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ANALYSIS OF DURABILITY AND DIMENSIONAL STABILITY OF HYDROTHERMAL CARBONIZED WOODEN PELLETS

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ABSTRACT

Hydrothermal carbonization (HTC) is a chemical pretreatment of wood waste for convert it in biochar by the application of high temperatures and pressures in a reaction time that do not exceed 10 hours. One of the main applications of the HTC biochar is as pellets. In this research durability against fungal decay and dimensional stability associated with relative humidity changes of HTC pellets were analyzed and evaluated. A comparison of these properties between HTC pellets and wooden EN+ pellets has been carried out.

HTC pellets are significantly more durable against fungal attack, more dimensionally stable against relative humidity changes and denser than wood pellets, which confers better properties for logistics processes like storage and transport.

KEYWORDS: Wood; hydrothermal carbonization; pellets; durability; dimensional stability.

INTRODUCTION

Hydrothermal carbonization (HTC) is a chemical process for converting different types of wet wood or wood waste in a biochar with similar characteristics to coal. This process is carried out by the application of temperatures higher than 180°C, high pressures and a reaction time that do not exceed 6 to 8 hours. The process was described in the early 20th century by Bergius (1913), but recovers now more industrial interest due the importance acquired by biofuels produced with alternative biomass sources under wet conditions. Bergius (1913) carried out first experiments of HTC and also described the hydrothermal transformation of cellulose into coal-like materials (Titirici et al. 2007). The industrial application of this process was scaled-up at the Max-Planck-Institute of Colloids and Interfaces in Potsdam, Germany (Antonietti 2006).

HTC is based on a simple chemical process based on the splitting of water from carbohydrates (dehydration) in wood (Ramke et al. 2009), obtaining as products of an exothermic reaction, water and a coal, henceforth called HTC biochar (see Fig. 1).

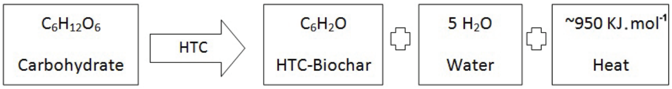


Fig. 1: HTC Chemical process (adapted from Ramke et al. 2009).

HTC process exhibits solid products with higher energy density, which are easily friable and more hydrophobic in comparison to the original biomass (Lyman et al. 2011).

The HTC process can change depending mainly on the wooden raw input material selected and chosen parameters of temperature, time or pressure. In general, for the same raw input material, relative carbon content increases and relative oxygen concentration decreases with increasing chemical reaction time and temperature. This increasing carbonization is reflected in particular by the increased heating value of the biochar. In addition, for the same process parameters of temperature, pressure and time, raw input material with high lignin content produces a biochar with higher carbon content and consequently higher heating value (Dinjus et al. 2011).

The main advantage of HTC is that it can convert wet input wooden material in solid biofuels at relatively high yields without the need for energy-intensive drying before or during the process. This opens up the field of the additional potential use of a variety of non-wood biomass sources: wet animal manures, human waste, sewage sludges, municipal solid waste, as well as aquaculture and algal residues (Libra et al. 2011). However, with lower moisture content in the raw input biomass, more amount of biochar is obtained from the same amount of biomass (Hitzl 2011).

Acharjee et al. (2011) described that HTC of lignocellulosic biomass makes the biochar more hydrophobic and it becomes even more hydrophobic with the increase of temperature at the same reaction time.

HTC biochar can be used for various applications in the bioenergy value chain, but also in agriculture and gardening as renewable peat. Nevertheless, in order to become a commercial technology, it is essential to identify applications, which offer technical or economic advantages over conventional biomass processes (Erlach et al. 2011). The main application for HTC biochar is as solid biofuel. Pelletization is an applicable technology for HTC biochar, without the addition of any binder. That facilitates its industrial use (Felix 2012). Moreover, pelletization makes pretreated pellets denser than raw wooden pellets because the friability and homogeneity increases with the temperature in the HTC process (Yan et al. 2009). The properties of biomass pellets depend on the pelletization conditions of temperature, pressure, moisture content, biomass type, binder and milling and extrusion machines. The role of moisture content in the pelletization process and products is a key production factor. Moisture can act as a binder and lubricant at the same time (Reza et al. 2012).

