Production of High Energy-Dense Solid Biofuel and Biopolymer Filler via Hydrothermal Carbonization of Carob Fruit

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In this study fresh carob tree fruits (CF), a very widespread botanical species in the Mediterranean basin, were hydrothermally carbonized (HTC) at 200, 230, 250, and 280 °C for a residence time of 0.5 h and a biomass-to-water mass ratio (B/W) of 0.1. CF hydrochars were characterized in terms of elemental and proximate analysis for their possible valorization as solid biofuels. Increased reaction severity showed a decrease in solid mass yield recovery but an increase in hydrochar fixed carbon content and energy density. Hydrochars showed a high heating value (HHV) up to about 27.7 MJ/kg with a corresponding energy densification ratio (EDR) higher than 150%. CF hydrochars were also investigated as potential carbon-dense material as fillers in bio-plastic. Therefore, the CF hydrochar particles, at different concentrations, have been introduced in biopolymer matrices, such as PolyButylene Adipate Terephthalate (PBAT), by melt mixing and the rheological and mechanical behaviour of the bio-composites have been evaluated considering their potential application in the packaging sector.

1. Introduction

Thermochemical upgrade of biomass represents one of the most favourite options for energy production due to the large and equally globally availability of the source. If, on the one hand, in the last two decades the number of studies dealing with the energy valorization of waste biomass via dry thermochemical technologies as torrefaction (Prins et al., 2006), pyrolysis (Patra et al., 2021) and gasification (Volpe R. et al., 2016) have considerably increased. On the other hand, more recently, wet thermochemical technologies like hydrothermal carbonization (HTC) (Lucian et al., 2021) and hydrothermal liquefaction (HTL) (Di Lauro et al., 2022), have attracted further attention due to the possibility of direct conversion of high moisture waste biomass (water content often higher than 60 wt%) without the need of high energy demanding drying pre-treatments. During HTC, water, at subcritical conditions, typically between 180 and 280 °C and corresponding saturated water pressures of 10-60 bars, catalyzes degradation of biomass components through subsequent reaction of dehydration, hydrolysis and decarboxylation (Kruse and Dahmen, 2015) with the production of a high carbon dense solid material, named hydrochar, an aqueous liquid fraction containing oxygenated compounds as organic acids (acetic, formic, levulinic etc.) and furfurals like 5-HMF. A small fraction of the staring materials is also converted in a gas phase mainly constituted of carbon dioxide (Hitzl et al., 2015). Between other proposed applications, rather than biofuels, pyrolyzed char particles have been mainly investigated as fertilizers for poor soils (Wang et al., 2022) and as fillers for the formulation of sustainable composites (Infurna et al., 2023a). According to previous works, the addition of biochar particles produced by slow pyrolysis of biomasses led to the increase of system rigidity, penalizing significantly the ductility (Infurna et al., 2023b). Another important effect, due to the presence of biochar particles, is related to the modification of the optical properties. Particularly, as known, the biochar particles show dark colour, i.e., brown to black colour, and this influence significantly the colour of biopolymer-based manufacturers. As expected, the dark colour of biochar particles determines a well-pronounced UV absorption that could be useful for some specific applications, such as covering and mulching biopolymer films. The hydrothermal treatment of biomasses, being
made at lower temperatures in comparison to that of fast and slow pyrolysis, could preserve native functional groups of the biomasses and this could be considered useful for the formulation of novel biocomposites. In this work, we processed the carob through hydrothermal cracking of the biomass at lower temperatures, i.e., between 200 and 280 °C, aiming to maintain the native functional groups and then, these hydrochar particles have been added through melt mixing to PBAT.

2. Materials and Methods

2.1 Materials

Carob fruits were collected in Palermo province, and the fresh fruits grounded by a knife miller to produce a homogeneous pulp residue named CF. The so obtained material was portioned and stored in a freezer at – 20 °C in sealed plastic bags in order to preserve the characteristics before its use. CF samples were defrosted slowly at room temperature (about 20 °C) before each HTC reaction test. CF samples were defrosted and dried in a ventilated oven at 55 °C, until constant weight, before any analytical characterization. CF sample showed average moisture content (M%) of 20.05 ± 0.75%.

