Mass and energetic yields of hydrochar from brewer's spent grain

J. Velebil[*], J. Malaťák and J. Bradna

Czech University of Life Sciences Prague, Faculty of Engineering, Department of Technological Equipment of Buildings, Kamýcká 129, CZ 165 21 Prague, Czech Republic
[*]Correspondence: velebil@tf.czu.cz

Abstract: Brewer's spent grain (BSG) was hydrothermally carbonized at combinations of three temperatures (180 °C, 215 °C, 250 °C) and three reaction times (2 h, 5 h, 12 h). For comparison, the corresponding barley malt was also tested at the same conditions. Elemental composition, volatile matter, ash and heating values were determined for original biomasses as well as resulting hydrochars. The mass yield of dry BSG hydrochar ranged from 45 to 73%. The energetic yield defined as retention of total lower heating value in the hydrochar on dry basis ranged from 66 to 85%. Specific lower heating value of dry material rose from 20.6 MJ kg^{-1} to 30.3 MJ kg^{-1} at the most severe conditions. Nitrogen and sulphur content in hydrochar were not strongly dependent on reaction conditions.

Key words: hydrothermal carbonization, malt, calorific value, heating value, biochar, elemental composition.

INTRODUCTION

One of the main components for beer brewing is malt. That is germinated and then dried cereal, usually barley, which provides starch and sugars that can be later consumed by yeast. Brewer's spent grain (BSG) is then the main by-product (85% of all by-products by weight) of brewing beer which is collected after filtering the wort. It contains water insoluble malt remnants composing mainly of water insoluble proteins and cell wall residues of the husk, pericarp and seed coat within the spent grain (Mussatto et al., 2006). BSG is composed mainly of lignocellulosic fibres (cellulose, lignin and arabinoxylan might make up around 70% of dry weight of BSG). Another roughly 20% is taken up by proteins. The rest are lipids and starch remnants. The composition changes with barley variety and differences in the brewing process even within one brewery so the reported values vary significantly. (Santosa et al., 2003; Mussatto et al., 2006; Xiros & Christakopoulos, 2012)

Brewer's spent grain can be used traditionally for animal feeding. For its high content of fibre and protein it has been used largely for dairy cows to increase milk production, but its use for other animals, such as poultry, pigs or fish, has been also investigated. Human consumption is possible when adding moderately small quantities of BSG flour into bakery products, with reported health benefits. When converted to so-called germinated barley foodstuff it has been found to be beneficial to patients with ulcerative colitis (Mussatto et al., 2006; Steiner et al., 2015). If not used for nutrition

BSG may possibly serve in brick-making to increase porosity, in paper manufacture or after pyrolysis treatment as adsorbent. BSG can be used also in a number of biotechnological processes as substrate for cultivation of microorganisms or substrate from which enzymes or other biochemical products can be obtained. (Mussatto et al., 2006; Xiros & Christakopoulos, 2012)

Finally, when there is not sufficient demand for these uses it may be also utilized energetically. Since fresh BSG is usually a very wet substrate, biogas production in an agricultural biogas plant would omit the need to dry the material. (Malakhova et al., 2015) found methane yield of BSG in co-fermentation up to $58.7\,l\,kg^{-1}$ of raw BSG. Different option may be hydrolysis treatment to produce liquid fuels (Raud et al., 2015). Another technique that can process wet material is hydrothermal carbonization (HTC). In general, hydrothermal treatment of biomass can lead to a variety of products depending on the substrate, reaction temperature and pressure etc. (Kruse & Dahmen, 2015). Hydrothermal carbonization occurs in water environment mainly in temperature range of ca. 180–250 °C. The reaction pressure corresponds to that of saturated water vapour or is increased by generated gases, which are mostly CO_2 (Poerschmann et al., 2014). The solid product is most often called biochar or hydrochar. Suitable substrates are generally all carbohydrates, while proteins and lipids do not usually turn into hydrochar by themselves, but may be adsorbed onto it or their change into hydrochar may be facilitated by other substrates (Heilmann et al., 2011; Kruse & Dahmen, 2015). Submersion of substrate in water is a crucial condition in HTC and other solvents do not produce the same effects (Heilmann et al., 2011).

The advantages of hydrothermal treatment are complete hygienization and to some extent also degradation of some pollutants (Weiner et al., 2013). Under hydrothermal conditions the structure of original material and its cells are destroyed to a high degree, so the resulting hydrochar can be more easily dewatered. This is useful mainly for highly moist waste biomass which would have to be disposed of possibly without energy gain, but with HTC the energy efficiency may become better (Malaťák & Dlabaja, 2015).