Some economical analysis conclude that when biodegradable waste is available at zero cost, the total production costs of HTC biochar pellets are similar to those of wooden pellets (Erlach et al. 2011).

Industrial production of pellets involves some logistic operations that occur since the pellet is produced in the factory to the moment when it is ready for combustion in the boiler or stove in the final destination. Transport, storage and handling of pellets have a key importance, both economically as well as in the final product quality.

Mechanical durability of pellets is directly influenced by transportation, storage and handling. It is also the main physical quality parameter considered by industry (Wilson 2010). It strongly depends on the amount of dust contained in the pellets bag or containers. If the pellet crumbles easily may be problems of dirt in the stove, reduced combustion efficiency and increased emissions (Pepiciello 2011). Abrasion index is a common test for pellet durability. According to Reza et al. (2012), HTC pellets have an abrasion index of 0.28 against 1.03 % for untreated wood pellets.

Another key aspect for the logistic processes of HTC pellets is its hydrophobic nature. Changing hydrothermal conditions and direct contact with water affects the mechanical durability of pellets. It is expected that HTC pellets should have a more hydrophobic behaviour as wooden pellets. Furthermore, the biodegradation of biomass depends heavily on its moisture content. This moisture content largely depends on the hydrothermal conditions in the surrounding atmosphere, but it also depends on the biomass composition (Acharjee et al. 2011). Moreover, the moisture content on the biomass used has a significant influence on energy efficiency of the process and also in the product quality.

Taking into account all described scientific knowledge, the objective of the research has been to investigate the durability against fungal decay and dimensional stability associated with relative humidity changes in the surrounding environment in order to evaluate advantages or disadvantages in the logistic processes of transport, storage and handling of HTC pellets compared to wood pellets.

MATERIAL AND METHODS

Test material

HTC pellets

The company INGELIA has supplied HTC pellets. This company has an industrial HTC plant of in Náquera (Valencia, Spain), which uses wood waste from agriculture and forestry.

The HTC process also includes a pretreating phase in order to achieve suitable conditions for the chemical reaction phase. The pretreating phase includes a milling step and a washing step. After the pretreating phase, the lignocellulosic biomass is stored in a hopper to be fed to the HTC reactor. The process begins with the mixture of the wet biomass with additional water and an acid mean for accelerating the chemical reaction (Hitzl 2011). This mixture is fed into a vertical reactor of continuous operation, once it has been preheated to a temperature of 180°C. Once this process temperature and a pressure of 13 bar are reached, the carbonization enters its monomerization and polymerization phases. The process continues with a step for releasing energy to the reaction medium due to the exothermic nature of the process itself. The total duration of the HTC process is about 10 hours. The product obtained is constituted by a liquid phase and solid particles of carbonized biomass. Next, the solid phase is separated from the liquid phase by a pressure system. Finally, a pelletizer machine densifies the biochar to produce the HTC pellets.

Wooden EN+ pellets

Wooden pellets of the brand EKOPellets were used for the comparative tests. The wooden pellets have EN+ A1 certification following EN 14961-2 (2011). The pellets were packaged in

15 kg plastic bags in order to protect them against moisture changes.

Methodology

Durability

To evaluate the durability of pellets against fungal decay, Bravery test (Bravery 1978) and EN 113 (2004) has been adapted. The fungi species used in the experiment are *Coniophora puteana* and *Rhodonia placenta*.

The pellets were selected measuring their length with caliper, being between 17-25 mm long.

