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Upgrading of moist agro-industrial wastes by hydrothermal carbonization

Verónica Benavente*, Emilio Calabuig, Andres Fullana

Chemical Engineering Department, University of Alicante, PO BOX 99, E-03080 Alicante, Spain

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ABSTRACT

This work focuses in the application of the hydrothermal carbonization (HTC) technology as a possible moist agro-industrial waste management treatment. Through this technique, olive mill, canned artichoke and orange wastes (OMW, CAW and OJW, respectively) were carbonized in a lab-scale high pressure reactor at different temperatures (200–250 °C) and durations (2, 4, 8 and 24 h) in order to obtain useful bioenergy feedstocks. The effect of the residence time and temperature on the properties of the bio-char obtained was studied through different characterization techniques. Material and energy balances were also performed to determine the potential energy saving of hydrothermal carbonization versus dry thermal treatments like torrefaction (TF). It is found that the moisture content of HTC-hydro-chars decreases as the temperature and duration increase, which implies that wet biomass can be upgraded and, at the same time, dewatered through HTC. The best results are found for the OMW, whose moisture content decreases from over 70% to less than 30% for the experiments carried out under the more severe conditions. Consequently, it is be possible to reach energy savings over 50% by using HTC instead of TF technologies. Regarding the hydro-char properties, the hydrothermal carbonization of the three organic wastes treated leaded to hydro-chars that present carbon contents and heating values closed to those of brown coal and great energy densifications, depending on the type of waste. Accordingly, it can be concluded that it is feasible to manage moist agro-industrial wastes via HTC, which is ostensibly more efficient than TF in terms of energy consumption.

1. Introduction

The Mediterranean region concentrates an important fraction of wine, olive oil, canned fruits and vegetables industries worldwide. Currently, part of the canning industrial wastes are intended to animal feeding, but a significant fraction ends in the landfill and increases the existing problem of lack of space. Meanwhile, fresh wine and olive mill wastes, which are high polluting by-products, are usually managed through biological treatments such as composting to produce fertilizers. However, this technology needs large processing volumes to treat the large amounts of wastes that are generated every year and, on the other hand, the digestate storage is also a problem because of the associated costs and the vast occupied space. Thus, to decrease such amounts of wastes, it would be interesting to use them as bio-energy feedstocks. Nevertheless, the combustion characteristics of agro-industrial wastes pose some technical and economic challenges and, as a consequence, the use of this kind of wastes as a bioenergy source has not been extended. Agro-industrial wastes present moisture contents that in most cases reach the 80%. As a result, this kind of wastes has low calorific values and difficult and costly handling, transport and storage. Then, to make them suitable for energy production and reach all their potential as alternative energy sources, the aforementioned limitations must be overcome.

A range of pre-treatment and upgrading technologies have been developed in order to improve the biomass characteristics as bioenergy feedstocks. Among these methods, dry pyrolytic treatments such as torrefaction are being widely evaluated to produce carbonaceous solids from different biomass materials. Torrefaction (TF) is a mild pyrolysis process at temperatures between 200 and 300 °C that converts biomass into an upgraded solid that is more suitable for international long-distance shipping for use in centralized heat and power generation [1]. Though, before conversion through dry pyrolysis, wet biomass needs to be actively dried. Therefore, moisture is a limiting factor in the thermal process efficiency due to the great deal of energy required in the pre-drying step of moist wastes.

To avoid the costly pre-drying step, wet pyrolysis, often called hydrothermal carbonization (HTC), is mentioned as an efficient

* Corresponding author. Tel.: +34 96 590 38 67; fax: +34 96 590 38 26.
E-mail address: veronica.benavente@ua.es (V. Benavente).

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technology to carbonize moist biomass [2–7]. In the HTC process, biomass is heated in a high pressure reactor at temperatures lower than 350 °C. As a result, the feedstock is decomposed by a series of simultaneous reactions that occur in liquid phase, including hydrolysis, dehydratation, decarboxylation, aromatization and recondensation [7], that lowers both the oxygen and hydrogen content of the feed. The reaction products are gases, mainly carbon dioxide, carbon monoxide, hydrogen, methane, ethane and propene, and a mechanically easy to separate mixture of solid, referred to as hydro-char, and liquid, which contents the solvent used in the HTC reaction and solubilized organic products [5,7–11].

Through HTC technique, the water that is inherently in green biomass could be used as solvent to pressurize the reaction medium and then, it is not necessary to remove it from the material before to apply this method. During HTC, the phase change from water to steam is largely avoided due to the high pressures involved in the process. Then, the required energy to heat the water is smaller in comparison to that required to evaporate the same mass of water before dry pyrolytic treatments. Additionally, carbonization reactions and disruption of colloidal structures have been shown to improve the dewaterability properties of the hydro-char [12]. As a consequence, the HTC process is expected to have a great potential of energy saving versus dry thermal conversion techniques regarding to the avoided pre-drying step and the improvement in the dewatering properties of the hydro-char compared to those of the raw material.

