

## Hydrothermal carbonization and torrefaction of cabbage waste

B. Tamelová\*, J. Malat'ák and J. Velebil

Czech University of Life Sciences Prague, Faculty of Engineering, Department of Technological Equipment of Buildings, Kamýcká 129, CZCZ165 21 Prague, Czech Republic

\*Correspondence: [tamelova@tf.czu.cz](mailto:tamelova@tf.czu.cz)

**Abstract.** In recent years, waste biomass has been increasingly becoming an energy source. The utilization of biomass includes a number of potential treatments: thermochemical, physicochemical and biochemical. In the food industry, significant amounts of biodegradable wastes are produced which have to be quickly treated to not pose an environmental problem. In this work cabbage waste (*Brassica oleracea var. capitata*) was treated by hydrothermal carbonization and torrefaction.

Hydrothermal carbonization experiments were carried out in a pressure reactor vessel Berghof BR-300 (inner volume 400 mL, temperature regulation by Berghof BTC 3000). The carbonization took place at target temperatures 180 °C and 225 °C. Torrefaction tests were carried out in a thermogravimetric programmable oven LECO TGA701 under nitrogen atmosphere at temperatures 225 °C, 250 °C and 275 °C. The residence time was 30 min for both processes. Proximate and elemental composition, as well as calorific value was analysed in all samples. To express the influence of the treatments on combustion behaviour, stoichiometric combustion calculations were performed.

The analyses show a positive effect of both torrefaction and hydrothermal carbonization on fuel properties in the samples. Most obvious is the reduction in oxygen content which depends on the process temperature. After hydrothermal carbonization at 225 °C the oxygen content was lowered by 46.7%. The net calorific value increased proportionally with temperature in both processes. After hydrothermal carbonization at 225 °C the net calorific value increased on average by 3 MJ kg<sup>-1</sup> to 20.89 MJ kg<sup>-1</sup>. Both tested processes significantly increased the fuel value of this biodegradable waste.

**Key words:** biomass, biochar, elemental analysis, energy properties.

### INTRODUCTION

In recent years, waste biomass has become an important part in renewable energy production. The use of waste biomass involves a wide range of potential thermochemical, physico-chemical and bio-chemical processes (Hamelinck et al., 2005).

Brassica varieties are grown today for food everywhere in the world. Cruciferous vegetables are one of the most important dietary vegetables consumed in Europe due to their availability on local markets, affordability and consumer preference (Šamec et al., 2011). Headed cabbage (*Brassica oleracea var. capitata*) and Chinese cabbage (*Brassica rapa cv. pekinensis*) are one of the most widely grown vegetables grown for

human consumption (Liu et al., 2014). The cabbage head generally develops during the first year in the plant's life cycle, flowering and seed production usually occur in the second year (Šamec et al., 2017). The weight of the white cabbage head generally ranges from 0.5 to 4 kg and can be green, light green or white in colour. In most cases, up to 40% of the outer leaves and the cabbage cores are discarded and treated as waste, often used as livestock feed, for composting or for biogas production (Nilnakara et al., 2009).

One of the ways to further utilize waste biomass is the technology of hydrothermal carbonization and torrefaction.

Hydrothermal carbonization (HTC), often referred to as wet torrefaction, is the process of transforming biomass into carbonaceous material at a relatively low temperature (150–250 °C), elevated pressure, and in water environment (Kannan et al., 2017). Biomass is completely immersed in water during the process with an overpressure of up to 4.6 MPa (Lynam et al., 2011). The HTC reaction time is in the range of 5–240 min (Chen et al., 2012). The mechanisms of hydrothermal carbonization are associated with a series of hydrolysis, condensation, decarboxylation, and dehydration reactions (Pala et al., 2014). The reaction products include gases (mainly carbon dioxide, carbon monoxide, hydrogen, methane, ethane and propene), and a mechanically easily separable mixture of solids, referred to as hydrochar, and liquid, which contains the solvent used in the HTC reaction as well as solubilized organic products (Berge et al., 2011; Benavente et al., 2015). Compared to torrefaction, HTC has the advantage of not requiring an energy-intensive drying process for wet materials (Pala et al., 2014).

