

Hydrothermal Carbonization of Corncob and Characterization of the Obtained Hydrochar

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The hydrothermal carbonization (HTC) is a thermochemical process of biomass conversion that uses water as the reaction medium, which does not have any toxicity and categorizes the method as an environmentally friendly process. The solid product obtained by this process is commonly called hydrochar, and has many applications: it can be used for energy purposes, for soil amendment processes, also by producing activated carbon adsorbents, catalysts, and nanostructured materials. In this investigation was used as lignocellulosic biomass milled corncob, which was sieved before the process. For the experimentation were used three-quarter parts of the capacity of a Parr reactor of 25 ml, adding a volumetric relation of biomass:distilled water of 1:3. The hydrothermal carbonization was applied in a temperature range between 180 and 350 °C under subcritical water conditions and during the same period: four hours. These resulting hydrochars, were characterized by Fourier Transform Infrared Spectroscopy (FT-IR), adsorption analysis, thermogravimetric analysis (TGA) and scanning electron microscopy. The results of this characterization showed that after the hydrothermal carbonization, the functional groups from fresh biomass were preserved, as evidenced in the IR analysis. Appreciable changes in carbon densification, which increases with increasing HTC temperature, improved the potential properties as a solid fuel of this material; the Higher Heating Values obtained are comparable to the values reported for fossil fuels such as carbon which indicates that a replacement thereof can be performed by hydrochar in industrial processes. In addition, the adsorption capacity was observed in samples hydrotreated at low temperature, which generates adsorptive properties and makes it able to be used in processes for removal of dyes, metals and water. The results presented indicate that treatment of hydrothermal carbonization is a low-cost waste management of lignocellulosic biomass with economic feasibility, which generates a versatile solid product with diverse applications, making HTC an excellent way to take advantage of this kind of renewable resources.

1. Introduction

The rapid increase in volume, types of biomass and its waste, as a result of the rapid increase in world population and improved living standards, is becoming an increasing problem as waste biomass emits methane, and open burning generates CO₂ and other local pollutants. Hence, improper management of waste biomass is contributing towards climate change, water and soil contamination, and local air pollution. Furthermore, this waste is of high value with respect to material and energy recovery.

The biomass and its waste composition are essentially cellulose, hemicellulose, and lignin, along with other components in small proportion. The percentage of these mentioned components and other properties are crucial to the choice of conversion or transformation process biomass. In general, the main properties of the biomass to be considered for the choice of treatment to be applied are as McKendry (2002a) proposes: (i) moisture content, (ii) calorific power, (iii) proportion of fixed carbon and volatile, (iv) ash content, (v) content of alkali metals, (vi) proportion of cellulose / lignin. Although generally the determining factor is the type of product to be obtained, followed by the type and availability of biomass or its waste (McKendry, 2002b). Among the thermochemical processes of biomass conversion, hydrothermal carbonization (HTC) is one of the promising for producing hydrochar and value-added chemicals.

The hydrochar produced by HTC may have extensive applications. The hydrochar performance, in particular, areas linked directly to the source of biomass and applied operating conditions. It has been investigated for use as solid fuel comparing with lignite, due to significant densification of organic matter (Oliveira et al, 2013; Parshetti et al, 2013.). Another good performance reported is it's used to remove environmental contaminants in water (Mohan et al., 2014). Moreover, the possibilities for use in CO₂ sequestration have also been studied (Ponce, 2012; Funke and Ziegler, 2010). Finally, among the most promising applications, two different studies have suggested the use of this hydrochar as electrode materials for super capacitors (Falco et al., 2013).

For this study, the biomass selected is corncob; for which the approximate composition is 45 % cellulose, 35 % hemicellulose and 15 % lignin (Harmsen and Huijgen, 2010). The main goal of this work was to study the hydrochar production from corn cob obtained by HTC.

