VALORIZATION OF BIOMASS WASTE USING HTC PROCESS FOR POTENTIAL ENVIRONMENTAL APPLICATIONS

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An efficient, economical and emerging method used for the valorization of biomass waste is hydrothermal carbonization (HTC). The aim of this study was to develop eco-materials from grape stems waste, using an environmentally friendly method. The structural and morphological properties of the eco-materials were investigated by means of ATR-FTIR and SEM-EDS. Based on the results, these eco-materials derived via HTC from grape stems waste can be further used in environmental applications, such as water depollution.

Keywords: HTC, biomass waste, eco-materials

1. Introduction

Worldwide, 2.01 billion tons of municipal solid waste are generated annually, of which at least 33% is not managed in an environmentally friendly way [1]. Globally, the waste generated by each person per day averages 0.74 kilograms but varies widely from 0.11 to 4.54 kilograms. Although they account for only 16% of the world's population, high-income countries generate about 34%, or 683 million tons, of the world's waste.

Globally, 140 billion metric tons of biomass are generated each year from agriculture. This volume of biomass can be converted into an enormous amount of energy and raw materials. Equivalent to about 50 billion tons of oil, agricultural biomass waste turned into energy can substantially replace fossil fuels, reduce greenhouse gas emissions and provide renewable energy for an estimated 1.6 billion people in developing countries who do not yet have access to electricity. As feedstocks, biomass waste is very attractive to large-scale industries and EU-wide businesses [2].

Biomass comes in the form of waste stalks, straw [3], leaves [4,5], roots [6], husks [7], nuts or seed husks [8,9], wood waste and livestock waste [10].

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Widely available, renewable and virtually free, residual biomass is an important resource. With the global campaign to combat climate change, countries are now looking for alternative sources of energy to minimize greenhouse gas (GHG) emissions. In addition to being carbon-neutral, the use of biomass for energy reduces dependence on fossil fuel consumption, thereby contributing to energy security and climate change mitigation [11].

Thermochemical conversion is considered to be one of those technologies that can handle any type of feedstock due to severe treatment at high temperatures and in some cases at high pressure [12]. This is the reason why it is often considered as the ultimate solution for waste processing. The products resulting from this process can generally be divided into three parts - solid, liquid and gaseous. By varying the process parameters (temperature, pressure, etc.), the reaction medium (gas-N_2, CO_2, O_2, water/liquid solvent, etc.) and the catalysts, the proportions of the three fractions can be changed. In general, temperature and pressure range from 200°C to 1600°C and pressure from atmospheric to 400 bar. This gives an indication of a broad spectrum of the thermochemical conversion process.

The HTC process offers a unique way to recover materials from biomass waste that are otherwise difficult and costly to recover. This new technology is a very stable and simple process that simulates an accelerated process similar to natural coal formation.

The HTC process usually takes place between 180°C and 260°C, in the absence of air, at high pressures of 5-40 bar, using water as the reaction medium. The HTC process is very complex, consisting mainly of reactions such as decarbonylation, decarboxylation, dehydration, hydrolysis polymerization and recondensation [13]. These reactions lead to a solid phase consisting of hydrothermal coal (HC) with properties similar to fossil coal, a liquid phase in which valuable chemicals such as furfural (FF) and hydroxymethyl furfural (HMF) can be found; and a gas phase consisting mainly of CO, CO_2 mainly from decarboxylation reactions. Also, the use of a suitable catalyst can greatly influence the yield in HC as well as other valuable chemicals present in the liquid and gas phases.

Depending on the temperature under saturated pressure conditions, biochar [14,15], bio-oil and gaseous products such as CO, CO_2, CH_4 and H_2 [16] are the main products of a hydrothermal process below 250°C, at 250~400°C and above 400°C, respectively. Therefore, the hydrothermal process at each temperature range is called hydrothermal carbonization (HTC), hydrothermal liquefaction (HTL) and hydrothermal gasification (HTG), respectively. The carbon produced from the HTC process has a higher C content than that produced from dry processes [17], and the reaction temperature, pressure, residence time, and water-biomass ratio are reportedly the main parameters that determine product characteristics [14,17,18].

The solid product from the HTC process is the hydrothermal carbon, which had a wide range of environmental applications which are presented in Fig. 1.

