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Conversion of tomato-peel waste into solid fuel by hydrothermal carbonization: Influence of the processing variables

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ABSTRACT

In this work, the influence of the variables temperature, residence time, and biomass/water ratio on the hydrothermal carbonization (HTC) of tomato peel was investigated. The implementation of a Design of Experiments – Response Surface Methodology approach allowed to identify the importance of each variable, as well as their interactions, in both the reactivity (solid yield) and energy densification (increase in higher heating value). The HTC residence time and specially temperature had a major effect on the process, increasing the solid yield and promoting energy densification. Ratio had a minor effect although under certain temperature and time conditions, it was a decisive parameter. Solid yields in the range 27.6% and 87.7% with corresponding high heating values 23.6–34.6 MJ kg^{-1} were obtained. From the statistical processing of the experimental data obtained pseudo-second order models were developed. It was proven that these approaches envisaged the hydrochar final characteristics successfully. From the elemental analysis and the FTIR spectra, it was possible to investigate the HTC pathway, which was defined as a combination of several processes; considering dehydration and decarboxylation reactions and especially lignin depolimerization reactions, which lead to the formation of monomeric radicals.

Moreover, the surface morphology of selected hydrochars by Scanning Electron Microscopy (SEM) showed the original structure scaffold, with minor changes between hydrochars prepared under different conditions.

1. Introduction

In the frame of a new energy scenery in which the participation of renewable energy sources is mandatory, biomass stands out due to wide availability and environmental reasons. Various forms of pre-treatment can be considered in order to improve the physico-chemical characteristics of biomass for its subsequent combustion. These include drying (Song et al., 2012), pelleting (Miranda et al, 2011), ultrasonication (García et al., 2012), washing with chemicals (Tan and Wang, 2009), torrefaction (van der Stelt et al., 2011), etc. An example that has become a particularly interesting topic for research during the last few years is energy densification by hydrothermal carbonization (HTC) of raw materials (Román et al., 2012). By this technique, biomass is heated in water under autogenous conditions, in some cases in the presence of chemicals, to yield a carbonaceous fraction called hydrochar (HC), which is more stable and has enhanced C content. Due to their simplicity and low cost, HTC processes have gained great prominence over other biomass pre-treatments (Song et al., 2012).

Moreover, the energy balance of the process is very interesting. The fact that biomass does not need to be dried allows saving a quite large amount of energy (the vaporization enthalpy of water equals 2258 kJ kg^{-1} at 10^5 Pa), which would be necessarily supplied in a pyrolysis process. Berge et al. (2011) performed an analysis on the HTC process energetics for several substrates, based on the high heating value (HHV) of solid, liquid and gaseous phases, and combustion reactions. They found that HTC processes are exothermic and moreover, the heating process is energetically very favorable, because the required energy to heat the reacting water (in a closed system to saturation conditions) is very small in comparison with traditional thermochemical processes (2.4 times lower, according to their estimations). Kruse et al. (2013) have made scaling-up studies on HTC and found that the process is very energy-efficient.

Abbreviations: R, biomass/water ratio; CCD, Central Composite Design; DoE/RSM, Design of Experiments/Response Surface Methodology; HHV, higher heating value; HTC, hydrothermal carbonization; t, Residence time; SEM, Scanning Electron Microscopy; SY, solid yield; T, temperature; FTIR, Fourier transform infrared.

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In recent years, many works on HTC of lignocellulosic biomass have been done (Román et al., 2012, 2013). In general, for a given feedstock, the main variables influencing the process, the product distribution and the properties of the hydrochar obtained are temperature, pressure, residence time and ratio biomass/water, as well as the addition of chemicals to the reaction media. Of these variables, temperature has the strongest influence on the process according to most pieces of research (Román et al., 2012; Basso et al., 2015); enhanced temperature promotes gasification reactions, as well as the dissolution of carbonaceous products into the aqueous phase. This involves the obtention of lower solid yields, greater carbon densification, and, in consequence, higher HHV of the hydrochars.

On the other hand, the influence of residence time on HTC process is less important especially if long residence times are considered, suggesting that the main equilibria governing the process are especially prominent during the first hours of reaction. However, it is worth mentioning that residence time effect on HTC is very variable, depending on the raw material and also, for a given raw material, on the fixation of the other variables (such as temperature). In this way, different authors report an upward or downward evolution of HTC solid yield, or even an absence of effect, depending on the experimental conditions. Besides, the correspondence of a greater reactivity (measured as lower solid yield) with HHV is not as straightforward. For example, Román et al. (2012) reported that using longer residence times promoted HTC only for low time intervals; also, their findings suggested that a prolongated reaction entails a greater energy densification. Dissimilarly, Basso et al. (2015) found that at 250 °C, increasing the residence time at certain conditions involved an increase on the solid yield and a slight energy densification.

