

Investigation of applicability of wetland biomass for producing biochar by hydrothermal carbonization (HTC)

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Abstract

The production of carbonaceous materials from biomass has recently attracted much attention. The hydrothermal carbonization process (HTC) is of great importance because it can generate chars (HTC-chars) that are rich in organic carbon from biomass with high water content; these chars have the potential to be used in a wide range of applications. In this review we discuss an investigation into the production of carbonaceous materials from four types of wetland biomass (reed, typha, juncus and carex) using hydrothermal carbonization. Furthermore, the influence of reaction temperatures on the carbonization process was examined by varying the temperature over a range of 180 to 230 °C. A comparison between the properties of the resulting chars was performed, focusing on elemental analysis and nitrogen adsorption. Depending on the biomass, the HTC-chars were found to contain around 53 to 60% of the carbon originally present in the biomass. There was a clear positive correlation between reaction temperature increase and the carbon proportion of the HTC-char of all variants. The atomic ratios H/C and O/C of the chars were found to be more similar to lignite than those of the raw material. The study shows that wetland biomass has great potential for the production of HTC-char.

Keywords: *Hydrothermal carbonization, wetland biomass, HTC-char, BET*

Zusammenfassung

Untersuchung zur Anwendbarkeit von Moorbio- masse für die Biokohleher- stellung durch hydrothermale Karbonisierung (HTC)

Die Herstellung von kohlenstoffhaltigen Materialien aus Bio- masse ist ein hochaktuelles Thema. Der hydrothermale Kar- bonisierungsprozess (HTC) ist dabei von Bedeutung, weil er HTC-Kohlen, die reich an organischem Kohlenstoff sind, aus Biomasse mit hohem Wassergehalt erzeugen kann. Diese haben das Potenzial, vielfältig eingesetzt werden zu können. In diesem Beitrag werden Untersuchungen für die Herstel- lung von kohlenstoffhaltigen Materialien aus vier Arten von Moorbio- masse (Schilf, Rohrkolben, Binsen und Seggen) mit- tels der Technik der hydrothermalen Karbonisierung vorge- stellt. Neben den Biomassevarianten wurde der Einfluss der Reaktionstemperatur auf den Karbonisierungsprozess durch Variation der Temperatur im Bereich von 180 bis 230 °C geprüft. Ein Vergleich zwischen den Eigenschaften der erzeugten Kohlenvarianten wurde durchgeführt. Dies wurde mittels Elementaranalyse und Stickstoffadsorption realisiert. Es wurde festgestellt, dass die HTC-Kohlen je nach Biomasse ungefähr 53 bis 60% des Kohlenstoffs der ursprünglichen Biomasse enthalten. Der Kohlenstoffanteil der HTC-Kohle steigt bei allen Varianten mit der Erhöhung der Reaktions- temperatur an. Die Atomverhältnisse H/C und O/C der Koh- len zeigten eine größere Ähnlichkeit zu Braunkohle als zum Ausgangsmaterial. Die Studie zeigt, dass sich die Moorbio- masse für die Herstellung von HTC-Kohle eignet.

Schlüsselworte: *Hydrothermale Karbonisierung, Moorbio- masse, HTC-Kohle, BET*

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1 Introduction

Some properties of biomass make it unsuitable for use as energy feedstock (van der Stelt et al., 2011), in carbon sequestration or improvement of soil fertility (Libra et al., 2011). However, not only does biomass have an interesting internal structure, it also has the advantage of being available in large quantities at low cost. Therefore, pre-treatment technologies can be used to improve the properties of biomass and convert it into useful and homogenous products, more efficient energy carriers or carbon storage deposits (Pala et al., 2014). To convert biomass into materials with a higher carbon content than the original biomass different biological or thermo-chemical processes can be used (Libra et al., 2011). There are two thermo-chemical processes at low temperatures which can improve the properties of biomass: hydrothermal carbonization (HTC) and torrefaction. (Pala et al., 2014). The main difference between these two processes is the amount of water present in the biomass.

Torrefaction is restricted to biomass with low water content because of the high energy needed to dry the feedstock prior to reaction (Libra et al., 2011). Torrefaction, also called mild pyrolysis, is typically performed in an inert gas environment at temperatures ranging from 200 to 350 °C using reaction times which vary between 30 minutes and several hours (Prins et al., 2006a; 2006b).