Several works focused on HTC of BSG have been already written mostly focusing on composition of hydrochar or process water (Poerschmann et al., 2014; Poerschmann et al., 2015; Riedel et al., 2015). In these works, BSG was seen as a suitable material for HTC. The aim of this work is to help evaluate the potential of BSG for energy utilization by following the energetic yield in HTC of BSG across three different carbonization temperatures (180 °C, 215 °C, 250 °C) and three different times (2 h, 5 h, 12 h). Since mass and energetic yields in hydrothermal carbonization are influenced by other parameters as well (reactor loading, mixing, etc.) it was deemed useful to compare BSG to a different biomass for better comparison with literature. The barley malt used for brewing was chosen.

MATERIALS AND METHODS

Materials and chemicals
Barley malt and corresponding brewer's spent grain (BSG) were supplied from a local brewery. The initial moisture of the BSG was 75% wt. To preserve it, it was dried in a fruit drier in flowing air at 60° until no moist patches could be seen. The material was then thoroughly mixed to ensure homogeneity. BSG was then stored in a

refrigerator. The moisture of stored BSG was measured every time it was used for an experiment, the average value being 7.0% wt.

Malt was supplied as whole grains. It was stored in a closed container at 20 °C. Its moisture was measured when received and then every week to determine moisture content changes over time. To measure moisture a sample was always ground and immediately weighed.

For adjusting the acidity of reaction mixtures citric acid was used (analytical grade, Lach-Ner). For calibration of analysers, calibrating standards were supplied by LECO. For calibration of volatile matter (VM) in TGA 701 coal standard with 40.4% wt. VM was used. CHN module was calibrated with ethylenediaminetetraacetic acid. S module was calibrated using coal standard with 1.16% wt. sulphur. The calorimeter was calibrated with 1 g pellets of benzoic acid.

Experimental procedure

Mixtures for HTC experiments were composed of such an amount of substrate to achieve 25 g of dry matter (DM) with the last known moisture content. Tap water would then be added to achieve a total 200 g of mixture (laboratory scales A&D GF-3000, accuracy 0.01 g). The actual amount of DM in case of BSG would be calculated using moisture of a concurrently measured sample, for malt the weekly value would be used. The final mixture DM content in all experiments was $12.5 \pm 0.2\%$. Citric acid would then be added to adjust the acidity of mixture to pH3 – pH4 (pH-meter Thermo Scientific Orion Star 111). Malt was not ground in the mixtures.

The HTC treatment took place in a laboratory reactor, a stainless steel pressure vessel, Berghof BR-300 with an internal volume of 400 ml. It was not filled completely to allow for the expansion of the mixture at higher temperatures. Inert atmosphere was not introduced. The reactor was heated on an electric heater (Heidolph MR Hei Standard) which was controlled by a regulator (Berghof BTC-3000). In all experiments the reactor would be heated to the target temperature and maintained on it for the chosen time. The reaction was not stirred. Heating up and cooling down phases took each approximately 40–50 minutes. The reaction time was determined as the time when the temperature stayed above target temperature minus 2 °C and it never went above the target temperature plus 5 °C. The only variables in the experiments were reaction temperature and time. All other parameters were maintained the same throughout all experiments. Three different temperatures and times were chosen: 180 °C, 215 °C and 250 °C and 2 h, 5 h and 12 h. Experiments with all combinations have been performed for both substrates.

Upon completing an experiment, remaining pressure would be released and reactor opened when it reached 40 °C. Liquid phase was filtered on a qualitative filter paper and hydrochar left in the reactor was completely taken out. The filtered liquid contained no visible hydrochar particles so all carbon unrecovered in hydrochar is considered to have been dissolved in the process water or has escaped in formed gases. All solid product was then dried until reaching a constant weight (Memmert UN 30) at 105 °C. The mass yield of the hydrochar was then calculated as percent ratio of dry mass of hydrochar to dry mass input in each particular experiment.

