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Preparation & Characterization of Biochar from Rice Husk by Pyrolysis Method

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ABSTRACT

In nations where rice cultivation is prevalent, the responsible management of substantial quantities of rice waste is necessary to mitigate potential environmental concerns. This study aims to produce biochar from rice husks through the pyrolysis method, specifically without using inert nitrogen gas by utilizing a low-oxygen pyrolysis technique. The study employed many experimental parameters, including the process temperature, residence time, and heating rates. The FTIR results revealed a decrease in the stretching of O-H bonds in rice husk biochar at elevated temperatures (500°C), suggesting the degradation and disintegration of cellulose, hemicellulose, and lignin. Various bands associated with hydroxyl, carboxyl, aromatic bonds, amine groups, and other aromatic compounds were observed at lower pyrolysis temperatures. The observed functional group in rice husk biochar closely resembles the outcomes obtained from commercial biochar, except for the absence of C=O stretching. It was seen that the biochar structure exhibited an increase in pore size with increasing temperature. At higher temperatures, a decrease in pore size was observed on the surface of the biochar. It has been observed that when subjected to elevated pyrolysis temperatures, commercial biochar has a greater pore size compared to rice husk biochar, albeit fewer in number than the latter. Based on the findings, it can be inferred that the most favourable conditions for the rice husk biochar production by the low oxygen pyrolysis method are attained at temperatures of 300°C for durations of 60 and 90 minutes, as well as at 400°C for 90 minutes.

Keywords: *Rice husk, Biochar, Double crucible method, Pyrolysis*

1. INTRODUCTION

Over 2 million tonnes of agricultural waste, including rice husks, coconut shells, and empty fruit bunches, are produced annually in Malaysia. When this material accumulates in landfills, it creates environmental issues by contaminating the groundwater and polluting the air. Pyrolysis is the most common and effective process for turning rice husks into biochar (Liu & Zhang 2009). Rice husk, which makes up about 20% of the weight of the rice, is made up of cellulose, lignin, silica, and moisture (Singh Karam et al., 2022). The properties of rice husk biochar (RHB) are influenced by various parameters such as heating rate, residence time, and pyrolysis temperature.

High-purity nitrogen is used to purge the system of oxygen before pyrolysis. Before the pyrolysis process starts, the inert gas must be purged into the pyrolysis system to remove the unwanted air or oxygen. This was to prevent oxidation from occurring during high temperature pyrolysis process. However, a complicated experimental setup is needed to produce biochar using a nitrogen medium. Another alternative taken in this research is using the double crucible method to prevent intrusion of oxygen into char without using nitrogen gas. In this method, the ground rice husk was placed in a smaller alumina crucible covered with an alumina lid. The small crucible containing ground rice husk is put in a bigger alumina crucible. The gap inside the bigger crucible is filled up by raw rice husk to reduce oxygen inside the crucible and finally, the bigger crucible is covered with a lid. In this method, the bulk volume of air inside the bigger crucible is replaced by raw rice husk, again when the crucible is heated up; firstly the volume of air inside the crucible is expanded and a portion of the air comes out from both the small and bigger crucible; secondly, the volatile part of rice husk is reacted with oxygen and it is assumed that the entire amount of oxygen is exhausted from the crucible during the heating process.

In this study, the morphology surface, functional group identification and pyrolysis parameters are significant in identifying the characteristic rice husk biochar produced by slow pyrolysis using the double crucible method as soil amendment application.

2. METHODOLOGY

2.1. Materials

The raw materials of this study are rice husks collected from Perlis, Malaysia. The rice husk was initially thoroughly cleaned of any contaminants using tap water before being allowed to dry naturally. After drying, the rice husk was ground into powder using a grinder.

2.2 Method

The pyrolysis process was done using the double crucible method. In this method, the ground rice husk was placed in a small alumina crucible covered with an alumina lid. Subsequently, the small crucible will be placed into a bigger alumina crucible. Thus, a gap will form between the smaller and larger crucibles. This gap is filled with ungrounded rice husk and the larger crucible is covered with a lid (Figure 1). Next, the slow pyrolysis process of turning rice husk into char was carried out using a high-temperature box furnace at different temperatures (300, 400 and 500°C), residence times (60, 90, 120 mins) and constant heating rates (10°C/min).

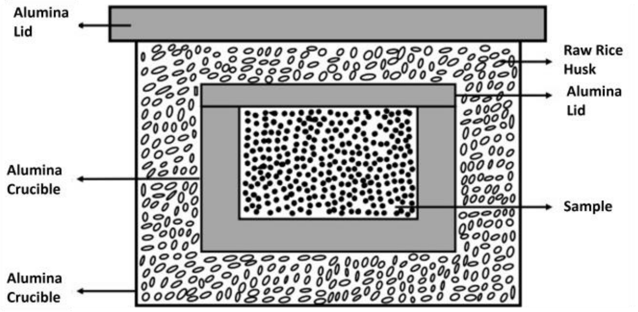


Figure 1. Double crucible setup.