2. Experimental Methodology

2.1 Materials

The biomass used for this study was corncob, an agro-industrial waste which was obtained locally. The corn cob was dried at 80 °C for 18 h and was then milled and sieved to a particle size between 1 - 2 mm. The estimated actual density is 0.88 g·mL⁻¹, with a moisture content of 6 % (Caldera, 2014). Each test was performed with a ratio biomass: water of 1:3.

2.2 Experimental Procedure

The hydrothermal processes were carried out using 4.4 g feedstock dispersed in 14.0 mL of distilled water at room temperature. The mixture was then transferred to a 25 mL Parr pressure reactor (Parr Instrument Company, Moline, Illinois) which was heated at a rate of 10 °C/min to the last reaction temperature, which depending on the test was: 180, 200, 250 or 350 °C. The pressure recorded between 180 and 350 °C were between 550 and 1150 psi. The reactor was maintained at this temperature for 4 h. The reaction mixture, consisting of a liquid solution and solid phase (hydrochar) was collected in a glass beaker for separation by filtration and the solid was washed thoroughly with distilled water and then dried in an oven at 80 °C overnight. The hydrochar samples obtained were denoted as HTC-180, HTC-200, HTC-250 and HTC-350 according to the corresponding operation temperature.

2.3 Characterization of hydrochar materials

The characterization of the untreated and HTC treated biomass were determined using thermogravimetric analysis (TGA), it was performed by measuring the change of hydrochar weight by increasing temperature from 25 °C to 900 °C in a controlled atmosphere using a V20.10 TGA Q500 equipment (Universal V4.7A TA Instruments). As result of this process, the moisture, volatile and ash content for fresh biomass and hydrochar was obtained. From these values, the fixed carbon (FC, w%) content is determined to estimate the calorific value GCV (MJ kg⁻¹) of the biomass samples, employing Eq. (1). This value is used for comparison with other coals and estimating gross calorific value (GCV) from the Eq. (1), which was developed by Dermibas (1997), this correlation was experimentally verified by Ponce (2012) who reported an error from 4 % to 6%.

$$GCV [MJ/kg] = 0.196 \cdot FC [MJ/kg] + 14.119 \quad (\text{Eq. 1})$$

For the morphological analysis of the raw biomass as well as the hydrotreated samples use the SEM, all samples were prepared by suspension, requiring you to be subjected to coating with pure gold in an ion cover Brand SAIA, model Sputter SCD-050-12 mA 60 s to generate a layer of 10 Å thick, in order to make the conductive sample. The images obtained from the samples were taken in a scanning electron microscope JEOL brand; model JSM-6380, under program control microscope control.

The hydrochar samples were characterized by Fourier Transform Infrared Spectroscopy (FTIR) using a Thermo Scientific iS5 spectrometer with Attenuated Total Reflectance (ATR) iD5 probe (ZnSe). The total number of scans was 50 with spectral resolution of 4 cm⁻¹. Samples were analyzed in triplicate, absorbance spectra averaged and baseline corrected using Omnic Spectra software (ThermoScientific).

For adsorption it was used methylene blue at a concentration of 72 ppm and the absorbance of the solution was measured using a spectrophotometer Genesys 10S (ThermoScientific) before and after contact with the hydrochar for 24 hours. Previously a calibration curve of 6 points using methylene blue solutions of concentrations between 4.8 ppm and 96 ppm was performed.

3. Results and Discussion

At the end of each hydrothermal carbonization treatment, for all cases, after cooling the reactor, was recorded an increased pressure of about 100 psi. This indicates that there is a HTC product in gas phase. These gases can be associated with CO₂, which is reported as a major product of the reaction mechanism HTC (Funke and Ziegler, 2010).