The main product of the HTC is 'hydrochar' (hydrothermal biochar), a hydrophobic solid fuel with much better grindability, lower moisture content and higher calorific value compared with the untreated biomass (Bach et al., 2013). The amount and quality of the hydrochar are dependent on a number of parameters, especially on the treatment temperature, the original material and the residence time (Lu & Berge, 2014).

Torrefaction is a process of biomass thermal treatment where the biomass is heated in the temperature range of 200–300 °C in an inert atmosphere. The torrefaction temperature provides the activation energy for the destruction of chemical bonds in organic matter, i.e. cellulose, hemicelluloses and lignine. The effect is a change in material structure and release of gases, volatile liquids and tars (Toscano et al., 2015). During torrefaction, the moisture content decreases, increasing the energy density of torrefied biomass (Couhert et al., 2009). Further, the oxygen content is reduced, the torrefied biomass has a lower O/C ratio than the original biomass (Bridgeman et al., 2008; Van der Stelt et al., 2011). The final solid product from torrefaction is dry, blackened material, which is described as torrefied biomass or biochar (Baskar et al., 2012).

In terms of physical properties, the colour of the torrefied biomass element changes to brown and even to black with increasing torrefaction temperature, the volume decreases and particles change shape (Chen et al., 2014). Literature shows that torrefaction process generally improves the fuel properties of biomass (Chen & Kuo 2010; Tamelová et al., 2018).

Many authors have studied torrefaction and hydrothermal carbonization of lignocellulosic biomass (Prins et al., 2006; Couhert et al., 2009; Chen et al., 2011; Phanphanich & Mani 2011; Bach et al., 2014). However, fewer studies have focused on wastes from agriculture and food industry (Benavente et al., 2015; Tamelová et al., 2018; Wang et al., 2018).

Since these materials tend to be more heterogeneous than woody biomass and often not suitable for a direct energy valorisation, torrefaction process could be a useful solution to overcome this issue (Toscano et al., 2015).

The aim of this article is to assess the fuel value of white cabbage before and after hydrothermal carbonization and torrefaction.

For these samples, elemental analysis, calorific value and combustion heat have been determined. Stoichiometric combustion parameters such as the theoretical amount of air for perfect combustion or the amount of dry flue gas are also determined and the calorific value of the treated samples will be determined depending on the water content.

## MATERIALS AND METHODS

### Sample preparation

The waste from the cleaning of white cabbage (*Brassica oleracea var. capitata*) was obtained from an agricultural company processing white cabbage. The material contained waste cabbage leaves and cores. Three 100 g samples were used for moisture determination. For subsequent tests, the material was left to dry in forced flow of ambient air. Then, the material was milled with a RETSCH SM100 cutting mill to size under 1 mm.

### Experimental procedure of hydrothermal carbonization

Hydrothermal carbonization of white cabbage was carried out in a Berghof BR-300 reaction vessel with an internal volume of 400 mL paired with a Berghof BTC 3000 temperature controller. The reactor vessel is made of stainless steel. For each test run, 50 g of cabbage sample was put in the reactor and 200 mL of water was added. Target temperatures for hydrothermal treatment were 180 °C and 215 °C with residence time 30 minutes. Subsequently, the vessel was cooled to about 50 °C. During the measurement, the reaction temperature and pressure were recorded. Reaching the target temperature and cooldown both took ca. 40 min. When the reactor was cooled, the remaining overpressure was released, the reactor was opened, and the pH of the resulting process liquid was measured. The solid residue in reactor was filtered and dried in a Memmert UN 30 oven at 60 °C for 24 h.

