Co. KG, Schwabach, Germany). Heating and maintaining the temperature was controlled by a regulator (Berghof BTC-3000; Berghof GmbH, Eningen, Germany). Final reaction temperature in all experiments was 200°C. Heating from room temperature took 40 min, cooling down to 50°C about the same time. At 50°C, the remaining pressure was released, the reactor was opened and pH of liquid phase was measured. Liquid phase was then filtered and the biochar in rector was completely taken out. Biochar samples were weighed in wet state and after drying in dryer (Memmert UN 30; Memmert GmbH + Co. KG, Schwabach, Germany) at 105°C for 5 hours. The mass yield was then calculated as:

$$MY = 100 \frac{m_b}{m_s} \qquad (1)$$

where:

MY – mass yield of biochar (%); m_b – dry weight of biochar (g); m_s – dry weight of sucrose in the initial solution present in the reactor (g)

Elemental analysis of biochar samples for carbon, hydrogen and nitrogen was performed on a CHN analyzer (Elementar vario EL III; Elementar Analysensysteme GmbH, Langenselbold, Germany). Noncombustible content, i.e. ash and water content was determined by drying and burning of samples. Higher heating value was found by calorimetric method (calorimeter IKA 200; IKA®-Werke GmbH & Co. KG, Staufen, Germany). Using higher heating value and elemental composition, lower heating value was calculated by a formula in ISO 1928:2010 derived for zero nitrogen and moisture content.

$$LHV = HHV - 212H - 0.8O \qquad (2)$$

where:

LHV – lower heating value of dry sample (J/kg); HHV – higher heating value of dry sample (J/kg); H – hydrogen content in dry matter (% wt.); O – oxygen content in dry matter (% wt.)

To measure a contribution of matter dissolved in liquid product to biochar weight, two 10 g samples of liquid were dried in Petri dish for each experiment. Drying conditions were the same as for biochar samples (105°C, 5 h). The dishes were weighed to 0.0001 g (laboratory scales KERN ABT 320-4M; Kern & Sohn GmbH, Balingen, Germany). The concentration of residue in process liquid was calculated as the ratio of weights of the residue left to process liquid when dried on a Petri dish. The adjusted mass yield is then:

$$MY^* = 100 \frac{m_b - \left(m_{bw} - m_b\right)\frac{c_r}{1-c_r}}{m_s} =$$

$$= MY - 100 \frac{m_{bw} - m_b}{m_s\left(1/c_r - 1\right)}$$

(3)

where:
MY^* – mass yield with deduction of residue from pro-liquid (%); MY – mass yield of biochar (%); m_b – dry weight of bio(g); m_s – dry weight of sucrose in the initial solution present in the reactor (g); m_{bw} – wet weight of biochar (g); c_r – concentration of residue in process liquid (g/g)

RESULTS AND DISCUSSION

All experiments were performed at a constant target temperature of 200°C which was held for specified time. Reaction time is defined by time when the temperature was over 198°C. Ramping up to a target temperature and cooling are sufficiently quick, therefore reaction time below the limit temperature is not considered.

Mass yield of biochar was the main observed parameter. It became clear that the biochar as well as resulting process liquid contain some volatile matter that is partly released even under temperatures below 105°C. Part of this content is released while drying and part is left in biochar. Therefore all biochar samples had to be dried under the same conditions.

Final form of the reaction products

The resulting biochar obtained by carbonization of sucrose can be described as a black porous solid, see Fig. 1. After being dried, it will maintain 5% wt. moisture in laboratory environment with relative

air humidity 50–60%. During hydrothermal treatment the biochar would deposit on reactor surfaces, even on the stirring bar, under all tested process conditions. The process liquid, on the other hand, does not contain any suspended biochar. In case of the reactor being mixed the biochar tends to make a harder and thinner layer compared to the reactor not being mixed. In that case the biochar has larger pores and holds more process liquid.

The biochar carbonized at 200°C and 2-hour reaction time from initial solution that had 16% wt. of sucrose was analysed for elemental composition and fuel properties (Table 1). First set of samples was analysed after the hydrothermal treatment. Second set was dried and stored for 2 months in laboratory conditions with relative air humidity 50–60% and temperature 20°C. Elemental compositions of new and stored biochar were similar: approximately 65% carbon, 4.5% hydrogen and 30% oxygen. That is nearly identical to the results of Fiori et al. (2014). However, biochar that has been stored has lower volatile matter content by about 5%. This might mean that during drying and long-term storage a part of volatile matter in biochar or adsorbed on it is lost.