From thermogravimetric analysis curves obtained for biomass and hydrochar, there were calculated contents of moisture, volatile and ash. Through Eq(1), shown in experimental methodology, the gross calorific potential (GCP) was calculated and the results obtained are shown in the Table 1. Moisture decreases slightly with increasing treatment temperature of the sample, except for HTC-350, coinciding with (Parshetti et al., 2013). Volatile biomass emerges from hydrochar at greater amount as the temperature is increased, as is reported in (Parshetti et al., 2013). Dehydration and decarboxylation reactions in the process are checked with the result. The FC is greater at higher temperature tests and also the GCV because it is a directly proportional relationship (Eq. 1). GCV obtained are comparable with that reported at 220 °C by (Olivera et al., 2013). Furthermore, higher density of energy is obtained to samples obtained at higher at higher temperature. The loss of volatile generates a condensation in the carbonaceous structure and therefore the GCP is increased because the decomposition (loss of volatiles) is decreased and the combustion favored.

Table 1: Thermogravimetric analysis of biomass and hydrochar product.

Sample	Moisture (W %)	Volatiles (W %)	Ash (W %)	FC (W %)	GCP (MJ/kg)	Density of Energy
Carbon ^a	15.13	34.84	9.33	40.73	22.10	-
Biomass	6.48	60.14	13.54	19.54	17.95	-
HTC-180	0.52	74.15	1.37	23.96	18.82	1.05
HTC-200	0.52	72.39	1.30	25.79	19.17	1.07
HTC-250	0.50	65.69	1.26	32.60	20.51	1.14
HTC-350	0.61	52.20	1.15	46.04	23.14	1.29

^a Reference values for low-grade carbon, Parshetti et al. 2013.

Gravimetric analysis curves shows in Figure 1 that biomass initiates combustion at 201.05 °C and ends at 302.99 °C in four stages, having the highest peak of the curve at 302.99 °C, which is located in the range of carbonization temperatures for hemicellulose and cellulose (Parshetti et al., 2013), however, it can be appreciate the small curve corresponding to lignin, above 400 °C, probably due to low percentage of lignin from the biomass (Harmsen and Huijgen, 2010). While for HTC-180 and HTC-200 tests the hydrochar combusted in one stage at 316.05 °C and 321.02 °C respectively. HTC-350 for two temperatures of combustion 337.80 and 399.04 °C is observed, however the increase in combustion temperature is negligible considering its final use as an energy source.