24 selected pellets were oven-dried at 103°C for 24 h. Later, they were cooled down to room temperature in a desiccator during 30 minutes and weighed to determinate the initial dry mass with a precision balance 0.0000 g (m_0). After that, the samples were stored in a climate chamber at 20°C and 65 % HR during 14 days. To avoid fungal attack risk each pellet was covered with a mesh. The meshes were cut for the size of each pellet and weighted (m_m).

The culture medium was prepared with a 2.5 of agar and 4.0 % of malt extract. The mix was made in an Erlenmeyer flask of 1.000 ml and sterilized in the autoclave for 2 hours. After that, the Petri dishes were filled with the culture medium and were left to cool in sterilization conditions during one day.

A cork borer was used to mark the inocula of the fungi in the Petri dishes where the mycelium was growing. With the help of a spatula, the inocula were deposited in the center of the petri dishes with the culture medium and then were placed in the fungi chamber for 8 days (Fig. 2).

Two sample supports were introduced per each petri dish to avoid any direct contact of the samples with the nutrient medium. Then, two samples of the same kind of pellets were deposited per each petri dish. The petri dishes were closed, sealed and introduced in the culture fungi chamber for 12 weeks. The culture vessels were checked every week according EN 113 (2004).

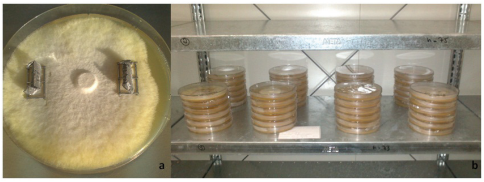


Fig. 2: a) Petri dish with Rhodonia placenta and two samples b) Petri dishes in culture room.

After the 12 weeks, the culture vessels were removed from the culture room. The samples were withdrawn from the petri dishes and cleaned with the help of a sponge and scalpel, maintaining the meshes to keep loose material. The samples were oven-dried at 103°C for 24 h. After that, the samples were cooled down to room temperature in a desiccator for 30 minutes and weighed again to determine the dry mass after test (m_2).

The formula to calculate the mass loss is:

$$Mc = (m_0 - (m_2 - m_m)/m_0) \times 100 \tag{1}$$

Dimensional stability

To evaluate how changes in relative humidity affect the dimensional stability of pellets, three parameters were considered: Moisture content, swelling and density.

To evaluate the pellet swelling, the standard EN 318 (2002) was taken as reference. To evaluate the moisture content, the methodology described in CEN/TS 14774 (2007) was used.

The pellets were oven-dried at 103°C for 24 h. Later, they were cooled down in a desiccator for 30 minutes and weighed (p_0). The diameter was measured in the two points marked with the caliper (D_{a0} and D_{b0}).

In order to change the moisture content, the pellets were introduced in a climatic chamber. First, the pellets were placed at 20°C and 40 % HR. After 24 h, the pellets were weighed (p_{40}) and the diameter was measured in the two marked points (D_{a40} and D_{b40}). This procedure was repeated two times at the same temperature but changing the HR to 60 and 80 % (p_{60}, p_{80}, D_{a60}, D_{b60}, D_{a80} and D_{b80}).

Finally, the pellets were immersed in water for two days to measure their mass and diameter in saturation. After immersing, it was observed that the EN+ pellets were completely broken up after 1 minute, being impossible to measure mass and diameter.

The formula to calculate the moisture content was:

$$h = ((p_n - p_0) / p_0) \times 100 \qquad (\%) \tag{2}$$

where: h - moisture content (%),
p_n - mass of pellets in a n % HR (g),
p_o - oven-dried mass of pellets (g).

The formula to calculate the swelling was:

$$\alpha_n = ((Dm_n - Dm_0) / Dm_0) \times 100 \tag{3}$$

where: α_n - swelling (%),
Dm_n - mean value of two diameters at different moistures (mm),
Dm_0 - mean value of two diameters in oven-dried conditions (mm).

