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Research Paper

Comparative Study of Biochar and Hydrochar Derived from Agricultural Waste: Characterization and Chemical Properties

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Abstract

Carbonaceous substances, including hydrochar and biochar, have been produced from agricultural residue via hydrothermal and pyrolysis processes. The surface morphology of the materials was assessed using FTIR, XRD, BET, and SEM techniques. The identification of diffraction peaks at approximately 22° by XRD analysis suggested the existence of carbonaceous material. This is confirmed by FTIR analysis, which identifies cellulose vibration at 2931 cm^{-1}. The results of the SEM analysis revealed that BC-Rice husk and HYC-Rice husk are heterogeneous in shape and surface area; conversely, HYC-Rambutan and Duku have a uniform, ball-like shape and aggregate. This is further corroborated by surface area data, which indicates that the material composed of rice husk has a larger surface area than the material composed of fruit peel.

Keywords

Carbon Based Materials, Biochar, Hydrochar, Fruit Peel, Agricultural Waste

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1. INTRODUCTION

Biochar is mostly generated through thermochemical processes, such as pyrolysis and hydrothermal carbonisation. Gasification, torrefaction, and combustion, among other processes, are not suited for the creation of biochar. Gasification, as demonstrated by Jeyasubramanian et al. (2021), produces solid products such as char and soot particles, which account for 25-37% of the total yield. Nevertheless, the char can have a maximum ash content of 60% and exhibits a limited surface area (Zhu et al., 2019). The primary outputs of the gasification process, namely syngas and methane, are utilised for the purpose of energy production (Hamidzadeh et al., 2023). The attributes of gasification render it an imprudent option for biochar generation. Meanwhile, torrefaction is a preliminary process to pyrolysis that enhances the manageability of biomass (Tomczyk et al., 2020) and boosts its energy density (Zhang et al., 2019). Similar to torrefaction, combustion does not generate any biochar. The primary emphasis of combustion research is mostly on energy generation rather than the production of carbonaceous material (Awogbemi and Von Kallon, 2023).

During pyrolysis, biomass experiences both physical and chemical transformations as a result of heat in the absence of oxygen or with limited levels of oxygen. This process yields biogas (in gaseous form), bio-oil (in liquid form), and biochar (in solid form) (Palapa et al., 2021; Song et al., 2022). Pyrolysis parameters, including temperature, heating rate, and pyrolysis time (Patel and Panwar, 2023), can vary significantly, resulting in products of different qualities.

Pyrolysis has been categorised into different types, including slow, fast, flash, vacuum, intermediate, and hydro pyrolysis, based on operating factors such as heating rate and residence time (Wijitkosum, 2022). Slow pyrolysis is a commonly employed pyrolysis method that yields a significant amount of biochar (Zhang et al., 2019). According to Hamidzadeh et al. (2023), the output yield of oil in fast pyrolysis is increased by reducing the residence time and increasing the heating rate (Suarez et al., 2023). According to Potnuri et al. (2023), this approach can obtain an oil output of up to 75%, which is half the calorific value of traditional oils. Flash pyrolysis is a variant of fast pyrolysis that is employed to obtain a substantial amount of liquid product along with aerosol. This technique has been documented by Yihunu et al. (2019). Vacuum pyrolysis is a process that operates under reduced pressure, similar to slow pyrolysis. However, it differs in that it minimises the temperature at

