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Full Length Article

Preparation and characterization of agricultural waste biomass based hydrochars

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HIGHLIGHTS

- Carbon content increased with increasing temperature.
- Prepared hydrochars contain hydroxyl, carbonyl, carboxyl, ether and ester groups.
- Spherical/semi-spherical particles were prepared.
- Semi-graphitized amorphous carbonaceous structure formed.

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ABSTRACT

In this study hazelnut shell and olive residue were hydrothermally carbonized in a stainless steel autoclave. Chemical, structural and physicochemical properties of obtained hydrochars were investigated in dependence of the reaction parameters and characterized by use of various techniques. Reaction temperature was found to have a much stronger influence on hydrothermal carbonization (HTC) of biomass than reaction time after 2 h. Hydrochar samples consist of spherical/semi-spherical particles in nano to micron size with aromatic framework. Hazelnut shell based hydrochars have higher number of O-containing reactive functional groups compared with the olive residue based hydrochars. Because of the knowledge gaps in hydrochar characterization, more comprehensive product characterization and reporting are needed to advance our understanding of HTC processes, products and applications. By the help of the results of this study, it will be possible to choose the appropriate hydrochar characteristics in various applications of hydrochars.

1. Introduction

Carbonaceous materials received a great attention in the last decade because of their wide range of applications such as water purification [1], or as electrode materials for super-capacitors [2], catalysts [3–5], catalyst support material [6] and solid fuel [7,8]. The hydrothermal carbonization (HTC) process is one of the most common thermochemical conversion technologies which first was demonstrated in 1913 [9] and has practiced extensively after 2000. At hydrothermal conditions biomass is converted to carbonaceous materials in water, under mild thermal conditions (150–350 °C), autogenous pressure and with relatively short reaction times [10].

Another advantage of the hydrothermal method is to allow carbonaceous sphere formation of nano and/or micro size. This carbonaceous spheres have a wide variety of surface functional groups such as —OH, —C=O and —COOH. Hydrothermal carbonization of biomass in aqueous media allows lots of oxygenated functional groups to occur on the surface of the carbonaceous material and these functional groups play a very critical role for some applications such as for dyes or heavy metal ion adsorption [11,12].

Generation of carbonaceous materials from waste biomasses as carbon sources has a critical importance since it is a renewable and environmentally benign method. The biomass feedstocks used in this work were hazelnut shell and olive husk. Hazelnut shell is an important agricultural residue in Turkey being the largest hazelnut producer in the world [13]. Olive residue is also an important biomass generated especially in the Mediterranean region of Turkey as a byproduct of olive oil production.

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In our previous work low temperature (180 °C) hydrothermal carbonization of saccharides and waste biomasses were successfully performed and evaluated in terms of the char formation mechanism [7]. In the present paper, the effects of operational conditions on the chemical, morphological and structural characteristics of hydrochars obtained from the two bio-residues were investigated. Even though the hydrothermal carbonization of biomass has been investigated by various workers [14,15], this work differs from those in regard to the use of wide variety of analysis techniques to improve the understanding of operation conditions on the chemical, structural, physicochemical properties and formation process of hydrochars.

2. Materials and methods

2.1. Materials

Hazelnut shell (HS) and olive residue (OR) were used as carbonaceous material precursors. Olive oil waste was provided from a local olive oil factory at Muğla from Turkey and formed the remaining material after the oil extraction from the olive kernel. Hazelnut shell was supplied from the Black sea region in the northern part of Turkey. The proximate and ultimate analysis of the raw biomass samples (HS and OR) are given in Table S1 in supporting information (SI). The air dried biomasses were milled and then sieved through a 425 μm mesh.