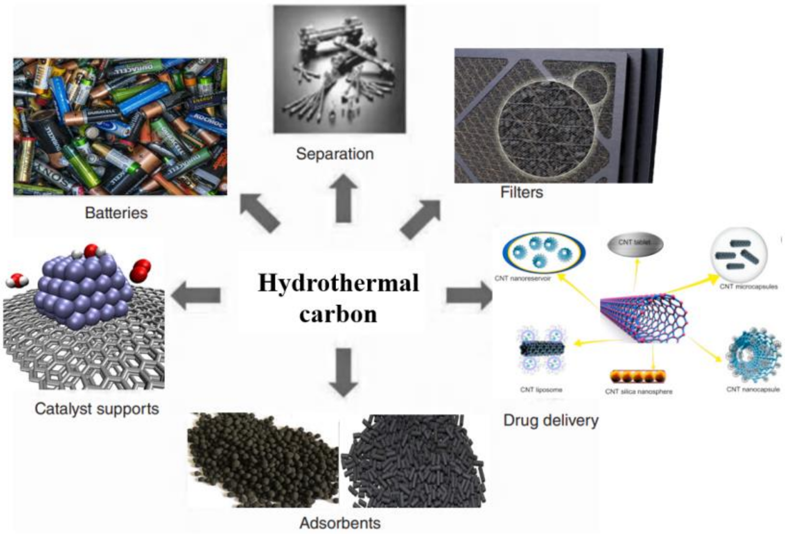


Fig. 1. Applications of hydrothermal carbon

Contamination of water with organic pollutants or heavy metals has attracted significant attention because of their high toxicity and non-degradability. Among their applications, porous carbon materials derived from sustainable resources represent an environmentally friendly and efficient way to adsorb pollutants from water. Several studies have reported their ability to adsorb both organic [19-21] and inorganic molecules [22-24].

In this paper, we prepared and characterized eco-materials obtained from biomass waste (grape stems) via HTC process with potential applications for environmental protection.

2. Materials and methods

Preparation of eco-materials

To obtain hydrothermal carbon eco-materials from grape stems (HTC-CS) a quantity of 30g of dry raw material (CS) was used, mixed with 300g of distilled water to obtain a mass ratio of 1:10. The mixture was loaded in a dynamic autoclave, operated at 220°C and the reaction time was varied from 1h to 6h and finally 12h. Stirring of 300rpm was used and the autoclave time to reach 220°C is ~2.5h. After completion of each reaction time, the autoclave was allowed to cool before opening. Three phases were obtained following the hydrothermal process:

- gaseous phase which is evidenced when the autoclave is opened; it mainly consists of small molecules such as CO, CO_2, CH_4.
- The liquid phase which was separated from the solid phase by filtration using a Buchner funnel, it was put in the refrigerator for future analysis.
- The solid phase was washed with hot distilled water several times until the wash water remained clear and up to neutral pH.

HTC derived eco-materials were dried at 80°C to constant mass and deposited in the desiccator to avoid hydration of the material with water molecules from the air.

Characterization of eco-materials.

Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) (Interspec 200-X Spectrophotometer, Interspectrum, Tõravere, Estonia) was used to characterize the raw material (CS) and the HTC derived eco-materials. To determine the structure and morphology of the eco-materials, Scanning electron microscopy (SEM) coupled with energy-dispersive spectra EDS (QUANTA 450 FEG microscope, Eindhoven, The Netherlands), equipped with a field emission gun and a 1.2 nm resolution X-ray energy dispersive spectrometer, with a resolution of 133 eV) was used.

3. Results and discussions

FTIR-ATR analysis

Eco-materials obtained from grape stem waste by HTC process at 220°C, autogenous pressure, 300 rpm, residence time 1h, 6h and 12h were investigated structurally using FTIR-ATR and the spectra is presented in Fig. 2.

Following the analysis, it was found that grape stem waste raw material (CS) shows broad absorption peaks around 3287 cm^{-1} indicating the existence of hydroxyl groups of alcohols, phenol and carboxylic acids. The peaks observed at 2923 cm^{-1} can be attributed to C-H groups of aliphatic acids. Peaks around 1731 cm^{-1} can be attributed to C=O stretching vibrations. Peaks around 1589 cm^{-1} correspond to C=C stretching which can be attributed to the aromatic C-C bond of lignin. The structure of lignin can also be confirmed by the strong C-O band at 1031 cm^{-1}.