Analyses and calculations

After determination of mass yields of hydrochars, the samples were crushed to produce homogenous powder. Consequently they were analyzed for moisture, volatile matter, ash, elemental composition and heating value. The first three parameters were analyzed in a thermogravimetric analyser (LECO TGA 701). The temperature programme first dried samples at 107 °C to constant weight. Volatile matter was determined in nitrogen atmosphere at 900 °C for 7 minutes. Lastly the samples were burned in oxygen at 550 °C, again until constant weight, to find ash content. Each hydrochar was analyzed twice with 1 g per sample; the original materials, BSG and malt, were analysed three times.

Elemental composition was analysed in an instrument LECO CHN628+S with helium as carrier gas to find carbon (C), hydrogen (H), nitrogen (N) and sulphur (S) contents. The analyser operates by analysing the flue gases of samples burned in oxygen. C, H and S are measured in infrared absorption cells; N is measured in a thermal conductivity cell. For determination of C, H and N, 0.15 g of sample was wrapped into a tin foil and burned at 950 °C. Samples into the S module (0.2 g) were poured into a crucible and burned at 1,350 °C. Each sample was analysed to get at least three good measurements of each element.

Higher heating value was measured in a isoperibol calorimeter (LECO AC 600). The samples were pressed into pellets of around 0.7 g and analysed to obtain two reliable results; three for original biomasses. Higher heating value (HHV) was determined using its supplied software.

All reported values are averages for dry basis values. Results of analyses were converted to dry basis values according to ČSN ISO 29541. The elements C, N, S and ash were converted using formula:

$$w_{Xd} = w_{Xa} \times \frac{100}{100 - w_{Ma}} \qquad (1)$$

where w_{Xd} – dry basis elemental contents in % wt.; w_{Xa} – values of analytical samples; w_{Ma} – the moisture in analytical samples.

Hydrogen was converted using:

$$w_{Hd} = \left(w_{Ha} - \frac{w_{Ma}}{8.937} \right) \times \frac{100}{100 - w_{Ma}} \qquad (2)$$

Oxygen content was calculated by subtracting C, H, N and S elemental contents and ash content, all on dry basis, from 100%.

Lower heating value (LHV) was then calculated according to ČSN ISO 1928 using elemental analysis results:

$$LHV = \{ HHV - 212 w_{Hd} - 0.8 \times (w_{Od} + w_{Nd}) \} \times (1 - 0.01 M_T) - 24.43 M_T \quad (3)$$

where M_T – the converted moisture basis, for dry basis it is zero.

All yield values are calculated in the same way. They are defined as the mass yield, as defined in the previous section, multiplied by ratio of contents on dry matter basis of each particular substance in hydrochar to that in the original biomass. Energetic yield is the yield of LHV. Since carbonization decreases the content of H, the HHV yield would be always somewhat lower.

RESULTS AND DISCUSSION

Overall results and energetic yield

After carbonization all hydrochars were not completely homogenous. After carbonization of malt, relatively empty husks tended to gather towards the surface and hydrochar formed arguably mostly from the malt endosperm was found mostly in the bottom half of the reactor. BSG hydrochar was mostly homogenous with its original structure still recognizable. However at higher temperatures and long times of carbonization the hydrochar tended to form a lump of hydrochar toward the surface while a tarry residue formed at the bottom.

Tables 1 and 2 show mass yield and analysis results for hydrochars from BSG and malt, as well as the original biomasses. Values are sorted by reaction temperature and then by reaction time which seems to correspond to reaction severity as the values of carbon content and heating values rise in the same order while volatile matter content decreases. As not a high number of experiments have been made for each set of conditions, small differences cannot be judged as statistically significant. However general trends are clear. Work of Poerschmann et al. (2014) showed carbonized BSG with similar composition giving comparable values of mass yield and elemental contents while also following composition of process liquid and sorption capability of hydrochar. Ash composition is another important factor in energy utilization, however it was not analysed in this work. In literature (Poerschmann et al., 2014) it can be found that after HTC of BSG some elements had an increased content in hydrochar, especially calcium.