The most important factor for energy utilization is the *LHV* which is dependent on moisture and ash content (Malaťák, Bradna 2014; Ružbarský et al. 2014). Lu et al. (2013) showed that an advantage of hydrothermal carbonization is that the heating value of biochar tends to increase in comparison to the initial material. Here the *LHV* has almost doubled mainly thanks to reduction in oxygen content. Decrease of oxygen led to both higher *HHV* and *LHV* of the sample (Funke, Ziegler 2011).
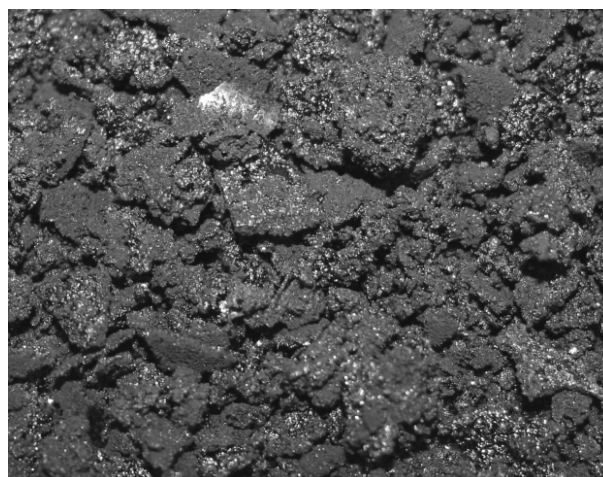

Fig. 1. Biochar – reaction conditions: 200°C, time 5 h, reactor not mixed

Table 1. Analysis of sucrose and its biochar: LHV for all samples and elemental composition of sucrose was calculated

Sample	Unit	Sucrose	Biochar 2h/16%	
			new	stored for 2 months
Ash	% wt.	0.00	0.00	0.00
Volatile matter	% wt.	–	57.27	52.38
Non-volatile matter	% wt.	–	42.73	47.62
Carbon	% wt.	42.11	65.60	63.19
Hydrogen	% wt.	6.48	4.69	4.53
Oxygen	% wt.	51.41	29.71	32.28
HHV	MJ/kg	16.24	25.62	25.28
LHV	MJ/kg	14.83	24.60	24.29

HHV – higher heating value; *LHV* – lower heating value

At the moment when the reactor is opened the process liquid is saturated with gases that mostly effervesce out when the liquid is poured out. The amount of gases increases with amount of sucrose in the original solution and with reaction time.

Influence of matter transferred from process liquid into biochar

Effects of changing process parameters on mass yield of biochar were studied in this paper. One of these effects might be the contribution of matter dissolved in process liquid to mass of the biochar. It was shown that biochar from hydrothermal carbonization may contain high portion of volatile matter which consists of various compounds (Funke,
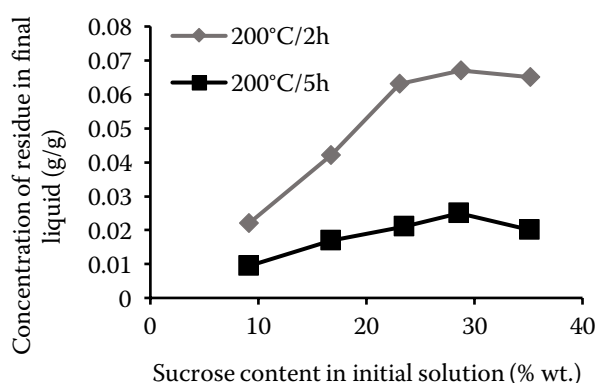

Fig. 2. Relative amount of residue of process liquid after drying
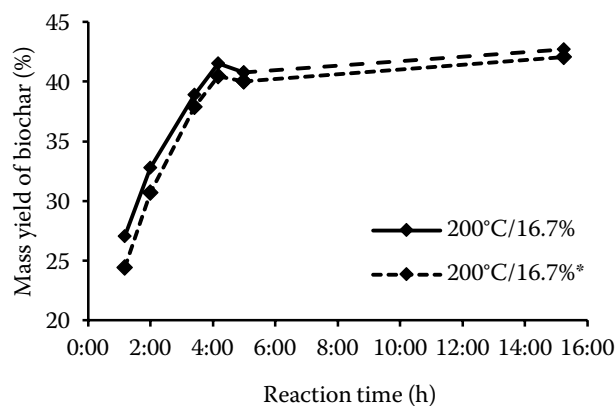

Fig. 3. Influence of reaction time on mass yield of biochar
*values where the calculated weight of residue from process liquid was deducted

Ziegler 2010; Spokas et al. 2011). When the process liquid from sucrose carbonization was dried a tarry residue was left which could be again partly dissolved in water. Assuming that the composition of liquid phase is uniform throughout the reactor then the amount of this residue that is transferred into the biochar can be estimated.

The relative amount of residue after drying liquid ranged from 0.01 to 0.07 g/g of process liquid after 5-hour drying time. The results are summarized in Fig. 2. The relative residue increased with sucrose content in original solution and decreased with reaction time.