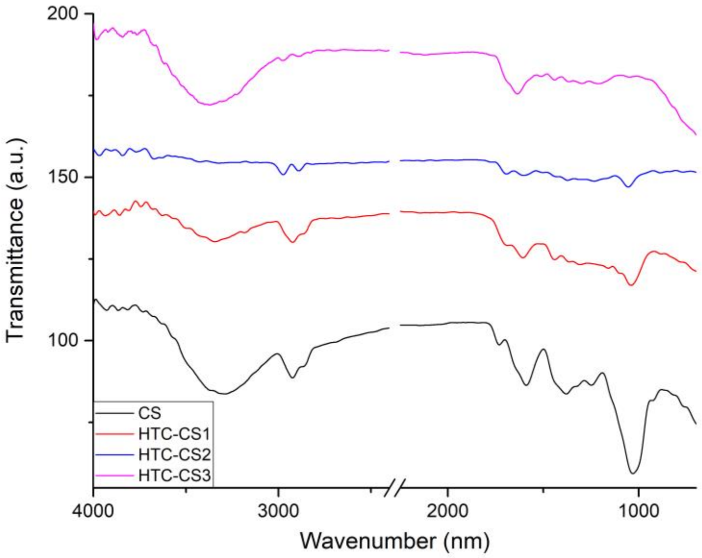


Fig. 2. FTIR analysis of the raw material (CS), HTC-CS1, HTC-CS2, HTC-CS3

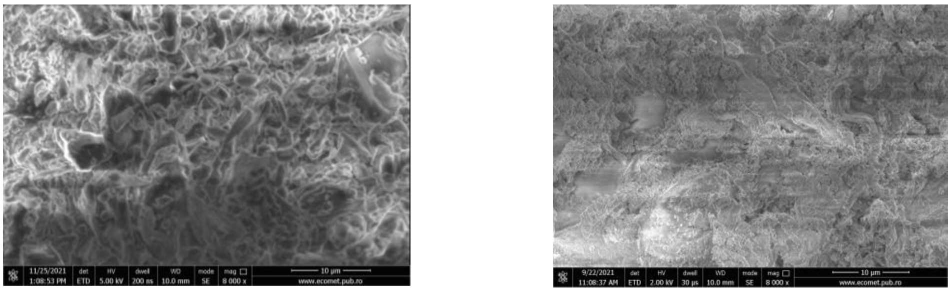
Similar results were presented by Farinella et al. [25] with grape bagasse generated in the wine production process and by Miralles et al. with grape stalk waste [26].

It was observed that in the case of HTC-CS1 and HTC-CS2 materials that the HTC process induced further broadening and decreasing intensity of the O-H stretching of the hydroxyl groups at 3700-3200 cm^{-1} due to the loss of hydrogen [27]. For the HTC-CS3 material the characteristic peak for the O-H remained wide and with a high intensity, suggesting that after 12h reaction time the surface of the materials is highly functionalized with -OH groups, that are responsible for the retention of many different pollutants from waters [28]. In addition, it was observed that for all the HTC treated materials, the transmission intensities at 1740-610 cm^{-1} arising from C=O stretching of ketones and other carbonyl structures are reduced after a higher reaction time of the HTC process at 220°C [29].

Furthermore, the decline of the peak at 1031 cm^{-1} e the C-O and C-O-C stretching, characteristic for the anomeric region of cellulose-like structures, indicates that both decarboxylation and dehydration occurs, as suggested by the van Krevelen diagram [30].

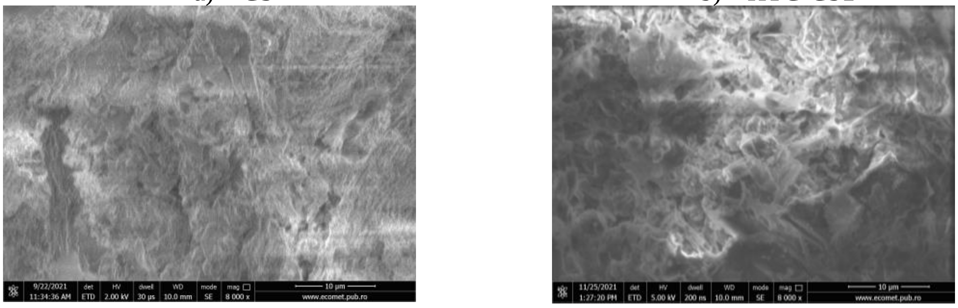
SEM-EDS analysis

Fig. 3 shows the SEM images of the raw material (CS) and the eco-materials (HTC-CS1, HTC-CS2, HTC-CS3) obtained via HTC, that is a process in which nanostructures are created in the carbonized material increasing its adsorption capacity considerably [31]. The SEM images of the raw biomass reveal a relatively heterogeneous surface structure typical for lignocellulosic biomass [32]. Carbonization disrupts the smooth structure of the biomass, creating cracks and pores on the biochar surface and fragmentation of particle (smaller and spherical particles) with increase of reaction time. The samples obtained via HTC at 220°C presented structures similar to those reported and illustrated by other authors [33,34]. The micrographs of the samples did not show sugar crystals probably because most of the sugars were hydrolyzed and dissolved [35]. In the b) c) and d) images shown in Fig. 3, it can be observed a disorganization in the particles, indicating that almost all the hemicellulose was removed. These results indicated that the solid residue was depleted in hemicellulose, which agrees with the FTIR analysis.