Table 1. BSG hydrochar: Mass yield and composition of original BSG and resulting hydrochars at all reaction conditions

Temperature	Time	Mass yield	Carbon content	Hydrogen content	Nitrogen content	Sulphur content	Oxygen content	Volatile Matter	Ash	Higher Heating Value	Lower Heating Value
°C	h	%	% wt.	% wt.	% wt.	% wt.	% wt.	% wt.	% wt.	MJ kg^{-1}	MJ kg^{-1}
Original material			51.9	7.44	4.38	0.34	31.8	83.8	4.10	22.2	20.6
180	2	72.9	59.3	7.32	4.57	0.35	24.0	76.3	4.48	25.2	23.7
180	5	71.7	60.9	7.22	4.64	0.37	22.2	74.6	4.71	25.6	24.0
180	12	70.9	61.8	7.28	4.40	0.36	21.6	73.7	4.60	26.3	24.7
215	2	64.8	63.5	7.37	4.35	0.34	19.9	71.7	4.53	27.3	25.7
215	5	59.2	66.0	7.40	4.58	0.34	16.9	69.8	4.80	28.3	26.7
215	12	56.1	67.3	7.42	4.67	0.35	15.0	67.2	5.29	29.4	27.8
250	2	51.5	69.5	7.50	4.68	0.36	12.9	65.4	5.06	30.4	28.8
250	5	49.2	70.2	7.72	4.32	0.33	12.5	63.3	4.90	31.3	29.7
250	12	45.0	69.7	7.42	4.37	0.38	12.4	56.7	5.72	31.9	30.3

The pH of the final process liquid was between pH3 and pH4 for malt and between pH4 and pH5 for BSG. It was always at least the same or higher compared to starting conditions, but there was not a clear trend. The pH rise was always well within one pH unit, so it was not expected to have a considerable impact on mass yield or other measured parameters (Reza et al., 2015).

Table 2. Malt hydrochar: Mass yield and composition of original malt and resulting hydrochars at all reaction conditions

Temperature	Time	Mass yield	Carbon content	Hydrogen content	Nitrogen content	Sulphur content	Oxygen content	Volatile Matter	Ash	Higher Heating Value	Lower Heating Value
°C	h	%	% wt.	% wt.	% wt.	% wt.	% wt.	% wt.	% wt.	MJ kg⁻¹	MJ kg⁻¹
Original material			46.3	7.01	1.61	0.16	43.0	88.6	1.93	18.6	17.1
180	2	36.7	58.9	5.36	2.99	0.25	30.5	69.3	1.99	24.0	22.9
180	5	47.2	64.8	6.01	2.78	0.22	24.7	63.3	1.52	25.8	24.5
180	12	55.6	67.3	5.53	2.59	0.21	22.9	57.4	1.41	26.8	25.6
215	2	51.9	67.6	5.66	2.69	0.20	22.4	55.8	1.52	27.1	25.9
215	5	52.6	65.9	5.45	2.57	0.19	24.5	54.2	1.39	26.9	25.7
215	12	52.7	68.7	5.51	2.69	0.19	21.2	53.2	1.72	27.2	26.0
250	2	49.4	65.6	5.51	2.71	0.22	24.3	52.3	1.65	28.4	27.2
250	5	48.3	66.0	5.39	2.66	0.20	24.2	49.6	1.55	28.7	27.6
250	12	47.5	66.4	5.46	2.74	0.20	23.4	47.8	1.73	29.3	28.1

Mass yield of hydrochar, see Table 3, from BSG was higher at milder conditions as was expected. BSG is made up mostly of fibres like cellulose which dissolve into solution or degrade only under more severe hydrothermal conditions (especially cellulose) (Heilmann et al., 2011; Reza et al., 2014; Reza et al., 2015). Mass yield of hydrochar decreased with temperature and time mostly due to decomposition of fibre. On the other hand, lower heating value increased from 23.7 MJ kg⁻¹ up to 30.3 MJ kg⁻¹ making it comparable to quality bituminous coal. The final energetic yield decreased overall, but not as sharply as the mass yield. For lower temperatures the mass and energy yields are relatively consistent with those for cellulose (Lu et al., 2013), but at 250 °C BSG yields are lower.

Table 3. Mass and energetic yield of BSG hydrochars

	Mass yield (%)			LHV (MJ kg⁻¹)			Energetic yield (%)		
	2 h	5 h	12 h	2 h	5 h	12 h	2 h	5 h	12 h
180 °C	72.9	71.7	70.9	23.7	24.0	24.7	83.6	83.4	84.9
215 °C	64.8	59.2	56.1	25.7	26.7	27.8	80.7	76.6	75.7
250 °C	51.5	49.2	45.0	28.8	29.7	30.3	71.8	70.8	66.1

The situation was different for hydrochar from malt, see Table 4. Malt still contains starchy endosperm which makes up most of its weight. The mechanism of hydrochar formation is different here. Sugars quickly solubilise in water at hydrothermal condition and most of the hydrochar has to be formed by polymerization from the solution (Nagamori & Funazukuri, 2004). It can be seen that at the mildest conditions the overall reaction proceeds slowly and the yield is quite low. With increasing time the reaction

becomes more complete and the yield rises or remains level. This trend, however, is reversed at the highest tested temperature (250 °C) which might be contributed either to decomposition of the husks or further carbonization and losing of H and O content. The latter, however, does not seem to be the case since elemental composition is very similar for the 2 h and 5 h samples at 250 °C. The general increase in mass yield with time or its stagnancy and increase of LHV with temperature resulted in similar energetic yields around 80% for all but two samples (2 h and 5 h at 180° C).