2.2 Hydrothermal carbonization procedure and residues recovery

HTC runs were carried out using a stirred (200 rpm) stainless-steel batch reactor with an internal volume of 500 mL. For each trial, the reactor was charged with approximately 38.0 ± 0.5 g of defrosted CF (approximately 30.0 g of feedstock on a dry basis d.b.) and about 300.0 ± 0.5 g of deionized water (DW), in order to achieve a biomass to water ration (B/M) of about 0.1. After the reactor was filled with the feedstock and DW it was sealed, evacuated and flushed three times with pure nitrogen to remove residual traces of oxygen. Once purged, the reactor was heated up to the selected temperature and kept isothermal for the prefixed reaction time (the heating step lasted for 25-40 min according to the temperature set point). Reaction temperatures and corresponding reaction pressures were: 200 °C – 16 bar, 230 °C - 28 bar, 250 °C - 40 bar and 280 °C – 60 bar. When the reaction time was passed, the reactor was rapidly cooled down to room temperature by using chilled (20 ºC) water flowing through a chilling coil inside the reactor body. Before opening the reactor, the gaseous phase produced was flowed through an outlet valve into a graduated cylinder filled with water, and its mass evaluated applying the ideal gas law, assuming atmospheric pressure, temperature of 30 ºC and CO2 as the sole gaseous product. It is well established in the HTC literature that CO2 is the prevalent gas product (often above 90 wt%) accompanied by small amounts of CO and light hydrocarbons (Hitzl et al., 2015). The solid-liquid reaction mixture was separated through a vacuum filtration unit and a pre-weighed cellulose filter. The solid fraction in the filter was washed few times with DW to remove the mother liquors and the solid residue dried in a ventilated oven at 55 °C until constant weight.

2.3 Biocomposites Formulation

Between the four different hydrochars, three of them, HCcrf200, HCcrf250 and HCcrf280, were selected for biocomposites formulation. The residual hydrochar from these three conditions were milled at the same process condition by means of a mechanical pestle and mortar in order to achieve dimensions lower than 100 μm. The bio-composite formulation was carried out by means of a Brabender mixer at 160 ºC, with a mixing speed of 60 rpm for 5 mins. Before compounding, PBAT and hydrochars were dried at 60 ºC under vacuum to avoid hydrolysis during compounding. The HCcrf200, HCcrf250 and HCcrf280 were added at a concentration of 10 wt% into PBAT matrix and the obtained mixtures were pelletized. In addition, the neat PBAT has been subjected to the same processing condition in order to be comparable with the composites. After 24 h of drying in an under vacuum oven at 60 ºC, to avoid the hydrolysis process, thin films (thickness of about 200 μm) of neat PBAT and of all composites have been obtained through compression moulding by means of Carver Laboratory Press at a pressure of 1500 psi (approximately 103 bar) for 5 mins at 160 ºC.

2.4 Analytical characterization

Proximate and elemental analyses, as well as HHV determinations, were carried out in order to characterize raw CF and the corresponding hydrochars. A LECO Thermogravimetric Analyzer TGA 701 was used carry out proximate analysis and quantify volatile matter (VM), ashes (ash) and fixed carbon (FC). Proximate analysis was carried as follows: 5 ºC/min ramp to 105 ºC in air, held until constant weight (< ± 0.05%) to remove moisture; 16 ºC/min ramp from 105 to 900 ºC, hold time 7 min, in nitrogen to determine VM as the mass lost; natural cooling down to 500 ºC in nitrogen; 30 ºC/min ramp in air to 800 ºC and isothermal until constant weight in to evaluate ash content as the remaining mass. FC was estimated by difference.
Elemental analysis was carried out in a LECO CHN 828 series Elemental Analyzer to determine carbon (C), hydrogen (H), nitrogen (N), content. A calorimeter LECO AC500 was used to measure HHVs according to the CEN/TS 14918 standard.

Rheological tests were performed using a strain-controlled rheometer (mod. ARES G2 by TA Instrument, New Castle, DE, USA) in parallel plate geometry (plate diameter 25 mm). The complex viscosity ($\eta^*$) and storage ($G'$) and loss ($G''$) moduli were measured performing frequency scans from $\omega=10^{-2}$ to $10^2$ rad/s at same processing temperatures. The strain amplitude was $\gamma=5\%$, which preliminary strain sweep experiments proved to be low enough to be in the linear viscoelastic regime.

Tensile tests were carried out using a Universal Testing Machine (Instron model 3365, UK), following ASTM D638-14 method, on seven rectangular shaped samples. The tests were performed, using tensile speed at 1 mm/min for 1 min in order to evaluate the Young's modulus and then the velocity was increased to 10 mm/min until sample breakage. The average values for elongation at break (EB), for elastic modulus (E), and for tensile strength (TS), were calculated.