a) CS

b) HTC-CS1

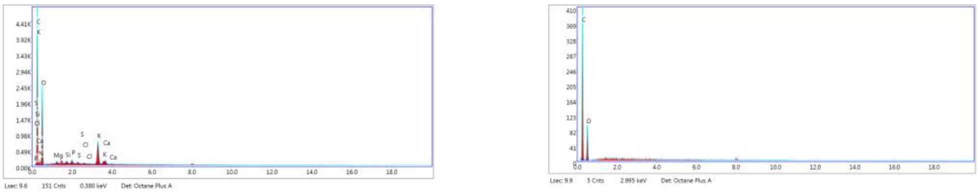


c) HTC-CS2

d) HTC-CS3

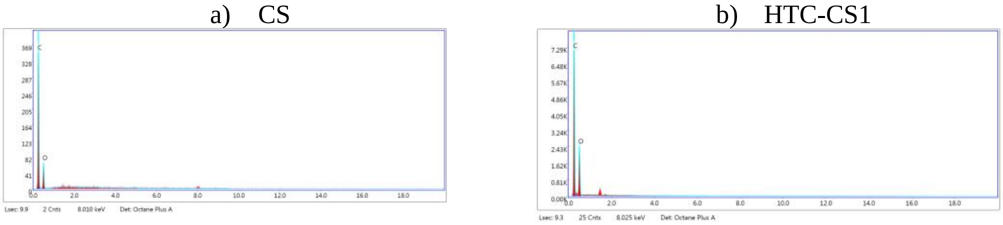
Fig. 3. SEM images at 8000x for a) CS, b) HTC-CS1, c) HTC-CS2 and d) HTC-CS3

The composition of the CS and HTC derived eco-materials is presented in Fig 4. From the EDS analysis it is indicates that the CS composition (Fig. 4. a)) consists of C (50.9%), O (41.02%), N (5.15%), Mg (0.27%), P (0.25%), Si (0.15%), S (0.1%), Cl (0.06%), K (1.79%), Ca (0.31%) while for the HTC derived eco-materials the composition mainly consists of C and O. For HTC-CS1 the composition consists of 67.69% C and 32.31% O (Fig. 4. b)), for HTC-CS2 73.6% C and 26.4 %, and for HTC-CS3 64.87% C and 35.13% O. This information suggests that for the HTC-CS1 and HTC-CS2 eco-materials the water-soluble compounds were dissolved and transferred into the liquid phase obtained in the process, thus leaving only C and O as the main elements found in the composition of these materials. With increase in reaction time, it was observed that the O content increases for the HTC-CS3 eco-material, which corelates with the information obtained from the ATR-FTIR analysis.



a) CS

b) HTC-CS1



c) HTC-CS2

d) HTC-CS3

Fig. 4. EDS analysis for a) CS, b) HTC-CS1, c) HTC-CS2 and d) HTC-CS3

4. Conclusions

Eco-materials were obtained from valorization of grape stems waste via hydrothermal carbonization process at 220°C, 1:10 CS:H_2O weight ratio, and 3 different reaction times, 1h, 6h, and 12h respectively. The eco-materials were characterized in terms of structural and morphological properties using ATR-FTIR and SEM-EDS analyses. When compared to the raw material (CS), the eco-materials HTC-CS1, HTC-CS2, and HTC-CS3 presented improved physical and chemical properties. The ATR-FTIR analyses showed that the HTC process led to the presence of a surface charged with different functional groups (hydroxyl, carbonyl) for the 3 eco-materials. Also, from the SEM-EDS analyses it was observed that the composition for these eco-materials consist mainly of high content of C (above 60% for the materials) and O (20-30%), while for the CS sample the C content was lower, and the sample also contained other trace elements like S, P, Mg, Ca and K.

The improved properties of the eco-materials obtained via HTC suggest that they can be used in different environmental applications. These eco-materials will be further tested in water depollution applications.

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