In contrast, HTC can be used with wet biomass, which is then converted into relatively high yields of carbonaceous solids without the need for an energy-intensive drying before or during the process (Glasner et al., 2011). During HTC, the solid material is surrounded by water, which is heated up to more than 180 °C (Funke and Ziegler, 2010; Heilmann et al., 2010; Mumme et al., 2011; Schneider et al., 2011). It is considered that, under HTC conditions, water splitting plays an important role in catalyzing the reaction (Peterson et al., 2008). This means that the biomass components are less stable. Cellulose decomposes over approximately 220 °C, hemicelluloses between 180 and 200 °C, and most of the lignins between 180 and 220 °C (Bobleter, 1994; Libra et al., 2011). The reaction mechanism comprises a dehydration of the carbohydrate and polymerization of the dehydration products (e.g. 5-Hydroxymethylfurfural) to produce carbon particles with polar functional groups (Kroto et al., 1985; Schüth, 2003).

HTC-chars are highly valued for many production processes. HTC is seen as a promising technology for CO₂-sequestration. HTC-char has also potential applications such as carbon fixation, water purification and energy storage (Heilmann et al., 2010; Hu et al., 2010; Rillig et al., 2010; Titirici et al., 2007).

Biomass from wetlands is generally of little use, but has great potential as a renewable energy source. Besides its use for feed and direct combustion, it can also be used as a raw material for industrial biochemistry (Wichtmann et al., 2010).

There are very few practical uses for wetland biomass, other than in HTC, which makes it of particular importance for this process. To date, there have been no other comparable investigations into wetland biomass use for HTC.

The main objective of this work is to investigate the applicability of wetland biomass for producing biochar by hydrothermal carbonization. We focus on two principal questions: Is it possible to convert this biomass into a higher value solid product such as HTC-char? How do the type of biomass and the reaction temperature affect the potential products and their properties? To examine these questions, four types of wetland biomass were considered. Results and observations obtained from product characterization will be detailed later to measure and assess the possible product applications. A key feature of this study is not only the hydrothermal treatment of wetland biomass in itself, but also the production of bio chars, which has potential value for real application on a larger scale as they are effective for pollutant sequestration.

2 Materials and methods

2.1 Materials

The wetland biomasses included in this investigation were reed, typha, juncus and carex. They were harvested from wetlands in Mecklenburg-West Pomerania, near Triebsees, in autumn 2011. The raw materials were cut, dried, milled and sieved under 4 mm size, with a water content of about 6%: their chemical composition was analyzed and is detailed later. All the materials were stored in plastic bags at room temperature until being used in the experiments.

2.2 HTC-reactor

The tests with the wetland biomasses were carried out in a stainless steel autoclave (Figure 1), which has an inner volume of 600 ml, and is hermetically sealed.

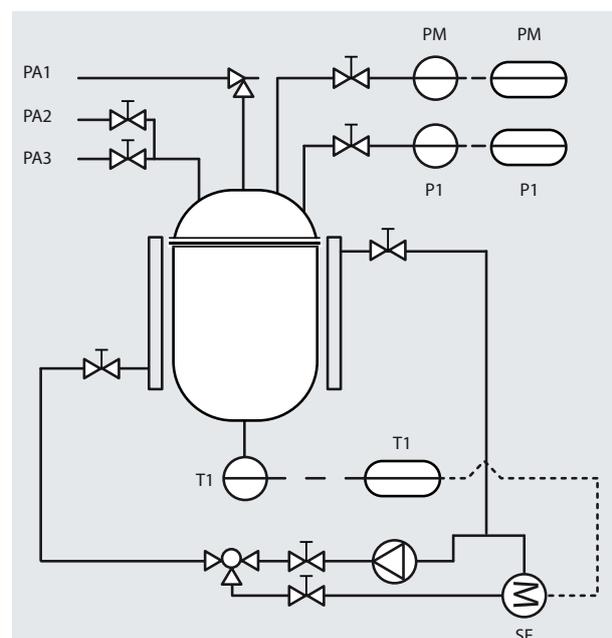


Figure 1
Schematic diagram for HTC-process

The cover is equipped with a pressure gauge (PM), a pressure sensor (P1) and a pressure relief valve (PA1), as well as gas inlet (PA2) and gas outlet (PA3). The Julabo heater (SE) is used as a heating circuit to provide the required heat in the process. The vessel has a double jacket through which hot oil, acting as heating medium, is circulated. The temperature of the medium is detected by a temperature sensor (T1) installed in the reactor vessel.