### Experimental procedure of torrefaction

Torrefaction process was simulated using a LECO TGA 701 thermogravimetric analyser in which the samples undergo a thermal programme in periodically weighed crucibles. First the samples were dried for 2 h at 105 °C, then nitrogen atmosphere was introduced, and the samples were heated to a target temperature and held at this temperature for 30 min. In total, three measurements were made at each target temperature of 225 °C, 250 °C and 275 °C. During the torrefaction treatment of the samples, the weight loss was monitored as a function of time.

### Moisture, ash, elemental composition and calorific value determination

The LECO TGA 701 thermogravimetric analyser also determined the total moisture and ash. Determination of the elemental composition of carbon (C), hydrogen (H), nitrogen (N) and sulphur (S) contents was performed on the LECO CHN628 + S analyser. Gross calorific value was determined in an isoperibolic calorimeter

LECO AC-600. All measurements were repeated at least three times to obtain reliable results. Net calorific value was determined by calculation using the results of calorimetry, elemental and proximate analysis. Based on these measured parameters, stoichiometric calculations were determined.

### Stoichiometric combustion calculations

The theoretical amount of oxygen for complete combustion  $O_{2,min}$  ( $m^3 \text{ kg}^{-1}$ ) is based on the equation:

$$O_{2,min} = V_m(O_2) \left( \frac{C}{M(C)} + \frac{H}{M(2 \cdot H_2)} + \frac{S}{M(S)} - \frac{O}{M(O_2)} \right) \quad (1)$$

Where  $C$ ,  $H$ ,  $S$ , and  $O$  are the contents of carbon, hydrogen, sulphur and oxygen in the sample (% wt.);  $V_m(O_2) = 22.39 \text{ m}^3 \text{ kmol}^{-1}$  is the molar volume of oxygen gas at normal conditions and  $M(C)$  ( $\text{kg kmol}^{-1}$ ) are molar masses of theoretical species that combine with  $O_2$ .

Where the theoretical amount of dry air  $L_{min}$  ( $m^3_N \text{ kg}^{-1}$ ) is determined from the equation:

$$L_{min} = O_{2,min} \cdot \frac{100}{C_{atm}(O_2)} \quad (2)$$

Where  $C_{atm}(O_2) = 20.95\%$  vol. is volumetric concentration of oxygen in air.

The theoretical amount of dry flue gases  $v_{fg,min}$  ( $m^3 \text{ kg}^{-1}$ ) is based on the equation:

$$v_{fg,min} = \frac{V_m(CO_2)}{M(C)} \cdot C + \frac{V_m(SO_2)}{M(S)} \cdot S + \frac{V_m(N_2)}{M(N_2)} \cdot N + \frac{C_{atm}(N_2)}{100} \cdot L_{min} \quad (3)$$

Where  $V_m(C)$  ( $m^3 \text{ kmol}^{-1}$ ) are the molar volumes of flue gas components;  $C_{atm}(N_2) = 78.05\%$  vol. is the concentration of  $N_2$  in air.

The theoretical amount of emission concentrations of  $CO_{2,max}$  ( $m^3_N \text{ kg}^{-1}$ ) is based on the equation:

$$CO_{2,max} = \frac{M(C) \cdot C}{V_m(CO_2) \cdot v_{fg,min}} \cdot 100 \quad (4)$$

Volumetric amounts of combustion products:

$$v(CO_2) = \frac{V_m(CO_2)}{M(C)} \cdot C + \frac{C_{atm}(CO_2)}{100} \cdot L \quad (5)$$

$$v(SO_2) = \frac{2 \cdot V_m(SO_2)}{2 \cdot M(S)} \quad (6)$$

$$v_{N_2} = \frac{V_m(N_2)}{M(N_2)} \cdot v(N_2) + O_{2,min} \cdot \frac{C_{atm}(N_2)}{C_{atm}(O_2)} \quad (7)$$

Conversion of the calorific value of  $Q_i^r$  at an arbitrary water content  $W$  to a different water content  $W_t$  is made according to the formula:

$$Q_{in}^r = \frac{100 - W_t}{100 - W} \cdot (Q_i^r + 0.02442 \cdot W) - 0.02442 \cdot W_t \quad (8)$$

Where  $W_t$  (% wt.), the total water content in the original sample;  $W$  the net calorific value of the original sample ( $\text{MJ kg}^{-1}$ ) and  $Q_i^r$  is the net calorific value at the target water content.