2.5 Data analysis

The hydrochar mass yield ($MY_{HC}$) and gas mass yield ($MY_G$) were evaluated through Eq (1) and (2) respectively, while liquid mass yield ($MY_L$) was calculated by difference through Eq (3). $m_{HC}$ and $m_G$ are the mass of hydrochar (d.b.) and gas, collected after the conversion, respectively and $m_{raw}$ is the mass (d.b.) of the solid starting material.

$$MY_{HC} = \frac{m_{HC}}{m_{raw}}$$ (1)

$$MY_G = \frac{m_G}{m_{raw}}$$ (2)

$$MY_L = 1 - MY_{HC} - MY_G$$ (3)

The hydrochar energy properties were computed through the energy yield (EY) and the energy densification ratio (EDR), defined as follows:

$$EY = \frac{HHV_{HC}}{HHV_{raw}} \cdot MY_{HC}$$ (4)

$$EDR = \frac{HHV_{HC}}{HHV_{raw}}$$ (5)

Where the HHV$_{HC}$ and HHV$_{raw}$ indicate the HHV values for the hydrochar and raw feedstock, respectively.

3. Results and Discussion

Table 1 reports the HTC residues mass yields. The data show that between 200 and 250 °C the mass yields of the solid, the liquid and the gas fractions did not differ significantly being approximately 40 wt% for hydrochars, 1-2 wt% for the gas fraction and about 58-59 wt% for the liquid residue. Differently, at 280 °C hydrochar mass yield drops to about 32 wt%, while both gas and liquid mass yields increase up to 4.0 and 64.3 wt% respectively. This behaviour can be ascribed to the high content of sugars and hemicellulose fractions into the feedstock readily decomposed also at the lower HTC process temperatures. At higher HTC temperatures as 280 °C the more recalcitrant biomass component as lignin could be significantly decomposed thus reducing the solid mass yields (Kim et al., 2016).

Table 1: mass yields of CF HTC residues; average values of three HTC runs at each experimental condition (RSD% ≤ 0.8).

<table>
<thead>
<tr>
<th>Sample</th>
<th>mass yields (wt% d.b.)</th>
<th>MY$_{HC}$</th>
<th>MY$_G$</th>
<th>MY$_L$*</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTC$_{CF, 200}$</td>
<td>39.9</td>
<td>1.1</td>
<td>59.0</td>
<td></td>
</tr>
<tr>
<td>HTC$_{CF, 230}$</td>
<td>40.4</td>
<td>1.8</td>
<td>57.8</td>
<td></td>
</tr>
<tr>
<td>HTC$_{CF, 250}$</td>
<td>38.4</td>
<td>2.2</td>
<td>59.4</td>
<td></td>
</tr>
<tr>
<td>HTC$_{CF, 280}$</td>
<td>31.7</td>
<td>4.0</td>
<td>64.3</td>
<td></td>
</tr>
</tbody>
</table>

*Evaluated by difference: $MY_L = 100 - MY_{HC} - MY_G$
Table 2 shows the proximate and energy properties of CF hydrochars. As commonly found in HTC literature, with the increase in temperature (and thus severity) of the reaction, hydrochars showed an increase in the fixed carbon while a decrease in the volatile matter with a reduced ash content when compared to the starting material. The increase in fixed carbon and the reduction of ash content are both of great importance in determining the quality of a biofuel due to the reactivity during combustion and the reduced possibility of slugging and fouling respectively (Reza et al., 2013). While the energy yield of the hydrochars maintained between 50 and 56% the EDR and the HHV, for the hydrochar obtained at 280 °C, raised up to 159% and 27.7 MJ/kg respectively, showing the high potentially of the hydrochar as a bio-combustible in substitution or in a mix with standard coals.