2.3 Experimental procedure

The reaction temperatures have an influence on the properties and composition of HTC-char. The series of HTC experiments as shown in Table 1 were conducted to determine the effect of the HTC-process parameters on the properties of the HTC-char. The different HTC-chars are designated as follows R_n , T_n , J_n and Ca_n ($n = 1, 2, 3, \dots$) where $n = 1$ indicates the influence of 180 °C, $n = 2$ indicates 200 °C, etc.. The study was carried out as indicated in Table 1.

Table 1

Process parameters for the different HTC-experiments

Biomass	Biomass amount g	Reaction temperature °C				Reaction time h
		180	200	220	230	
Reed						
Typha	30	180	200	220	230	15
Juncus						
Carex						

In each experiment the desired amount of biomass was dispersed in water with the acid catalysts, since the presence of catalysts effectively accelerates the hydrothermal carbonization. The volume of water (500 ml) and the amount of acid catalyst (here 0.5 g citric acid) were constant in all experiments.

The mixture was stirred for two hours before starting the experiment, then transferred to the reactor and sealed. It was then heated to the desired reaction temperature and left at this temperature for the designated reaction time as shown in Table 1. After this time the reactor was cooled progressively. At the end of the test a mixture of solids, liquids and gas remained in the reactor: The gas was vented and the mixture was collected.

The solid product was separated by vacuum filtration using a Buchner funnel with Whatman filter paper. The wet solid product was washed with bi-distilled water to remove the soluble intermediates deposited on the HTC-char, and then dried in an oven at 110 °C for six hours.

2.4 HTC conditions

The reactor pressure is autogenous and temperature-dependent; it was higher than the vapour pressure of water due to the formation of gaseous products during the reaction.

Compared with the heating curve using only water, the reactor pressure did not significantly exceed the steam saturation pressure before the temperature reached 210 °C, indicating the production of only small amounts of gaseous products during the preheating period. Hoekman et al. (2011) noted the same behaviour at temperatures above 200 °C. After cooling down the reactor, there was only a slight overpressure inside the vessel, suggesting that only minimal amounts of gas were generated during the HTC-process. The same observation was reported by Sevilla et al. (2011).

The internal reaction temperature and the corresponding pressure were measured and recorded during the entire test period at regular intervals of 10 minutes as shown in Figure 2.

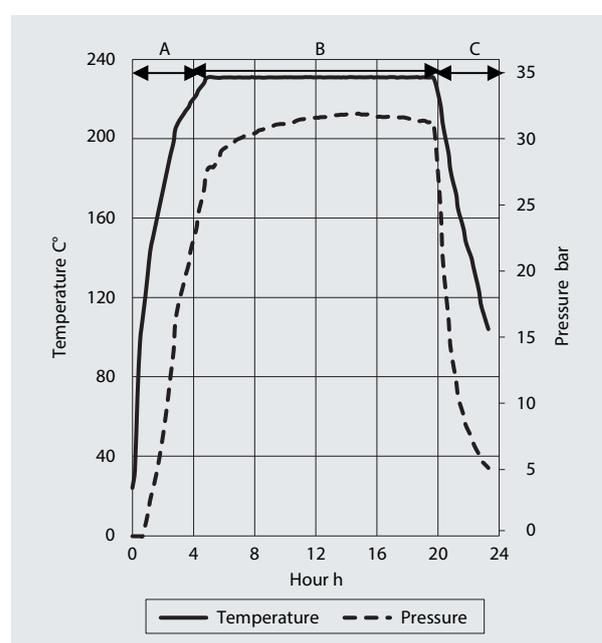


Figure 2

Temperature and pressure curves during the test period of HTC-process at 230 °C.

Figure 2 shows the approximate times for each reaction phase, the reaction time was defined as the time at the reaction temperature „B“ without heating „A“ and cooling time „C“.

2.5 Biomass and HTC-char characterization methods

The characteristics of the HTC-char were investigated with the objectives of qualitatively evaluating the carbonization process and identifying the changes in the solid material during the HTC-process, and determining the effects of the reaction severity (increasing the reaction temperature) on the properties of the HTC-char.

The specific surface area and the pore volume of the raw material and HTC-char samples were estimated using the standard Brunauer–Emmett–Teller (BET) method based on the principles of physical adsorption and desorption of nitrogen, where Accelerated Surface Area and Porosimetry analyzers

(ASAP 2010) were used for this purpose. The elemental analysis for carbon, hydrogen and nitrogen was performed using a microanalyzer (TruSpec CHNS Micro Company Leco).