## RESULTS AND DISCUSSION

Table 1 shows the results of the proximate and elemental analysis of white cabbage samples before and after hydrothermal carbonization and torrefaction treatment.

**Table 1.** Composition and calorific values of white cabbage before and after hydrothermal carbonization and torrefaction treatment at varying temperatures and 30 minute residence time

Sample	Water Content (% wt.)	Ash (% wt.)	Carbon (% wt.)	Hydrogen (% wt.)	Nitrogen (% wt.)	Sulphur (% wt.)	Oxygen (% wt.)	Gross Calorific Value (MJ kg <sup>-1</sup> )	Net Calorific Value
	<i>W</i>	<i>A</i>	<i>C</i>	<i>H</i>	<i>N</i>	<i>S</i>	<i>O</i>	<i>Q<sub>s</sub></i>	<i>Q<sub>i</sub></i>
Original sample	75.12	3.88	10.08	1.30	0.72	0.26	8.64	3.98	1.86
Dry basis		15.61	40.50	5.21	2.91	1.03	34.74	15.98	14.84
H-180-30		21.56	46.32	4.92	3.40	1.43	20.97	18.88	17.81
H-225-30		21.16	52.08	4.98	4.13	1.44	16.22	21.97	20.89
T-225-30		19.31	46.44	4.90	3.78	1.04	24.52	18.76	17.69
T-250-30		21.17	48.43	4.77	4.03	1.11	20.49	19.55	18.51
T-275-30		24.60	50.53	4.48	4.35	1.19	14.85	20.42	19.45

*H* – Hydrothermal carbonization, 180, 225 – temperature (°C), 30 – residence time (min.); *T* – torrefaction, 225, 250, 275 – temperature (°C), 30 – residence time (min.)

The results of the proximate and elemental analysis show a positive effect of HTC and torrefaction on the examined white cabbage sample. The original material had high water content 75.12% wt. as well as ash content at 15.61% wt. on dry basis. Abdul Samad et al. (2017) determined a comparable value of dry ash in a food waste sample to 16.89% wt. This can be contrasted with wood biomass where Van der Stelt et al. (2011) reported only 1.3% wt of ash in dry wood. With increasing torrefaction temperature, the ash content in the cabbage sample rose. At 250 °C the ash content increased to 21.17% wt. and at temperature 275 °C, the ash went up to 24.60% wt. Van der Stelt et al. (2011) reported the value of ash in wood after torrefaction at 250 °C for 30 minutes at 1.5% wt.

The carbon content increases during both processes with increasing temperature at the expense of oxygen and hydrogen, which leads to the reduction of H/C and O/C ratios (Pentananunt et al., 1990). During carbonization, dehydration and decarboxylation reactions of aromatic structures occur and subsequently the sample becomes more hydrophobic (Berge et al., 2011). The carbon content in dry original sample was 40.50% wt. and it rose with treatment temperature in both processes. During the HTC process, the carbon content increased by almost 6% wt. to a final value of 52.08% wt. at HTC 225 °C. With increasing torrefaction temperature, the increase in carbon is not as significant as that of HTC. The carbon value increases by about 2% wt. with an increasing temperature to a final value of 50.53% wt. In comparison, spruce torrefied at 270 °C for 16.5 min. had 52.50% wt. carbon content (Larsson et al., 2013), cotton stalk torrefied at 250 °C for 30 min. had 56.18% wt. (Chen et al., 2015) and orange peel torrefied at 275 °C for 30 min. achieved 67.05% wt. (Tamelová et al., 2018).