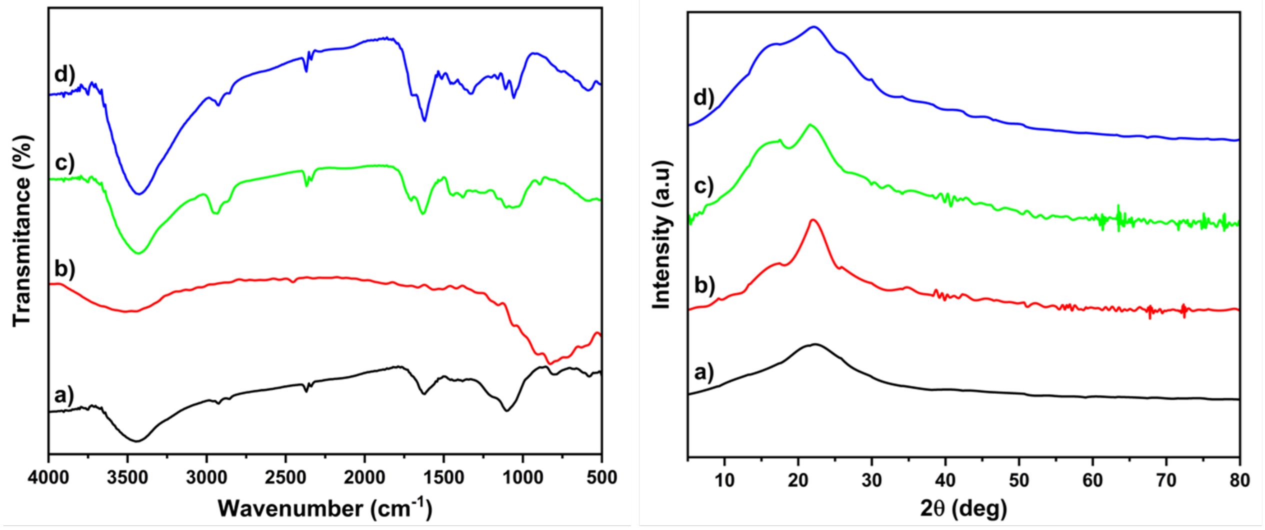

Figure 1. FTIR Spectra and XRD Pattern of BC-Rice Husk (a), HYC-Rice Husk (b), HYC-Duku (c), and HYC-Rambutan (d)

which biomass decomposes and the time it stays in a vapour state (Kambo and Dutta, 2015).

Hydrothermal carbonisation (HTC) is becoming increasingly popular since it requires less energy, eliminates the need for pre-drying, and produces hydrochar that may be utilised for wastewater treatment, solid fuel, and soil improvement (Mohadi et al., 2022). Hydrothermal carbonisation (HTC) is a thermochemical technique that involves the carbonisation of biomass at temperatures below the critical point and under self-generated pressure, with water serving as the reaction media. The primary process that governs HTC is hydrolysis (Kambo and Dutta, 2015; Fu et al., 2019). The optimal temperature for maximising char production is approximately 250°C. The crucial factors for HTC include the type of feedstock, operating temperature, residence duration, pressure, heating rate, pH of the reaction medium, type and concentration of catalyst, and substrate concentration . Increasing the temperature of HTC resulted in a decrease in the ash content and yield of CH hydrochar (Panahi et al., 2020). In addition, the HTC's low-temperature conditions caused hemicellulose to partially breakdown and cellulose and lignin to partially dissolve, resulting in the formation of CH hydrochar. In addition, a rise in temperature led to a reduction in the molecular O/C and H/C ratio in coconut biomass. Although it has a higher conversion efficiency than other thermal pre-treatments such torrefaction, gasification, and pyrolysis, its industrial feasibility is still unfavourable. During the HTC process, the reactor temperature and pressure are significantly elevated, resulting in a highly intricate, hazardous, and expensive procedure (Jeyasubramanian et al., 2021). Because of this, in this research a comparison was made between biochar made using the pyrolysis method and hydrochar made using the hydrothermal carbonization method. comparison of surface area, functional groups and surface formation of carbon materials.

2. EXPERIMENTAL SECTION

The materials was prepared by pyrolysis and Hydrothermal carbonization method. Rice husk, Rambutan peel and Duku Peel was obtained from waste product, washed and dried for three repetitions. The rice husk was dried at 60°C prior pyrolysis treatment. The pyrolysis treatment was conducted in furnace at constant N_2 flow for two hours at 500°C with reactor heating rate 10°C/min. Then, the reactor was cooled down to room temperature. Rambutan peel, rice husk and Duku peel was prepare by Hydrothermal carbonization using small hydrothermal reactor and heated at 200°C with reactor heating rate 5°C/min for 12 hours. Then, the reactor was cooled down to room temperature. The raw materials was characterized by XRD, FTIR, SEM, and BET surface area.

3. RESULT AND DISCUSSION

Figure 1 displays the FTIR spectra (A) and XRD pattern (B) of BC-Rice Husk, HYC-Rice Husk, HYC-Duku, and HYC-Rambutan. BC-Rice Husk and HYC-Rice Husk exhibited modest variations in their respective functional groups. The absence of the peaks at 1515 and 1611 cm^{-1} in the HYC-Rice husk sample indicates that there are no C=C bonds present in the aromatic rings of lignin. However, these peaks are observed in the BC-Rice husk sample. The peaks seen at 1515 and 1611 cm^{-1} are attributed to the presence of C=C bonds in the aromatic rings of lignin. On the other hand, the peak at 1161 cm^{-1} corresponds to the stretching vibration of C−O bonds in cellulose (Hamidzadeh et al., 2023). The presence of alcohol groups in cellulose, hydroxyl groups in water, and phenol in lignin can be identified by the stretching vibration of the −OH bond, which occurs in