The oxygen proportion was calculated from the difference of loss on ignition and the sum of organic carbon, hydrogen and nitrogen proportions (Jamari and Howse, 2012; Ramke and Blöhse, 2010). Ash content was measured according to ASTM D3172 method to determine the amount of non-combustible solid remaining after the combustion process.

H/C and O/C atomic ratios were computed for the raw material and the resulting HTC-char and analyzed using the carbonization diagram (van Krevelen, 1950).

The yield and carbon recovered were calculated according to equations 1 and 2 (Aydincak et al., 2012; Guo et al., 2008).

$$\text{Yield (\%)} = \frac{\text{mass of dried treated biomass}}{\text{mass of dried biomass}} \times 100 \quad (1)$$

$$\text{C-recovered (\%)} = \frac{\text{g biomass} \times \text{yield} \times (\text{treated biomass carbon \%})}{\text{g biomass} \times (\text{carbon content \%})} \quad (2)$$

3 Results and discussion

Table 2 lists the yields and the proportions of carbon, hydrogen, oxygen and nitrogen of the raw materials and of the HTC-chars. The yield of HTC-char increases as the temperature decreases.

By decreasing the reaction temperature from 230 to 180 °C there were increments in the range of 44.5 to 52%. These results are consistent with previous studies using other kinds of biomass (Hoekman et al., 2011; Yan et al., 2010).

As shown in Table 2, the highest char yields were formed from HTC of reed, while the lowest was associated with the carbonization of carex. This suggests that the yield of HTC-char also varies according to biomass type. Similar results have previously been obtained (Aydincak et al., 2012; Xiao et al., 2012). The influence of temperature was noteworthy for a second reason: the higher the temperature, the richer the carbon proportion in the HTC-chars. The HTC-chars produced at 230 °C show an increase in the carbon proportion of the solid residue of up to 52 to 66% compared with the carbon proportion in the untreated raw materials.

The HTC-process involves dehydration and decarboxylation reactions, resulting in the loss of some hydrogen and oxygen. The proportion of hydrogen lost varied only slightly with reaction severity. At the same time reductions in the oxygen proportion for the HTC-chars compared with the raw materials were observed, which means that the elemental composition (C, O, and H) of the solid materials changed markedly as the result of HTC (Dinjus et al., 2011; Xiao et al., 2012). The composition of the HTC-char is influenced by the removal of water and carbon dioxide during the HTC-process (Bergius, 1913; Funke and Ziegler, 2010; Libra et al., 2011). These variations became greater as the reaction temperature increased, which is consistent with a carbonization process (Sevilla and Fuertes, 2009b).

Table 2
Characterizations of the raw material and the HTC-chars produced

Parameter	Materials					
	Raw material	Produced carboneous product				
		Reaction temperature [°C]				
		180	200	220	230	
	reed	R ₁	R ₂	R ₃	R ₄	
Yield	%	-	58.30	51.50	41.93	40.30
C	%	43.82	52.32	56.97	63.79	66.71
H	%	5.82	4.22	4.24	4.68	4.55
N	%	0.54	0.95	1.37	1.61	1.53
O ^[a]	%	45.67	39.24	34.21	27.22	23.41
O/C ^[b]	-	0.78	0.56	0.45	0.31	0.26
H/C ^[b]	-	1.59	0.97	0.89	0.88	0.82
	typha	T ₁	T ₂	T ₃	T ₄	
Yield	%	-	53.40	47.40	37.80	35.10
C	%	42.74	52.69	56.73	64.08	67.30
H	%	5.58	5.45	5.03	5.29	5.09
N	%	0.78	0.46	0.72	0.88	0.78
O ^[a]	%	47.08	38.48	34.58	26.08	23.15
O/C ^[b]	-	0.82	0.55	0.46	0.31	0.29
H/C ^[b]	-	1.57	1.24	1.06	0.99	0.91
	juncus	J ₁	J ₂	J ₃	J ₄	
Yield	%	-	50.00	44.60	36.10	34.00
C	%	43.27	54.35	60.87	68.35	70.95
H	%	5.85	5.05	5.59	5.35	5.25
N	%	1.41	1.73	1.95	2.93	2.92
O ^[a]	%	45.23	37.72	30.31	21.86	19.54
O/C ^[b]	-	0.78	0.52	0.37	0.24	0.21
H/C ^[b]	-	1.62	1.13	1.10	0.94	0.89
	carex	Ca ₁	Ca ₂	Ca ₃	Ca ₄	
Yield	%	-	48.17	42.67	35.83	32.03
C	%	42.24	51.57	57.44	66.94	70.28
H	%	5.86	5.09	5.44	5.49	5.57
N	%	2.17	1.60	2.54	3.93	3.76
O ^[a]	%	44.09	40.89	33.67	22.22	19.25
O/C ^[b]	-	0.78	0.59	0.44	0.25	0.21
H/C ^[b]	-	1.66	1.18	1.14	0.99	0.95