To evaluate the density, the Archimedes´ principle was employed, following the Water Displacement Method described by Olesen (1971). To do this, a beaker was filled with 80 ml of distilled water and put in a precision scale. From a bracket situated above the scale, a thread was placed with a wire at his end, so that the wire was immersed in the water. The mass of water displaced (m_e in g) equals the pellet volume (V_p in cm^3).

The density was measured for 40 pellets in four conditions (anhydrous or 0, 40, 80 % HR and immersed in water during 2 days).

The density was calculated with following formula:

$$\rho_p = m_p / V_p = m_p / (m_e/\rho_w), \qquad (g.cm^{-3}) \tag{4}$$

where: ρ_p - pellet density (g.cm^{-3}),
m_p - mass of pellet (g),
V_p - pellet volume (cm^3),
m_e - value of the mass of water displaced by the pellet,
ρ_w - water density (g.cm^{-3}).

RESULTS AND DISCUSSIONS

Durability

Fig. 3 show the results of mass loss of the pellets exposed to the biodegradation by the fungus *Coniophora puteana* and *Rhodonia placenta*.

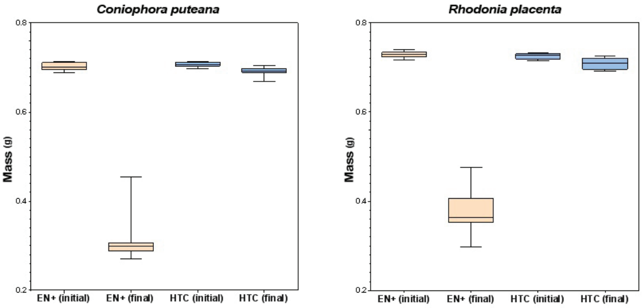


Fig. 3: Box-Whisker diagram for initial and final mass of EN+ and HTC pellets with Coniophora puteana and with Rhodonia placenta.

The mass loss caused by *Coniophora puteana* is significantly higher (approx. 25 times) in wooden EN+ pellets than in HTC pellets. 55.75 % of the wooden EN+ pellets mass was lost during the 12 weeks of the test. In comparison, Eaton and Hale (1993) reported a 60 % mass loss in 12 weeks for solid wood samples of Scots pine and 56 % for Southern yellow pine. On the other side, only 2.25 % of the HTC pellets mass was lost. Furthermore, the results of mass loss caused by *Rhodonia placenta* are similar. 48.46 % of the wooden EN+ pellets mass was lost. Only 2.11 % of the HTC pellets mass was lost. Reza et al. (2012) suggest that the low effect of fungi on HTC biochar or derived products can be caused by the higher lignin content that inhibits fungi growth.

Dimensional stability

Moisture content

The influence of changes in relative humidity on the moisture content is significantly higher for wooden EN+ pellets than for HTC pellets. The difference between the moisture content on HTC and wooden EN+ pellets is more significant with higher relative humidity. At 40 % HR, the moisture content was 1.76 times higher for EN+ pellets (2.88 % for HTC pellets in front of 5.14 % for EN+ pellets). At 60 % HR, the moisture content was 1.65 times higher (5.01 % for HTC pellets in front of 8.29 % for EN+ pellets) and at 80 % HR, the moisture content was 1.66 times higher (6.62 % for HTC pellets in front of 11.03 % for EN+ pellets). For the HTC pellets that were immersed into water for two days, the total moisture content was 24.29 %. This value can be considered as the saturation point. These results are consistent with those described by

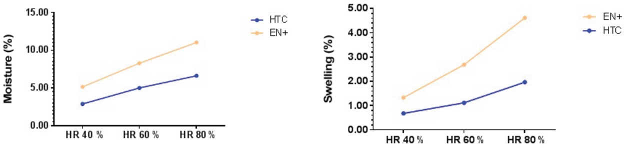
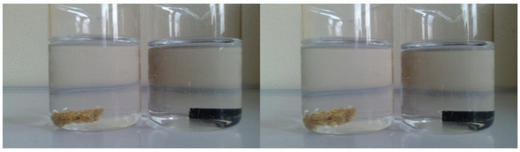


Fig. 4: Variation of moisture content and swelling in relation to relative humidity conditions.