Table 4. Mass and energetic yield of malt hydrochars

	Mass yield (%)			LHV (MJ kg^{-1})			Energetic yield (%)		
	2 h	5 h	12 h	2 h	5 h	12 h	2 h	5 h	12 h
180 °C	36.7	47.2	55.6	22.9	24.5	25.6	49.0	67.8	83.2
215 °C	51.9	52.6	52.7	25.9	25.7	26.0	78.6	78.9	80.2
250 °C	49.4	48.3	47.5	27.2	27.6	28.1	78.5	77.8	78.0

Mass yields of selected elements

The carbon content in hydrochars is always increased relative to that in the original biomasses. It increases mainly with carbonization temperature. Except for malt hydrochars at 180 °C it does not seem to be strongly dependent on time. The yields of carbon, see Tables 5–6, follow relatively closely energetic yields at milder conditions, but drop off more quickly at 250 °C and longer times in the case of both substrates.

Table 5. C, N and S contents and their yields in BSG hydrochars

	C (% wt.)			N (% wt.)			S (% wt.)		
	2 h	5 h	12 h	2 h	5 h	12 h	2 h	5 h	12 h
180 °C	59.3	60.9	61.8	4.6	4.6	4.4	0.35	0.37	0.36
215 °C	63.5	66.0	67.3	4.4	4.6	4.7	0.34	0.34	0.35
250 °C	69.5	70.2	69.7	4.7	4.3	4.4	0.36	0.33	0.38

	C yield (%)			N yield (%)			S yield (%)		
	2 h	5 h	12 h	2 h	5 h	12 h	2 h	5 h	12 h
180 °C	83.2	84.1	84.4	76.0	76.0	71.1	74.4	78.3	75.6
215 °C	79.3	75.2	72.7	64.4	61.8	59.9	65.4	59.4	57.8
250 °C	69.0	66.6	60.4	55.0	48.5	44.8	54.6	48.0	50.4

Table 6. C, N and S contents and their yields in malt hydrochars

	C (% wt.)			N (% wt.)			S (% wt.)		
	2 h	5 h	12 h	2 h	5 h	12 h	2 h	5 h	12 h
180 °C	58.9	64.8	67.3	3.0	2.8	2.6	0.25	0.22	0.21
215 °C	67.6	65.9	68.7	2.7	2.6	2.7	0.20	0.19	0.19
250 °C	65.6	66.0	66.4	2.7	2.7	2.7	0.22	0.20	0.20

	C yield (%)			N yield (%)			S yield (%)		
	2 h	5 h	12 h	2 h	5 h	12 h	2 h	5 h	12 h
180 °C	46.7	66.1	80.9	68.0	81.4	89.4	58.5	67.3	74.8
215 °C	75.7	74.8	78.1	86.7	83.7	87.7	65.0	62.3	63.1
250 °C	70.0	68.8	68.1	83.0	79.6	80.6	70.4	60.3	62.0

The hydrochar contents of N and S are relatively unaffected by carbonization conditions. In BSG hydrochar the N and S content are very close to those in original biomass, in malt hydrochar they are somewhat higher (Tables 5–6). The relatively unchanged nitrogen content was probably due to denatured proteins immobilized in the hydrochars (Heilmann et al., 2011; Poerschmann et al., 2014). The yields of N and S are then depending on the overall mass yield of hydrochars.