For the characterization process, the presence of the functional group in the sample was examined using the Fourier Transform Infrared Spectroscopy (FTIR) technique. The scanning electron microscope (SEM) has been used to examine the morphological characteristics of the samples.

3. RESULTS & DISCUSSION

3.1. Functional Group Identification

The analysis of the rice husk sample (Figure 2) revealed several important findings. The sample was found to contain absorbed water, indicating its hydrophilic nature. It also contained an alkene functional group, as evidenced by the C-H stretching vibration. Aromatic groups in hemicellulose and lignin were identified through C=O stretching peaks.

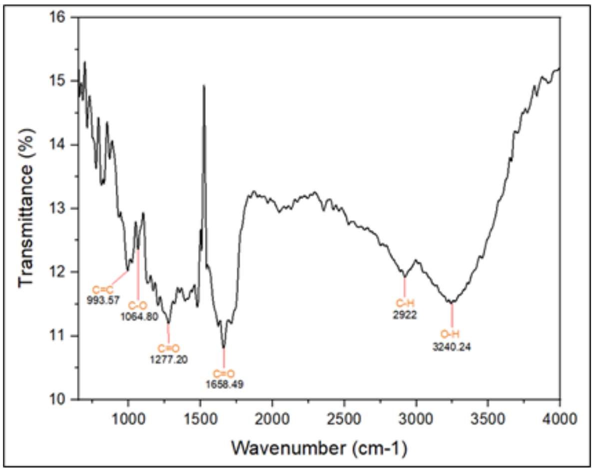


Figure 2. FTIR spectrum for rice husk sample.

Through CO group vibration, the presence of lactones associated with hemicelluloses was observed. The sample exhibited C-O stretching, potentially from primary alcohols or Si-O-Si stretching due to its high silicon content. Lastly, the presence of aromatic compounds, primarily from lignin, was indicated by the C=C bending vibration, contributing to the husk's structural rigidity.

Figure 3 illustrates the FTIR spectra obtained under varying temperature and residence time conditions in the absence of oxygen. The temperature is the primary factor influencing the surface functional groups of biochar (Yaashikaa et al., 2020). Table 1 provides detailed information about the functional groups and their corresponding peak positions.

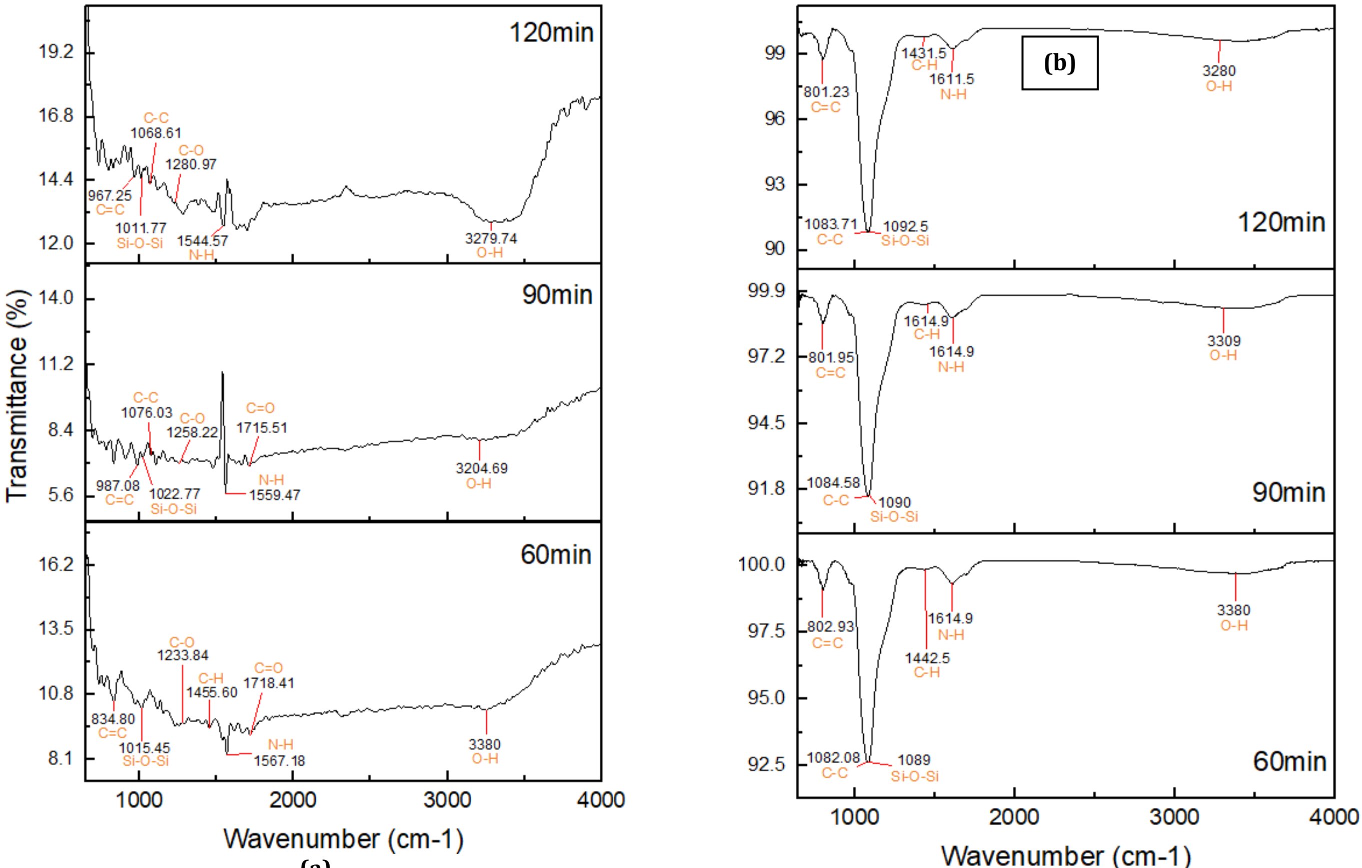
Several important findings occurred after the sample's characterization. The O-H stretching peak between 3252.94 cm−1 and 3380 cm−1 suggests the existence of water produced from hydroxyl groups. This peak decreases with increasing temperature and disappears at 500°C, indicating the breaking of hydroxyl bonds and the loss of hydrogen and oxygen atoms. The C=O stretching vibration peak indicates the presence of aromatic compounds and decreases in intensity with higher temperatures. The vibration of C=O stretching in aromatic rings is only observed at 300°C and its disappears at 400°C and 500°C due to thermal degradation and significant loss of oxygen atoms.