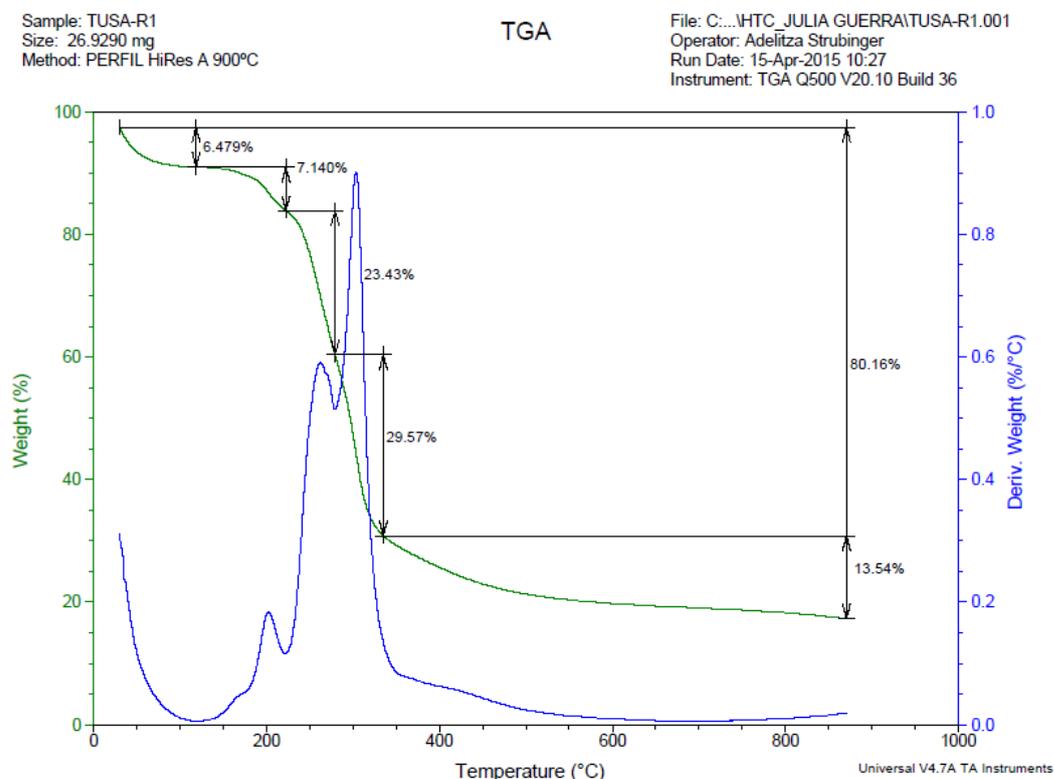


Figure 1: Thermogram for TGA of HTC-200.

The micrographs obtained for the biomass before and after the treatment: HTC-180, HTC-250 and HTC-350 products are shown in Figure 1 (a, b, c and d). The SEM micrographs in Figure 1 show that the morphological transformations of corncob after hydrothermal treatment are very similar to the ones of cellulose. The morphology observed in the particles show that these materials are made of globular body of different sizes, which have been attributed to glucose derivatives belonging to the hemicellulose. As hydrotreating temperature increases, a reduction in the sizes of the cellulose particles is evidenced, product of nucleation and polymerization reactions, which lead to a rupture of the fibrous structure at various points and formation of micrometric cellulose fragments. It is evident that as hydrotreating temperature increases, the size of the cellulose particles in the sample reduces its size, becoming very small for HTC-350 °C. The results shown here are in agreement with those reported by (Titirici et al, 2013), they study the morphological characterization of materials charred hydrothermally, concluding that this leads to the formation of small particles of cellulose, it is clearly shown that part of the biomass, natural macrostructure, persists even after the spherical particles start forming. These particles are supported by the plant structure of hydrotreating biomass.

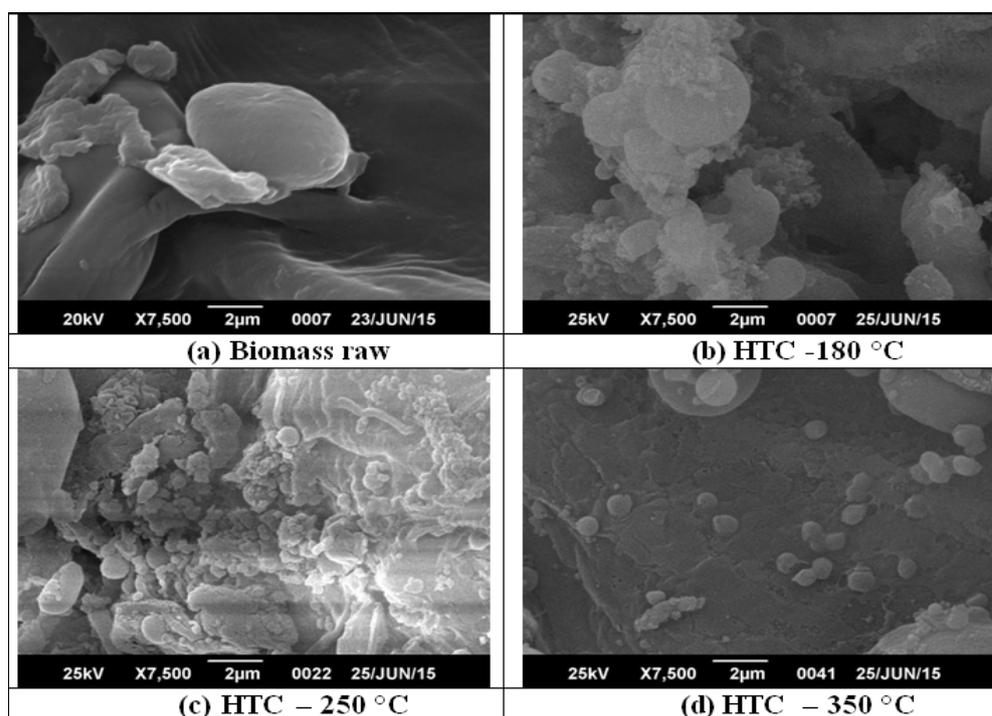


Figure 2: Micrographs obtained for biomass(a) and HTC products at: 180 °C (b), 250 °C (c) and 350 °C (d).