Van Krevelen diagram

Hydrochar achieves higher heating values thanks to increasing its carbon content and lowering mainly its oxygen and also hydrogen content. This conversion can be seen in a van Krevelen diagram, which has molar ratios O/C on its horizontal axis and H/C on the vertical axis. In Fig. 1 van Krevelen diagram of hydrochars and original biomasses can be seen. BSG hydrochars are moving to the left of the diagram with reaction severity (mainly with temperature, then with time) and at 250 °C they reach nearly the same ratios for all times, however with a little higher H/C ratio than in (Poerschmann et al., 2014). The ratios seem to follow a nearly linear trend. This was also the case for poplar wood or wheat straw in (Reza et al., 2014). Our BSG achieved similar ratios as olive mill waste in (Benavente et al., 2015). Malt hydrochars have very similar ratios for all but two conditions (180 °C at 2 h and 5 h). Comparing these results with heating values, it implies that a formula to estimate the heating value of hydrochars would have to consider more parameters than just elemental composition, for example volatile matter content.
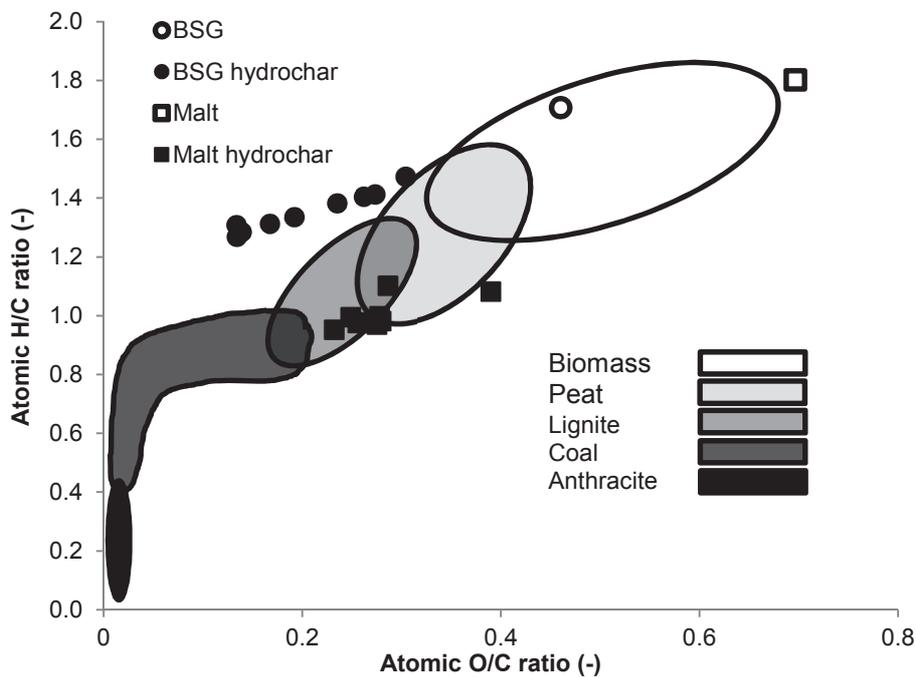
Figure 1. Van Krevelen diagram of BSG and malt hydrochar, areas of typical composition taken from (Van Loo & Koppejan, 2008).

CONCLUSIONS

The main aim of this work was to evaluate the possible energetic yield of hydrochar made by hydrothermal carbonization of brewer's spent grain. To compare it with a different biomass, the corresponding barley malt was also tested at the same carbonization conditions. On dry state basis the highest energetic yield (lower heating value returned in dry matter) was 84.9% at 180 °C and 12 h carbonization (but at shorter times it was almost as high). For malt nearly the same values were reached, but it took a time of at least 5 h or temperature 215 °C and higher to carbonize the most of dissolved sugars. In general, milder conditions produced hydrochar with lower specific heating values but with greater overall energy retention.

In practice other parameters will have to be accounted for to assess real efficiency of this process. Those are dewaterability of starting material versus that of hydrochar, the energy consumption to dry those materials or the energy consumption of hydrothermal conversion and others as well. The energy balance could be then calculated to see whether it is viable at all to hydrothermally convert this material from ecological, energetic or economical point of view. A life cycle assessment of environmental impact of hydrochar production has been performed in (Berge et al., 2015). It showed for example that the process water impact is not at all negligible. It contains still a large amount of dissolved organic carbon which would have to be removed, for example possibly by combining hydrothermal carbonization with wet oxidation (Riedel et al., 2015).

REFERENCES

Benavente, V., Calabuig, E. & Fullana, A. 2015. Upgrading of moist agro-industrial wastes by hydrothermal carbonization. *Journal of Analytical and Applied Pyrolysis* **113**, 89–98.

Berge, N.D., Li, L., Flora, J.R.V. & Ro, K.S. 2015. Assessing the environmental impact of energy production from hydrochar generated via hydrothermal carbonization of food wastes. *Waste Management* **43**, 203–217.