The possibility of using resources with high water content presents a very interesting challenge for HTC processes given that the water content in the raw material can itself be used during the process. This would represent an attractive option for these materials which otherwise are difficult to use in other thermochemical applications (such as combustion). Previous works in this line have examined the use of such high moisture content materials, such as grass cuttings (Hao et al., 2013), algae (Heilmann et al., 2010), maize (Mumme et al., 2011), invasive aquatic plants (Catallo et al., 2008), municipal solid waste (Basso et al., 2015) and sewage sludge (He et al., 2013).

The annual global production of fresh tomatoes is approximately 100 million tonnes. More than a third is grown for the food-processing industry, making this crop the world's leading culinary vegetable for processing (Tomato news, 2014). Spain is a major producer, with an annual production of more than 4 million tonnes (of which the Extremadura and Andalusia Regions contribute more than 75%). In addition, tomato processing is mainly concentrated in 2–3 months. The daily production of waste is thus very high, with the consequent problems associated to its handling. This has motivated a search for ways to use tomato processing waste, in particular the peel and seeds. Until now, such studies have focused on drying, combustion, and pyrolysis (Mangut et al., 2006). To the best of the authors' knowledge, no study has yet considered HTC.

With these premises, the main objectives of the present work were:

(a) To investigate the potential of HTC treatment to ungrade tomato peel, by increasing its carbon content and thus its heating value.
(b) To study the effect of main variables (HTC temperature, residence time and ratio biomass water) on the yield and characteristics of the hydrochar obtained. This study was performed following the DoE/RSM (Design of Experiments/Response Surface Methodology) approach. This is a particularly useful strategy for investigating interactions between variables, which would be hard to verify by a classical 'one variable at a time' approach.
(c) To complete HTC process investigation by additional characterization of selected samples by Scanning Electron Microscopy (SEM) and Infrared Spectroscopy (FT-IR).

2. Experiments

2.1. Materials

The biomass was provided by a tomato-processing industry (TOMALIA S.C.U.G.) located in Extremadura Region (Southwest Spain). At the industry, peel and seeds waste residues are produced in the pulper–finisher machines in which the tomato juice is extracted for further processing. The sample (peel and seed) was collected and transported in closed containers at 10 °C. The humidity of the sample (as received in the lab) was analyzed, according to the norm BS-EN-14774-1 (CEN/TS 335 Biomass standards, 2004), and a value of 50.2% was obtained. The two components of this residue, peel and seeds, were separated manually by density, placing it in a 25 L tank with water. After 24 h, peels remained in the surface, and were collected; subsequently both residues were dried overnight at 80 °C and ground to a powder of approximately 0.5 mm diameter. Only the peel was used in this study; after drying, it was stored in a closed flasks placed in a desiccators for further analysis.

2.2. HTC processes and hydrochar characterization

The HTC processes were performed in a stainless steel autoclave (Berghof, Germany). In a 0.2 L teflon vessel (unstirred), an appropriate amount of dried tomato peel (1.6–18.4 g) and 150 mL of deionised water at room temperature were added, in order to obtain the targeted biomass/water ratio, R (1.6–15% by weight). Then, the teflon vessel was sealed and placed into the autoclave and the system remained overnight at room temperature. This period of time was enough to guarantee that all biomass had bound together and descended by gravity to the bottom of the teflon vessel; under these conditions, the reactor empty volume was in all cases lower than 20%.

After this, the system was heated up in an electric furnace at selected temperatures (150–250 °C), during a chosen processing time (1.6–18.4 h). Previous experimentation made in the same installation were devoted to investigate how long the autoclave takes to reach the set temperature; these tests showed that this time period is in the range 20–25 min. The time period here defined considers the heating stage in the whole residence time, that is to say, zero time was considered at the moment in which the heating process started.

When the reaction time was reached, the autoclave was removed from the oven and subsequently placed in a cold-water bath. The cooling stage, which took about 15–20 min, was not counted as reaction time. After cooling, the solid phase was separated from liquid by vacuum filtration and subsequently dried at 80 °C to remove residual moisture. The dried hydrochars were stored in closed flasks placed into a desiccator until further analysis.

The hydrochars were characterized in terms of their solid yield (% mass weight), HHV (MJ kg^{-1} dry basis), elemental analysis, FTIR and SEM. In Table 1 the experimental conditions defined for each run have been collected.