^[a] Content by difference

^[b] Atomic ratio

The H/C and O/C atomic ratios for the raw materials and the resulting HTC-chars are shown in the van Krevelen diagram (Figure 3). This diagram offers a clearer view on the chemical transformation of the carbon-rich material whilst giving information about the possible reaction routes. The dotted lines indicate the dehydration process and the dashed lines represent the decarboxylation processes (Aydincak et al., 2012; Berge et al., 2011). The atomic ratios for bituminous coal and lignite coals are included for comparative purposes

(Berge et al., 2011). The starting raw materials are shown in the upper right corner of the diagram.

The HTC-chars are characterized by an increased carbon proportion expressed as lower O/C and H/C atomic ratios when compared with the raw materials. These ratios decreased as reaction temperature increased, as can be seen in Table 2. In experiment conditions of 230°C for the carbonization of raw materials, a reduction of about 42 to 45% of H/C atomic ratios and about 66 to 73% of O/C atomic ratios were calculated. In general, both the H/C and O/C atomic ratios decreased when the reaction temperature was raised. As shown in Figure 3, the conversion of wetland biomass is mainly dominated by the dehydration process (lower H/C). However, there is a deviation from the diagonal line; this suggests that a side reaction (decarboxylation) occurs during HTC because a complete dehydration reaction removes water molecules from the samples. This compares to observations for the hydrothermal carbonization of glucose, cellulose and starch (Sevilla and Fuertes, 2009a; 2009b). Ruyter (1982) reported that O/C atomic ratios of 0.2 to 0.3 are indicative of low-grade coals. Figure 3 illustrates that with increased reaction severity, the HTC-chars produced become increasingly similar to lignite and bituminous coal.

The pore volume and surface area of the raw materials and the HTC-chars are listed in Table 3. The specific surface areas of HTC-chars were 5 to 10 times greater than the raw materials.

Additionally, there was 5 to 26 fold increase in the measured pore volume after HTC indicating that the HTC-chars have higher specific surface areas, from which we can conclude that there was a significant increase in the quantity of nitrogen gas adsorbed.

Table 3

Surface area, pore volume and C-recovered of the raw materials and their HTC-chars

	BET surface area m ² /g	Pore volume cm ³ /g	C-recovered %
Reed	2.31	0.0048	
R ₄	24.66	0.1247	61.40
Typha	2.29	0.0041	
T ₄	18.69	0.0862	55.20
Juncus	1.57	0.0034	
J ₄	8.61	0.0191	55.57
Carex	2.26	0.0037	
Ca ₄	11.58	0.0541	53.30

The highest carbon recovered (in %) was found in the HTC of reed. It can be seen that the recovered carbon in the