Oxygen content decreases during both processes. Its value decreased by 57.25% in the dry state during torrefaction to a final value of 14.85% wt. at a process temperature of 275 °C. During HTC, oxygen is reduced by 53.57% compared to the original sample in the dry state to 16.22% wt. at temperature 225 °C.

When increasing the process temperatures of HTC and torrefaction, hydrogen content is being reduced compared to the original sample, albeit by a small degree.

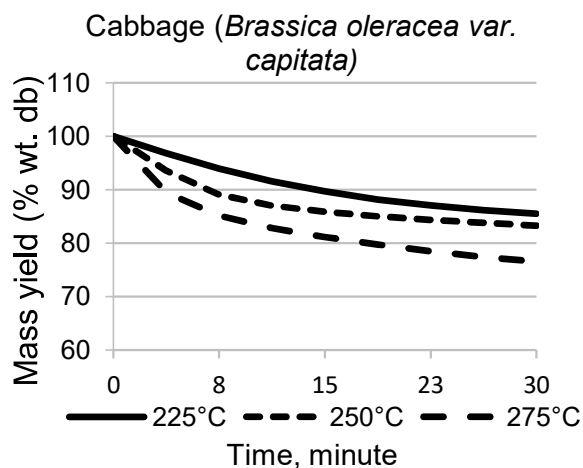
Nitrogen content increased with increasing temperature in both processes. The original sample contained 2.91% wt. nitrogen in dry state. After HTC at 180 °C for 30 min. this increased to 3.40% wt. After 30 min HTC at 225 °C it rose to 4.13% wt. Nitrogen content in torrefied samples was similar. After 30 min. torrefaction at 225 °C the value rose to 3.78% wt. and after 30 min. at 275 °C it reached 4.35% wt.

White cabbage has a relatively high proportion of sulphur. The greater proportion of sulphur is due to the fact that *Brassica* family species tend to show high concentrations of amino acids and other organic compounds derived from sulphur metabolism when accumulating other elements and heavy metals (Mazzafera, 1998). Sulphur in reduced form plays an important role in plant growth and plant growth regulation (Moreno et al., 2005). In dry sample, the sulphur content is 1.03% wt. This content increased with growing treatment temperature. The highest value (1.44% wt.) was reached after HTC at 225 °C. Comparing sulphur values with other biomass samples, for example Abdul Samad et al. (2017) reported the sulphur content of dry food waste sample at 0.16% wt. and, after torrefaction at a temperature of 330 °C and a residence time of 30 minutes, this increased to 0.26% wt. Miranda et al. (2009) determined the dry sulphur value for orange peel at 0.60% wt.

Gross calorific value increased with temperature after both process types. The gross calorific value of the white cabbage sample was 15.98 MJ kg<sup>-1</sup> in dry state. Compared to the original dry sample, it is increased by 5.99% wt. during the HTC process at 225 °C to value 21.97 MJ kg<sup>-1</sup>. HTC increases the calorific value by approximately 3 MJ kg<sup>-1</sup> to 20.89 MJ kg<sup>-1</sup> at process temperature 225 °C. Similar heating value values (21.17 MJ kg<sup>-1</sup>) were reported by Wang et al. (2018), who carbonized by HTC corn stalk at temperature 220 °C and 30 minute residence time.

Bach et al. (2014) reported net calorific value of spruce 22.97 MJ kg<sup>-1</sup> after HTC at 225 °C for 30 minutes. Benavente et al. (2015) showed net calorific value of orange waste 27.73 MJ kg<sup>-1</sup> after HTC at temperature of 225 °C and residence time 2 hours. Pala et al. (2014) hydrothermally carbonized grape pomace and reported net calorific value 25.65 MJ kg<sup>-1</sup> after 30 min at 225 °C.

During the torrefaction process, the net calorific value increased compared to the original dry sample by 2.85 MJ kg<sup>-1</sup> at 225 °C and further by another 1 MJ kg<sup>-1</sup> to the final value of 19.45 MJ kg<sup>-1</sup> at 275 °C. Pala et al. (2014) reported net calorific value 23.12 MJ kg<sup>-1</sup> in grape pomace torrefied at 275 °C for 30 min. When compared to wood biomass, Larsson et al. (2013) reported the Net calorific value of spruce of 21.1 MJ kg<sup>-1</sup> after torrefaction at 270 °C with residence time 16.5 minutes.