Table 1. Materials Surface Properties

Materials	Surface Area (m^2/g)	Pore Volume (cc/g)	Pore Size (nm)
BC-Rice Husk	72.2517	0.0602	3.334
HYC-Rice Husk	72.206	0.154	2.860
HYC-Duku	22.635	0.044	2.769
HYC-Rambutan	34.087	1.886	2.769

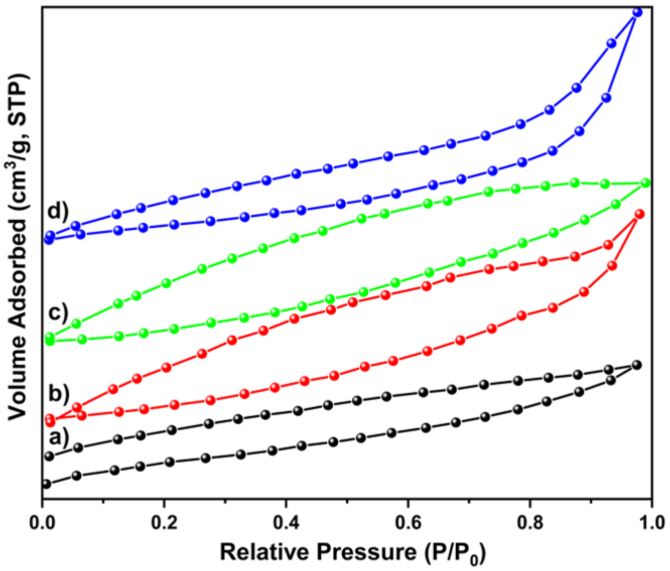

Figure 2. N_2 Adsorption-desorption Isotherm of BC-Rice Husk (a), HYC-Rice Husk (b), HYC-Duku (c), and HYC-Rambutan (d)

the range of 3400-3300 cm^{-1}. The peaks observed at around 1701, 1382, and 1035 cm^{-1} can be attributed to the presence of C=O bonds in cellulose and lignin, COOR bonds, and SiO_2 stretching vibrations, respectively. The spectra of HYC-Duku exhibited vibrations at 3425 and 1627cm^{-1}, indicating the presence of hydroxyl and carbonyl groups in both materials, specifically in the alcohol group. Additionally, a vibration was observed at 2931 cm^{-1}, suggesting the existence of C−H cellulose (Amri et al., 2023). The intense vibration at a wavenumber of 1635 cm^{-1} signifies the presence of the C=O functional group in the fundamental amide vibrations. Furthermore, a vibration at a frequency of 1442 cm^{-1} is indicative of C=C stretching in aromatic compounds. The spectra of HYC-Rambutan displayed vibrations at 2953 cm^{-1}, which are attributed to the C−H group. Additionally, a peak at 1,683 cm^{-1} was observed, which is connected with the C−O group. Furthermore, a peak at 1,013 cm^{-1} was observed, which is characteristic of the C=C group commonly found in cellulose compounds included in HYC materials. Therefore, XRD analysis reveals a broad spectrum of vibrations in all materials, demonstrating the amorphous nature of the carbon material. The presence of a broad peak at 23° in the 2θ reflection 002 is characteristic of amorphous silica and indicates the absence of a crystalline structure.

The BC-Rice Husk, HYC-Rice Husk, HYC-Duku, and HYC-Rambutan raw materials exhibited a comparable N_2 adsorption-desorption isotherm pattern (Figure 2). These findings suggest that surface area analysis can also provide measurements of pore volume and pore diameter. The isotherm patterns of BC-Rice Husk, HYC-Rice Husk, HYC-Duku, and HYC-Rambutan exhibit the distinctive Type III, indicating a weak interaction between active sites and nitrogen. Moreover, the affinity of the molecules is higher. The presence of a type III isotherm pattern suggests that the material exhibits a low adsorption energy (Mohadi et al., 2022). Table 1 presents BET measurement results for both adsorbents, including surface area, pore volume, and pore diameter. According to Table 1, rice husk was found to be the raw material that resulted in a large surface area. This research postulated that a greater concentration of lignocellulose leads to an increase in the size or number of pores or active sites in the substance.