Effect of reaction time on biochar mass yield

The effect of reaction time on biochar formation was tested with reaction between 1 and 15 hours. Reaction temperature was 200°C and the initial solution was composed of 200 ± 1 g distilled water and 40 ± 0.05 g sucrose. Solution pH was adjusted to pH 3 with citric acid. The reactor was always stirred throughout the whole experiment.

The mass yield of biochar for the shortest reaction time of 1 h was 27%. With increasing time it grew to 41.5% at 4 h reaction time. At longer times, the yield is relatively stable – slightly above 40%, see Fig. 3. No experiments were performed with reaction between 5 and 15 h, but it can be expected that no dramatic change will occur, similar to the results from Lu et al. (2013). Fiori et al. (2014) hydrother-
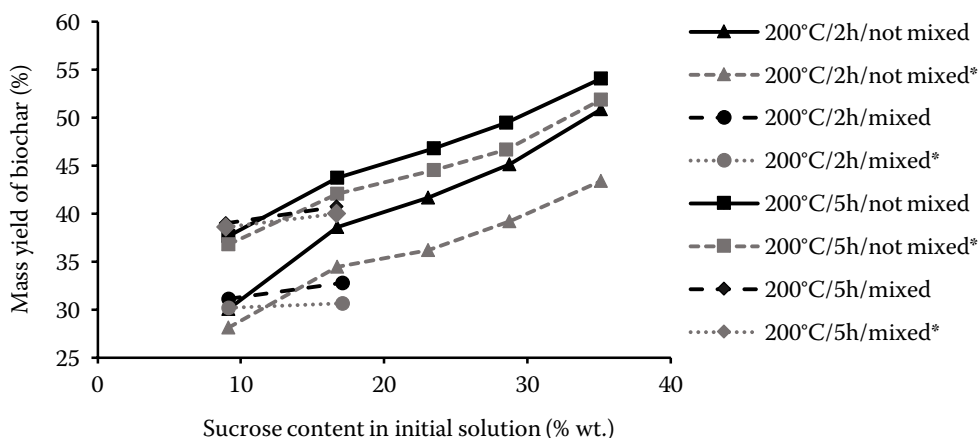
Fig. 4. Mass yield of biochar depending on the content of sucrose in the original solution at 2 different reaction times with and without stirring

*values where the calculated weight of residue from process liquid was deducted

mally carbonized sucrose at a higher temperature, 220°C, and reaction times from 1 to 8 hours. The mass yield there was higher and decreased with time from 55.7% to 47.5%. The difference may be due to a different procedure but it is likely that at higher temperatures the relation between mass yield and reaction time would alter.

Thanks to sucrose dissolving completely in the solution a phenomenon is avoided when the original material contributes to mass yield of the solid product of carbonization. This seems to happen for example with cellulose (Lu et al. 2013).

Effect of solution sucrose content on biochar mass yield

From previous experiments, it was obvious that the yield of biochar is dependent on the sucrose content of the original solution. There were four series of experiments in which the sucrose content in initial solution varied. Two reaction times were tried, 2 and 5 hours, both with and without stirring of reactor. In experiments with stirring the highest sucrose content was 16.7% wt. When the sucrose concentration is higher the biochar will form in most of solution volume and will stop the magnetic stirrer.

Solution sucrose content varied from 9.1 to 35%. The mass yield increased in a relatively linear fashion from 30 to 51% at two hours, and from 37 to 54% at five hours (Fig. 4). When the calculated weight of residue from process liquid was deducted, trends of

resulting curves followed well the measured values. At low sucrose contents, mass yields in mixed and non-mixed experiments were comparable. With increasing sucrose content mass yield grew more for non-mixed experiments. Biochar from those experiments had larger volume and retained more process liquid and thus there were bigger differences between the measured values and yield obtained after deducting the residue of dried liquid. The trend of higher yields without stirring was obvious even then. The final pH decreased with solids content from pH 2.4 to pH 2.

CONCLUSION

During the experimental part of this work, it was found that the final process liquid contains matter that is transferred into biochar affecting its mass yield even after drying. The concentrations of these substances were measured by drying the process liquid. The amount of these compounds increased with the sucrose content in the original solution, but significantly decreased with increasing the reaction time from 2 to 5 hours.

Furthermore, the article confirmed the hypothesis that the weight yield of biochar increases with increasing time of carbonization and with increasing solids content in the feed. The first part of this hypothesis was verified experimentally by measuring the mass yield of biochar at constant sucrose content of 16.7% while stirring. The reaction time

was varied in the range from 1 h to 15 hours. From 1 h to 4 h yield increased significantly, then stabilized above 40%. Increasing the solids content of sucrose in the original solution had a beneficial effect on yield of biochar, both at the time of carbonization for 2 h and 5 hours. The increase was greater if the substrate was not mixed.

Using the measured values sucrose could be used as model substance for comparison with hydrothermal carbonization of certain wastes or by-products in the sugar industry or food waste.

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