ČSN ISO 1928 Solid mineral fuels – Determination of gross calorific value by the bomb calorimetric method, and calculation of net calorific value. 2010 (in Czech)

ČSN ISO 29541 Solid mineral fuels – Determination of total carbon, hydrogen and nitrogen content – Instrumental method. 2012 (in Czech)

Heilmann, S.M., Jader, L.R., Sadowsky, M.J., Schendel, F.J., von Keitz, M.G. & Valentas, K.J. 2011. Hydrothermal carbonization of distiller's grains. *Biomass and Bioenergy* **35**(7), 2526–2533.

Kruse, A. & Dahmen, N. 2015. Water – A magic solvent for biomass conversion. *Journal of Supercritical Fluids* **96**, 36–45.

Lu, X., Pellechia, P.J., Flora, J.R.V. & Berge, N.D. 2013. Influence of reaction time and temperature on product formation and characteristics associated with the hydrothermal carbonization of cellulose. *Bioresource Technology* **138**, 180–190.

Malakhova, D.V., Egorova, M.A., Prokudina, L.I., Netrusov, A.I. & Tsavkelova, E.A. 2015. The biotransformation of brewer's spent grain into biogas by anaerobic microbial communities. *World Journal of Microbiology and Biotechnology* **31**(12), 2015–2023.

Malaťák, J. & Dlabaja, T. 2015. Hydrothermal carbonization of stabilized sludge and meat and bone meal. *Research in Agricultural Engineering* **61**(1), 21–28.

Mussatto, S.I., Dragone, G. & Roberto, I.C. 2006. Brewers' spent grain: Generation, characteristics and potential applications. *Journal of Cereal Science* **43**(1), 1–14.

Nagamori, M. & Funazukuri, T. 2004. Glucose production by hydrolysis of starch under hydrothermal conditions. *Journal of Chemical Technology and Biotechnology* **79**(3), 229–233.

Poerschmann, J., Weiner, B., Wedwitschka, H., Baskyr, I., Koehler, R. & Kopinke, F.-D. 2014. Characterization of biocoals and dissolved organic matter phases obtained upon hydrothermal carbonization of brewer's spent grain. *Bioresource Technology* **164**, 162–169.

Poerschmann, J., Weiner, B., Koehler, R. & Kopinke, F.-D. 2015. Organic breakdown products resulting from hydrothermal carbonization of brewer's spent grain. *Chemosphere* **131**, 71–77.

Raud, M., Tutt, M., Olt, J. & Kikas, T. 2015. Effect of lignin content of lignocellulosic material on hydrolysis efficiency. *Agronomy Research* **13** (2), 405–412.

Reza, M.T., Wirth, B., Lüder, U. & Werner, M. 2014. Behavior of selected hydrolyzed and dehydrated products during hydrothermal carbonization of biomass. *Bioresource Technology* **169**, 352–361.

Reza, M.T., Rottler, E., Herklotz, L. & Wirth, B. 2015: Hydrothermal carbonization (HTC) of wheat straw: Influence of feedwater pH prepared by acetic acid and potassium hydroxide. *Bioresource Technology* **182**, 336–344.

Riedel, G., Koehler, R., Poerschmann, J. & Kopinke, F.-D., Weiner, B. 2015. Combination of hydrothermal carbonization and wet oxidation of various biomasses. *Chemical Engineering Journal* **279**, 715–724.

Santos, M., Jiménez, J.J., Bartolomé, B., Gómez-Cordovés, C. & Del Nozal, M.J. 2003. Variability of brewer's spent grain within a brewery. *Food Chemistry* **80**(1), 17–21.

Steiner, J., Procopio, S. & Becker, T. 2015. Brewer's spent grain: source of value-added polysaccharides for the food industry in reference to the health claims. *European Food Research and Technology* **241**(3), 303–315.

Van Loo, S. & Koppejan, J. 2008. *The Handbook of Biomass Combustion and Co-firing*. Earthscan, London, 442 pp.

Weiner, B., Baskyr, I., Poerschmann, J. & Kopinke, F.-D. 2013. Potential of the hydrothermal carbonization process for the degradation of organic pollutants. *Chemosphere* **92**(6), 674–680.

Xiros, C. & Christakopoulos, P. 2012. Biotechnological potential of brewers spent grain and its recent applications. *Waste and Biomass Valorization* **3**(2), 213–232.