Besides, the ash content of the biomass and its chemical composition determines its application as a bio-fuel. Biomass from agricultural products is rich in alkali metals (Na and K), which melt at combustion temperatures and lead to slagging and fouling deposits on the surfaces of the equipment involved in the process (furnaces, boilers) [13,14]. Through HTC, part of the inorganic matter of the raw biomass is found to be transferred to the liquid phase [15]. Consequently, the hydro-char ash content is expected to be lower than that of the bio-char obtained by other pyrolytic techniques, which retains the 100% of the metals contained in the raw biomass [15]. Thus, in terms of energy consumption and ash content, HTC appears as a more energy efficient disposal treatment for moist organic residues and is expected to be beneficial to improve the quality of the hydro-char as bio-energy feedstock compared to dry pyrolytic treatments.

Several research works related to the conversion of organic wastes via HTC exist in the literature, since the HTC process, first described by Bergius in 1913 [16], was rediscovered by Bobleter in the 1980s [2] and applied to organic wastes at the University of Applied Sciences Ostwestfalen-Lippe in co-operation with the Max-Planck Intitute of Colloids and Interfaces inf Golm/Postdam (MPI) [5]. Within the last project, different organic wastes from households and industries were successfully carbonized. The produced hydro-chars were found to maintain approximately 75–80% of the carbon input. In addition, their elemental compositions and calorific values were very similar to brown coals, which make hydro-chars interesting for energy production. In the most recent literature, Lu et al. [17] found that the HTC of solid municipal waste leads to raise the departure energy density between 6.39 and 9.0 times. Xiao et al. [18] studied the HTC of cornstalk and observed that the heating value of the hydro-char was 66.8% higher than that for fresh biomass. In a similar way, Román et al. [19] treated walnut shells and sunflowers stems through HTC under different operating conditions to optimize the heating value of the hydro-char and obtained that the heating value increased from 1.5 to 1.75 fold when compared with the natural biomass. Regarding the variables studied, these authors found that temperature and water/biomass ratio were more influent on the hydrocarbonization process than residence time. Meanwhile, Oliveira et al. [6] applied the HTC process to several mixtures of agricultural wastes in order to analyze the hydro-char grade and the mass and energy losses during the treatment. They conclude that the mass and energy recoveries are increased as the waste mixtures are more lignocellulosic while the hydro-char grade improves as the waste mixtures were richer in low molecular weight carbohydrates. Pala et al. [20] compared the fuel, morphological and structural properties and the combustion characteristics of chars produced from grape pomace by both hydrothermal carbonization and torrefaction. These authors found that the char produced by torrefaction was more aromatic in nature than that obtained by HTC. However, HTC led to chars with greater energy density and combustion reactivity, which showed that HTC appears as a promising process for a winery waste having high moisture content.

Studies indicate that the hydro-char properties and the performance of the products depend on both the experimental conditions and the type of raw material used. Our aim in this work was to upgrade moist agro-industrial wastes typical in the Mediterranean region via hydrothermal carbonization to obtain profitable bio-energy feedstocks. Olive mill, artichoke and orange wastes, which have not been assessed yet, were evaluated because they suppose a concerning problem for the producing companies due to the large volume of wastes involved. The Mediterranean area is the main producer of olive oil and canned artichokes worldwide. In addition, 67% of processed artichokes resulted in wastes. As a consequence, more than 10×10^6 and 7×10^5 t are produced per year, respectively. On the other hand, the production of orange juice is also important, especially in Spain, and consequently more than 5×10^5 t of orange waste are produced per year. HTC experiments were carried out under different time and temperature conditions to study their effect on the hydro-char properties and estimate the energy saving of hydrothermal carbonization versus dry thermal treatments, such as torrefaction.

2. Materials and experimental design

2.1. Materials

Fresh olive mill waste (OMW) was supplied by Extremadura Agricultural and Food Technological Centre during the 2012–2013 campaign. The OMW appearance was typical of sludge. Specimens used for reactions and analyses were taken from below the surface layer of the OMW to gain a homogeneous sample, as the surface of the sludge becomes oxidized. In a similar way, fresh canned artichoke waste (CAW) and fresh orange juice waste (OJW) were collected from different artichoke canning industries and orange juice industries located in the south east of Spain. In this case, both CAW and OJW were milled in a grinder to attain homogeneity and sieved to obtain a particle size between 1 and 3 mm. Moisture and ash content of OMW, CAW and OJW prior HTC experiments were obtained.

2.2. HTC experimental procedure

Two series of experiments were addressed to study the effect of residence time and temperature on the reaction products. In the first series, OMW was thermally treated at 225 °C during residence times of 2, 4, 8 and 24 h. In the second series, OMW, CAW and OJW were processed under 200, 225 and 250 °C during 2 h. The reaction conditions were chosen because they are known to be effective for the hydrothermal degradation of a wide range of lignocellulosic materials (190–240 °C) [5,7,21]. The reactor pressure was not controlled in the experiments and was kept autogenic with the vapor pressure of water at the corresponding reaction temperature: 1.5 MPa at 200 °C, 25 MPa at 225 °C and 40 MPa at 250 °C, as indicated by the pressure gauge attached to the reactor.