The infrared spectra of the raw biomass and hydrochar samples revealed their complex chemical bond structure consisting of mixture of mineral and organic matter Figure 3 shows the spectra collected for all samples and normalization condences to the absorption band from 1030 to 1040 cm^{-1} .

The primary differences in the FTIR spectra for the raw biomass and the hydrochar samples are encountered in the increase of assigned signals of oxygen bonds (Figure 3). It can be observed that peaks at ~ 3300 , 1700, 1600, 1220, and 1140 cm^{-1} gradually increase its signal, with the increase of the hydrotreating temperature in relation to the biomass. The broad band in the region of 3600–3200 cm^{-1} is attributed to the O-H (e.g., water, alcohol, and phenol) and N-H (amines) stretching vibrations. Aliphatic bands, C-H (CH_3 and CH_2) stretching vibrations between 3000 and 2800 cm^{-1} , were presented in both biomass and hydrochar samples.

The peak at ~ 1700 cm^{-1} can be attributed to the stretching of C=O bonds, which are present in ketones, aldehydes, quinone, esters, and carboxylic acid functional groups. The strip t ~ 1600 -1630 cm^{-1} , particularly to the HTC 250°C sample, could be attributed to Amide I (C=O stretching). While the one at ~ 1515 cm^{-1} was attributed to the C-N stretching and N-H in-plane bending absorption due to Amide II of secondary amide in protein, respectively, which was not present in the spectra of the biomass (Koch et al., 1998; Pradhan et al., 1999; Fuertes et al., 2010; and Haberhauer et al., 1998).

A band at $\sim 1400\text{ cm}^{-1}$ corresponding to C–H bending was identified in all hydrochar (Smith et al., 1995) and the bands between 1200 cm^{-1} and 1110 cm^{-1} are attributed to the stretching of C–O bonds (carboxyl, ester, and ether groups) and OH deformations of carboxyl-C (Fonts, et al., 2009).

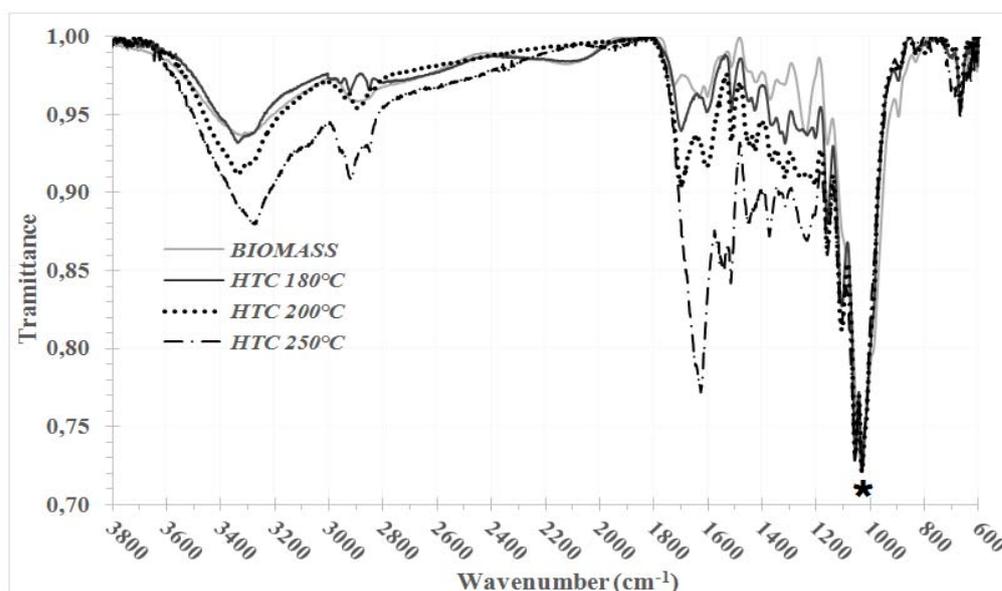


Figure 3: FTIR spectrum of raw biomass and hydrochar samples. For better visualization, the spectres were normalized to $1030\text{-}1040\text{ cm}^{-1}$.