Reza et al. (2012), in which the moisture content for wood pellets is 2.06 higher than HTC pellets for a relative humidity of 84 %.

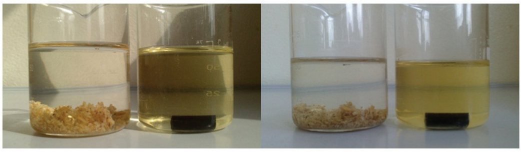
Swelling

The effect of changes in relative humidity on the swelling is also significantly higher for EN+ pellets than for HTC pellets. At 40 % HR, the swelling was 1.72 times higher than in HTC pellets (0.68 % for HTC pellets and 1.33 % for EN+ pellets). At 60 % HR, the swelling was 2.01 times higher (1.12 % for HTC pellets and 2.69 % for EN+ pellets). At 80 % HR, the swelling was 2.35 times higher (1.97 % for HTC pellets and 4.62 % for EN+ pellets). HTC pellets swell less than EN+ pellets when are subjected to the same conditions of relative humidity. Moreover, for the HTC pellets that were immersed in water for two days, the total swelling was 6.28 %.



5 seconds 30 seconds

1 hour 1 day



2 days 6 days

Fig. 5: Evolution in time of wooden EN+ pellets and HTC pellets immersed into water.

Visual analysis

As seen in Fig. 5, the disintegration of wooden EN+ pellets was almost immediate. In 30 seconds the EN+ pellets became detached some particles. In less than 5 minutes the disintegration was nearly complete. On the other side, HTC pellets only swelled slightly after 6 days of immersion, but without decomposition. These results are similar to those described by Hoekman et al. (2012), in which raw feedstock pellets began to disintegrate immediately and charred pellets maintained integrity for weeks.

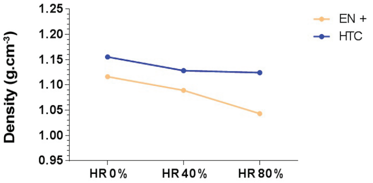


Fig. 6: Density of pellets in relation to relative humidity conditions.

Density

Density of HTC pellets is always significantly higher than EN+ pellets, for any condition of relative humidity. Density decreases with the increment of relative humidity of the surrounding environment. The basic density (d_b) of HTC pellets was 0.926 g.cm^{-3}. Furthermore, as shown in Fig. 6, the oven-dry density (d_0) of EN+ pellets was of 1.116 g.cm^{-3} in front of 1.155 g.cm^{-3} for HTC pellets. At 40 % HR, the density ($d_{40\%}$) of EN+ pellets was of 1.089 g.cm^{-3} in comparison to 1.128 g.cm^{-3} for HTC pellets. At 80 % HR, density ($d_{80\%}$) of EN+ pellets was 1.043 g.cm^{-3} in comparison to 1.124 g.cm^{-3} for HTC pellets. These results are consistent with those described by Reza et al. (2012), in which the normal density (d12%) was always significantly higher for HTC pellets.

CONCLUSIONS

HTC pellets are significantly more durable against biodegradation.

HTC pellets are significantly more dimensionally stable in relation with changing climatic conditions. Wood pellets disintegrate immediately after be immersed in water while HTC pellets maintains integrity for long time.

Consequently, a higher durability against fungal attack and a higher dimensional stability favour logistic processes for HTC pellets. The maintenance of strict conditions of temperature and relative humidity in storage places (silos, bulk storage, maritime transport etc.) is not necessary. Moreover, the hydrophobic character with lower moisture content improves flowability of pellets avoiding problems in removal of silos or containers.

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