2.2. Hydrothermal carbonization experiments

The hydrothermal carbonization experiments were carried out in, a 1 L stirred pressure reactor (Parr, model 4571) under different reaction conditions changing the temperature (180, 220 and 260 °C) and the reaction time (2, 4 and 6 h). In a typical run, 40 g biomass was dispersed in 400 mL distilled water in the reactor and heated with 4 °C/min. It took about 45, 60 and 75 min to reach 180, 220 and 260 °C temperatures, respectively. After reaction solid product was separated from liquid via vacuum filtration. The carbonaceous material was washed with distilled water 3 times and dried in an oven at 80 °C for 24 h. The obtained hydrochars from hazelnut shell (HS) and olive residue (OR) were labeled according to biomass type, reaction temperature and reaction time respectively. For instance, HTC-OR (260 °C, 4 h) refers to hydrothermally carbonized olive residue at 260 °C for 4 h.

2.3. Analysis of hydrochars

X-ray Diffraction analyses of biomass and hydrochar samples were carried out by a Rigaku D/Max 2200ULTIMAN X-ray diffractometer, using CuK_{α} radiation. Elemental analysis of hydrochars and biomass were determined using a LECO 932 CHNS elemental analyzer. XPS spectra was recorded by a PHI-5000 Versaprobe using Al monochromatic X-ray anode and Gaussian peaks for the peak fitting. ^{13}C CP-MAS NMR analyses were conducted by a Bruker Avance 300 MHz (7T) spectrometer spinning at MAS rate nMAS = 7 kHz. Raman spectra were obtained from a Horiva (LabRam HR-800) analyzer with 532 nm laser in the range of 1000–2000 cm^{-1}. High resolution transmission electron microscope (CTEM) analysis was performed with an FEI Tecnai G2 (at 200 kV) transmission electron microscope to determine the particle size and shape of the hydrochar particles. Scanning electron microscope (SEM) images were obtained using a QUANTA 400F Field Emission SEM device.

3. Results and discussion

3.1. Recovered hydrochars yield

The effects of reaction parameters on the solid product yield are shown in Fig. 1. High carbonization rates lead to formation of gaseous and liquid products and solid product yield decreased with the separation of this by-products when compared with the initial weight of biomass. Hydrothermal carbonization of waste biomass may occur at 180 °C [7], even though cellulose and lignin do not undergo any significant changes below 220 °C temperature. It can be explained by the thermally unstable hemicellulose content of the lignocellulosic biomass (Table S1 in SI). At 180 °C, olive residue has a low solid product yield (high conversion rate) compared with hazelnut shell because of the higher hemicellulose content relative to hazelnut shell. Low concentrations have provided better carbonization for waste biomasses.

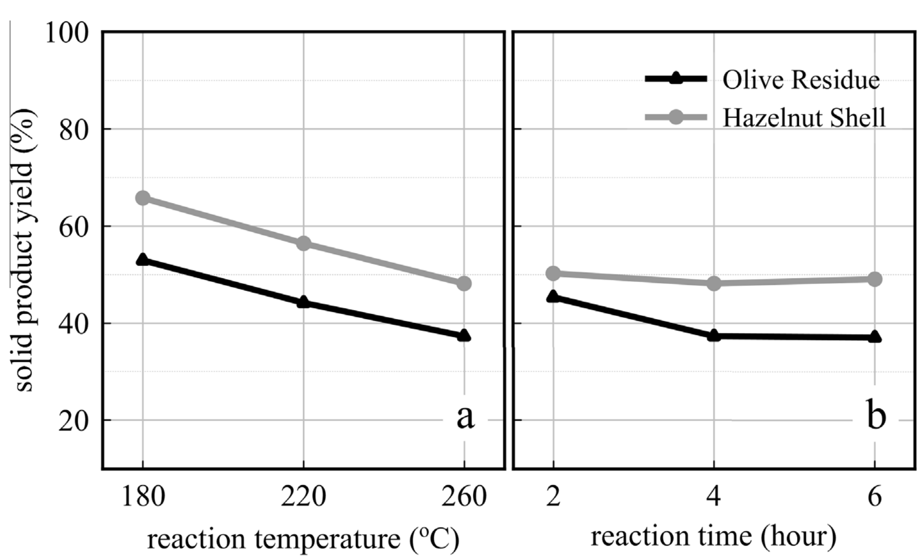

Fig. 1. Effects of reaction parameters on the solid product yield, (a) 4 h and (b) 220 °C.