As illustrated in Figure 3(a), the HYC-Rambutan exhibits a surface morphology characterised by particles that are more uniform in size and round, resembling a ball. Additionally, the surface is gritty. The aforementioned phenomenon arises from the lignin and cellulose compounds in rambutan peels undergoing degradation throughout the carbonisation procedure. The irregular shape and tendency towards heterogeneity of the HYC-Duku depicted in Figure 3(b) are consequences of the hydrothermal carbonisation treatment administered, which induces deaggregation, or the disintegration of the particles. The HYC-Rice husk surface morphology depicted in Figure 3(c) exhibited a pointed, irregular shape. As shown in Figure 3(d), the morphology of BC consisted of small pores interspersed with large openings that were cylindrical in shape. Conversely, the morphological characteristics of BC resulting from low-temperature pyrolysis (300-350°C) led to incomplete pore development and a lack of uniformity in the pore structure of BC-Rice husk.

4. CONCLUSIONS

The FTIR characterization of biochar and hydrochar produced from a variety of waste materials, including fruit shells and husks (rambutan and duku), reveals the presence of functional group peaks originating from lignocellulose.

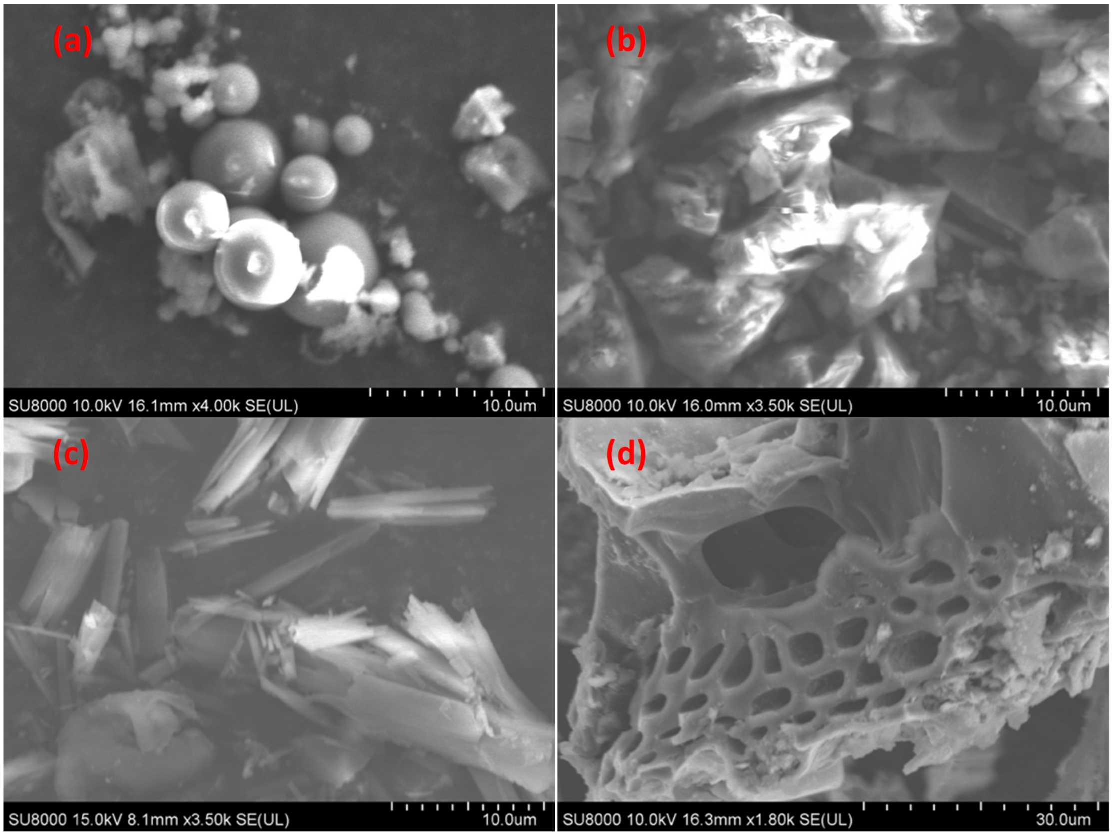

Figure 3. Mophological of HYC-Rambutan (a), HYC-Duku (b), HYC-Rice Husk (c), and BC-Rice Husk (d)

In addition, the amorphous nature of the carbon material is confirmed by XRD analysis, which reveals that all substances exhibit a broad range of vibrations. SEM surface analysis reveals that the husk contains cavities that can accommodate biochar and hydrochar. This is further corroborated by surface area data, which indicates that the material composed of rice husk has a larger surface area than the material composed of fruit rind.

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