Adsorption with methylene blue was conducted to biomass and hydrochar obtained results are shown in Figure 4, indicating the amount of adsorbed methylene blue per gram of solid evaluated. The decrease was observed in the adsorption of methylene blue in correlation with increasing temperature hydrotreating remain moderate the decline of adsorption at low temperature and very low adsorption for samples treated at higher temperatures compared to the original biomass. While this test is used to characterize pore sizes of the carbonaceous materials, also may give us information about the surface interactions may be occurring. As the molecule of Methylene Blue an intermediate polarity, low adsorption observed could be associated with superficial repulsion by increasing very polar functional groups hydrochar synthesized, which is in clear concordance with the observed functional groups through analysis of FTIR.

Specific adsorption of Blue Methylene

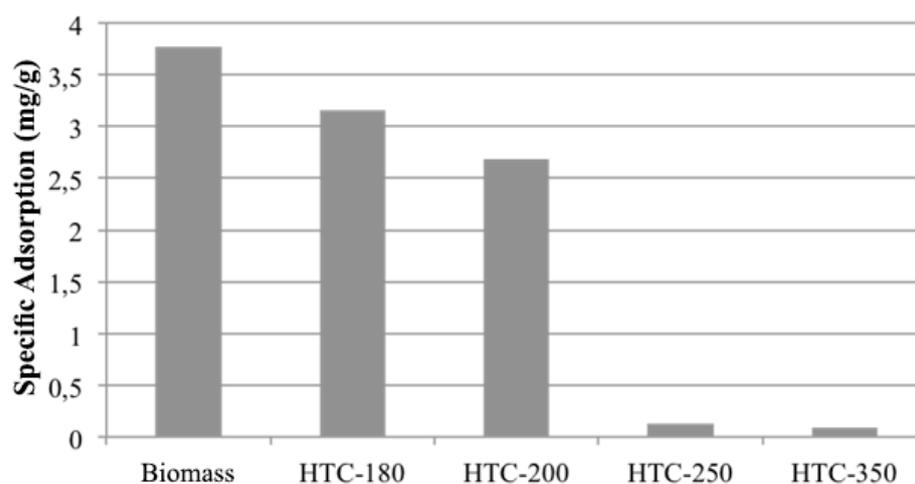


Figure 4: Results of the adsorption test on Methylene Blue.

4. Conclusions

Corn cob, under conditions of HTC, produced the formation of non-condensable gases which comes from the decomposition of these hemicelluloses in the original biomass. The thermochemical treatment applied (HTC) achieves an effect of carbonization of biomass. It was observed that the densification of the energy increases with temperature, and is in line with the increased energy potential, making significant use hydrochar obtained as solid fuel. Of scanning electron micrographs the formation of small particles of cellulose are seen, from the nucleation and polymerization reactions, where the particle sizes are reduced as the temperature increases. After HTC treatment, characterization by FTIR technique shows that biochar or hydrochar obtained by HTC contains more oxygen functional group of the raw biomass and the original functional groups of biomass are retained, this effect is intensified significantly at temperatures above 200 °C. The adsorption capacity of methylene blue as in the hydrochar obtained could not be conclusive for this material, due to the presence of oxygenated functional groups which are not characteristic of the carbonaceous materials discussed in this test. However, to indicate that the presence of these groups reduces the hydrophobicity observed in the original biomass, what appears to be a competitive advantage of the carbon obtained from HTC.

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