**Figure 1.** Mass loss curves during torrefaction of white cabbage.

Fig. 1 shows the weight loss over time during torrefaction temperatures of 225 °C, 250 °C and 275 °C. The greatest weight loss was recorded at 275 °C at almost 25%. The curves at 225 °C and 275 °C are offset by about 10%. Similar results were published by Meng et al. (2015) who pyrolyzed Chinese cabbage in the temperature range of 200-1,000 °C.

Tables 2 and 3 show the results of stoichiometric analysis. The tables show the difference between the treatment degree. Increasing temperature in HTC and torrefaction treatment changes the proportional representation of elements having the effect to increase specific theoretical volume of air for complete combustion and flue gas production, as well as the emission concentrations of individual combustion products. Very similar effects were reported by Tamelová et al. al., (2018) for citrus specimens. The effect was most pronounced in sample treated hydrothermally at 225 °C. In this case, the specific air consumption is 1.4 times that of the original sample. Similar results were determined for the torrefaction treatment, where the difference is up to 1.35 times the original sample.

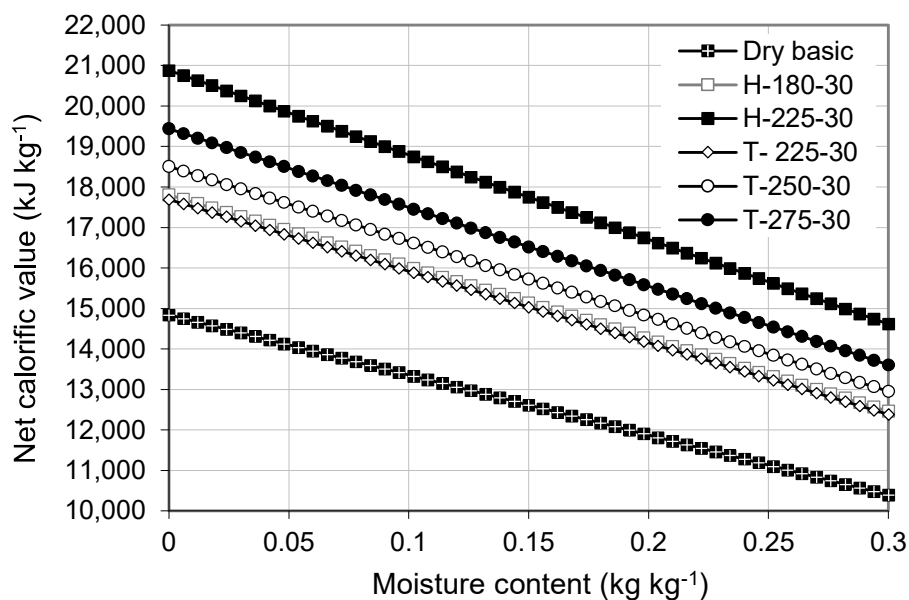
**Table 2.** Stoichiometric combustion of white cabbage and hydrothermally carbonized samples

			Original sample	H-180-30	H-225-30
$L_{min}$	Theoretical air consumption	(m <sup>3</sup> kg <sup>-1</sup> )	3.85	4.76	5.45
$v_{fg,min}$	Theoretical flue gas production	(m <sup>3</sup> kg <sup>-1</sup> )	3.79	4.62	5.26
$v(CO_2)$	CO <sub>2</sub> production	(m <sup>3</sup> kg <sup>-1</sup> )	0.75	0.86	0.97
$v(SO_2)$	SO <sub>2</sub> production	(m <sup>3</sup> kg <sup>-1</sup> )	0.01	0.01	0.01
$v(H_2O)$	H <sub>2</sub> O production	(m <sup>3</sup> kg <sup>-1</sup> )	0.73	0.74	0.77
$v(N_2)$	N <sub>2</sub> volume in flue gas	(m <sup>3</sup> kg <sup>-1</sup> )	3.03	3.76	4.28
$CO_{2max}$	Maximum CO <sub>2</sub> concentration in dry flue gas	(%)	19.84	18.58	18.36