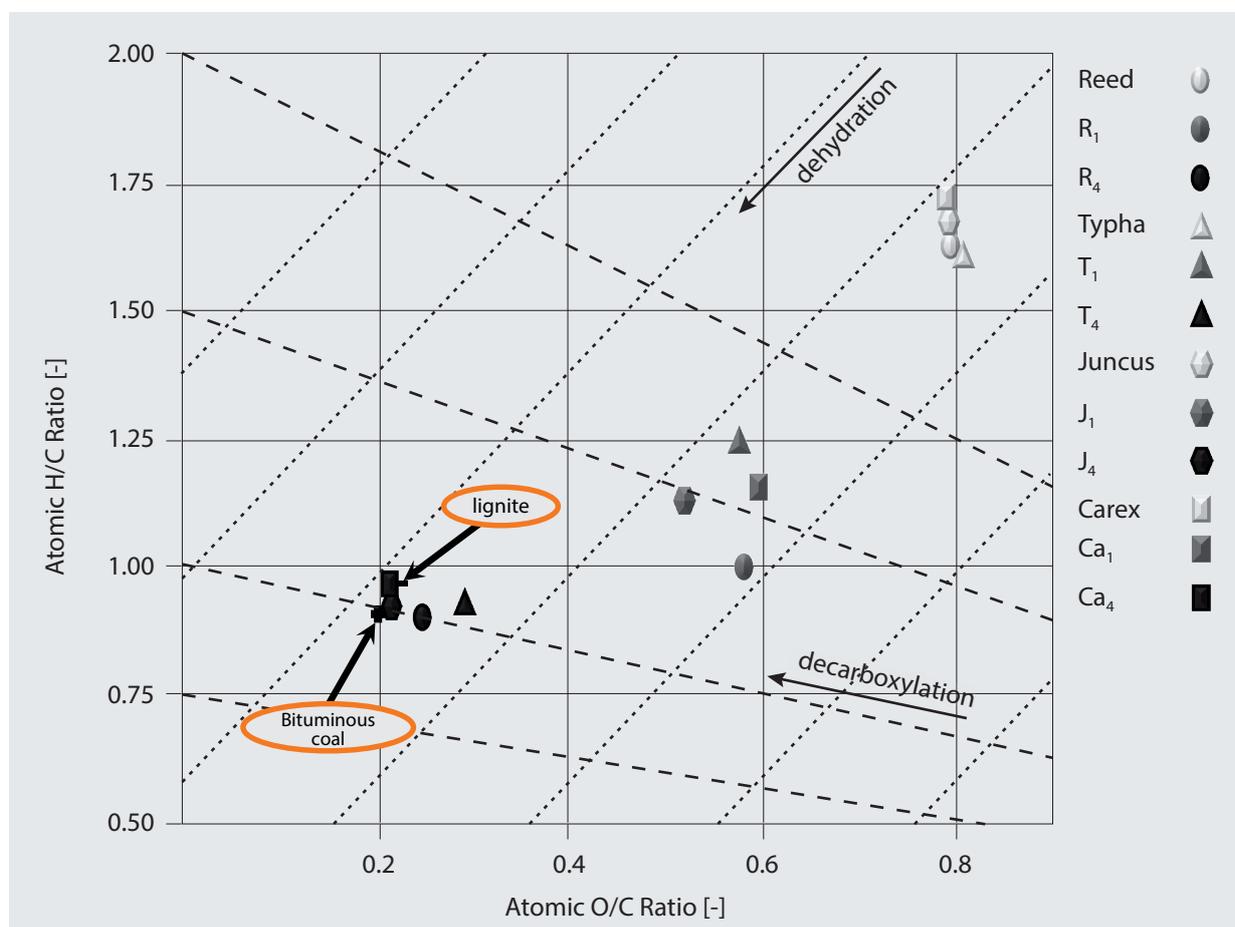


Figure 3: H/C and O/C atomic ratios of the feedstocks and chars resulting from HTC

HTC-chars (Table 3) ranged from 53.30% to 61.40% indicating that a large portion of the carbon in the biomass was stored. A similar observation was reported by Xiao et al. (2012).

4 Conclusion

The underlying motivation for using HTC is a move towards using more sustainable technologies to produce a variety of high-value carbonaceous material from widespread but little used biomass. In this study, a solid carbonaceous residue (HTC-char) was produced by the hydrothermal carbonization of wetland biomass under mild conditions (in an aqueous medium at >180°C). The HTC-chars obtained were carbon rich and chemically similar to lignite or bituminous coal, depending on the reaction temperature. The HTC-process decomposed the raw materials and produced products with greater carbon content. The HTC-processes showed, in the experiment conditions specified, that temperature is a significant parameter affecting the yield and characteristics of the produced HTC-chars. The coal-like solid particles produced can be used as fuels. Alternatively they are suitable for adsorption purposes because of their structure. The carbon proportion of the HTC-char increased with the increment of the reaction temperature, while the amount of oxygen elements decreased steadily indicating the elimination of this element during the HTC-process; the hydrogen proportion varied only slightly with reaction severity.

A feasibility analysis of char use as adsorbents for pollutant removal in order to develop an additional value for these products, and the effect of HTC-process parameters on the pollutant removal performance of the HTC-chars will be presented in another study. The results of this work both in terms of hydrochar yield and hydrochar properties showed not only an corroboration of the results of other publications, but they also showed the applicability of the wetland biomass for producing hydrochar, and that HTC represents an effective way to obtain a carbonaceous material with relatively robust characteristics. The results presented here firmly support further investigation of biomass to exploit its potential.

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