Table 2: Proximate analysis and energy properties of raw CF and corresponding hydrochars. Proximate analysis performed in duplicate; average values are showed (RSD% ≤ 1.5). Average values of three HHV measurements are reported (RSD% ≤ 0.9).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Proximate Analysis (wt% d.b.)</th>
<th>Energy Properties</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>VM</td>
<td>Ash</td>
<td>FC*</td>
</tr>
<tr>
<td>CFraw</td>
<td>71.9</td>
<td>2.6</td>
<td>25.6</td>
</tr>
<tr>
<td>HCCF200</td>
<td>57.4</td>
<td>0.6</td>
<td>42.0</td>
</tr>
<tr>
<td>HCCF230</td>
<td>54.2</td>
<td>0.9</td>
<td>44.9</td>
</tr>
<tr>
<td>HCCF250</td>
<td>50.3</td>
<td>1.3</td>
<td>48.4</td>
</tr>
<tr>
<td>HCCF280</td>
<td>45.6</td>
<td>1.2</td>
<td>53.2</td>
</tr>
</tbody>
</table>

*Evaluated by difference: FC = 100 - VM – ash

Elemental analysis confirmed that the energy densification of the CF hydrochars with the increase of reaction temperature is mainly driven by the increase of carbon content.

Table 3: Elemental analysis of raw CF and corresponding hydrochars, analysis performed in triplicate; average values are showed (RSD% ≤ 1.2).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Proximate Analysis (wt% d.b.)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C%</td>
<td>H%</td>
</tr>
<tr>
<td>CFraw</td>
<td>49.5</td>
<td>5.8</td>
</tr>
<tr>
<td>HCCF200</td>
<td>59.8</td>
<td>5.1</td>
</tr>
<tr>
<td>HCCF230</td>
<td>62.9</td>
<td>4.7</td>
</tr>
<tr>
<td>HCCF250</td>
<td>63.8</td>
<td>4.5</td>
</tr>
<tr>
<td>HCCF280</td>
<td>65.2</td>
<td>4.4</td>
</tr>
</tbody>
</table>

*Evaluated by difference: O% = 100 – C% - H% - N% - ash

Figure 1 shows the trend of complex viscosity of neat PBAT and PBAT containing hydrochar particles produced at different temperatures. Worth noting that the neat PBAT exhibited a well-pronounced Newtonian behaviour in the almost investigated frequency range and the HC addition led to a significant increase of the viscosity values, modifying the rheological behaviour of the biopolymer. The addition of HCCF200 led to both effects, first, the appearance of significantly pronounced yield stress, and second, viscosity values increase in the hole frequency range. Interestingly, the addition of HCCF250 and HCCF280 led to less pronounced effects on the rheological behaviour. The latter could be understood considering that the high production temperatures during hydrothermal treatment the carob less easily the surface functional groups and the interaction with the host matrix is less pronounced. Contrary, the HCCF200 contains numerous surface groups and this led to a more pronounced interaction/reaction with host matrix, inducing significant changes in rheological behaviour.
Figure 1: Complex viscosity as a function of the frequency of neat PBAT e PBAT containing 10 wt% of hydrochar particles

Figure 2a-c shows the values of the main mechanical properties, i.e. Young modulus, tensile strength and elongation at break, of neat PBAT and PBAT containing HCCF200, HC CF250 and HC CF280. The addition of the three kinds of HC led to a significant increase in the PBAT elastic modulus, and as noticeable, the increases are about three times for each sample, highlighting a well-pronounced beneficial effect of these particles on the PBAT rigidity. Interestingly, the tensile strength values remained almost unchanged by the addition of hydrochars, although the elongation at break of PBAT resulted significantly reduced. Therefore, the loss of system ductility must be taken into consideration when designing the application of PBAT/HC biocomposites.

Figure 2: (a) Young modulus, (b) Tensile strength and (c) Elongation at break of neat PBAT e PBAT continuing 10wt% of hydrochar particles (HC)
4. Conclusions

Hydrothermal carbonization of carob fruit demonstrated to be a valid technology for the energy upgrade of such a waste biomass. With the increase of HTC severity the produced CF hydrochars showed (at 280 °C) an increase in the fixed carbon and of high heating values up to 53.2% and 27.7 MJ/kgHC respectively. When comparing with the starting material, CF hydrochars showed also a significant reduction in the ash content and an energy densification ratio between 135 and 159%. All these data confirm the high potentiality of CF hydrochars as solid biofuels for boilers both in substitution or in a mixture with standard mineral coals. The addition of CF hydrochars at a concentration of 10 wt% to PBAT led to the increase of viscosity, highlighting a beneficial effect on the rheological behaviour of PBAT. The increase of viscosity values did not compromise the processing of the bio-composites through classical melt processing production by extrusion and, as demonstrated, the addition of hydrochars particles to PBAT significantly increased the Young’s modulus, improving the system rigidity, although, as expected, penalized the ductility.

Acknowledgments

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