**Table 3.** Stoichiometric combustion of torrefied white cabbage

			T-225-30	T-250-30	T-275-30
$L_{min}$	Theoretical air consumption	(m <sup>3</sup> kg <sup>-1</sup> )	4.64	4.91	5.22
$v_{fg,min}$	Theoretical flue gas production	(m <sup>3</sup> kg <sup>-1</sup> )	4.52	4.77	5.05
$v(CO_2)$	CO <sub>2</sub> production	(m <sup>3</sup> kg <sup>-1</sup> )	0.86	0.90	0.94
$v(SO_2)$	SO <sub>2</sub> production	(m <sup>3</sup> kg <sup>-1</sup> )	0.01	0.01	0.01
$v(H_2O)$	H <sub>2</sub> O production	(m <sup>3</sup> kg <sup>-1</sup> )	0.73	0.73	0.71
$v(N_2)$	N <sub>2</sub> volume in flue gas	(m <sup>3</sup> kg <sup>-1</sup> )	3.65	3.87	4.11
$CO_{2max}$	Maximum CO <sub>2</sub> concentration in dry flue gas	(%)	19.06	18.81	18.55

Fig. 2 shows calculated net calorific value for all studied samples against variable moisture content up to 30% wt. The amount of water in the fuel will determine the efficiency in energy utilization (Esteban et al., 2014) as well as the emission concentrations of the combustion plant (Johansson et al., 2004; Malat'ák & Passian, 2011). In hydrothermal carbonization, the difference in net calorific value between the original sample and the H-225-30 sample is 27.73% and for the T-275-30 sample it is 21.44%. From the graph in Fig. 2, the net calorific value can be deduced for arbitrary moisture content in the fuel. For example, as shown in Fig. 2 for sample H-225-30, 10% wt. moisture content decreases the net calorific value by 10.2%.



**Figure 2.** Net calorific value of all samples at variable moisture content.

## CONCLUSIONS

Torrefaction and hydrothermal carbonization are thermochemical treatments that can be used for a wide range of waste biomasses. As a suitable representative waste, white cabbage which is an important by-products in the food industry was chosen for this study. The main product of these processes is a biochar.

The fuel parameters of white cabbage before and after treatment by torrefaction and hydrothermal carbonization processes showed significant changes. Torrefaction is generally capable of producing better fuel compared to the original biomass, primarily by increasing the calorific value and reducing the oxygen content. For the samples examined, the highest net calorific value 20.89 MJ kg<sup>-1</sup> was obtained after hydrothermal carbonization at 225 °C with a residence time of 30 minutes. With increasing process temperature, the calorific value increased. The highest increase between two treatment temperatures in net calorific value occurred with HTC between temperatures 180 °C and 225 °C, rising by 3.08 MJ kg<sup>-1</sup>. The net calorific value after torrefaction increased by approximately 1 MJ kg<sup>-1</sup> between both temperature steps.

However, both processes had an undesirable effect in increasing the ash content. In the dry state, the ash content was 15.61% wt. After torrefaction at 275 °C and reaction time of 30 minutes, it increased to 24.60% wt. Such ash content limits the use of torrefied fuel in some areas, e.g. in small domestic appliances. The sample of white cabbage was found to have an unusually high amount of sulphur compared to, for example, wood biomass. In the dry state, the sulphur content was 1.03% wt. The sulphur content after both processes increased with increasing the temperature. The highest value of 1.44% wt. was measured after HTC at 225 °C.

The stoichiometric combustion characteristics of the treated white cabbage samples showed a positive effect of the treatments when compared to the original material.



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