The N-H bend (1550 cm^{-1} to 1650 cm^{-1}) peak is present across all temperature ranges and is attributed to nitrogen-containing compounds naturally found in rice husks. The peak in the range of 1430 cm^{-1} to 1470 cm^{-1} indicates the absence of methyl C-H asymmetric stretching at high temperatures, suggesting the decomposition of C-H bonds and the release of hydrogen in volatile compounds.

FTIR spectral analysis of rice husk biochar reveals the presence of aromatic C=C stretching, C=O stretching of conjugated quinones and ketones, and symmetric C-O stretching. As the pyrolysis temperature increases, C-O bonds' symmetric and asymmetric stretching diminishes, suggesting the degradation and depolymerization of cellulose, hemicelluloses, and lignin.

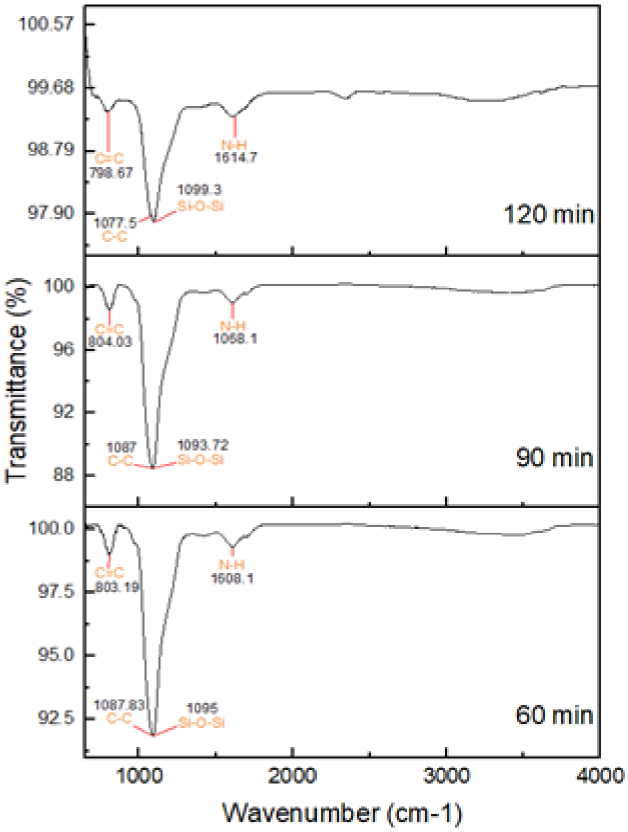
However, the aromatic compounds with C-C stretching (peak between 1020 cm^{-1} to 1090 cm^{-1}), are predominantly present under all tested parameters due to the presence of carbon-based compounds and the preservation of the original organic carbon framework of rice husk. The C-C bonds present in the organic compounds of rice husk are significantly retained in the resulting biochar.

Si-O-Si antisymmetric stretching and C=C bending in rice husk biochar can be attributed to the presence of silica and carbon-based compounds in rice husk. In addition, the retention of C=C bending is influenced by the C-C bonds present in rice husks.



(a)

(b)



(c)

Figure 3. FTIR spectrum of rice husk biochar at (a) 300°C, (b) 400°C and (c) 500°C with different residence time.

Table 1 Functional groups observed in the rice husk biochar sample

Wave number (cm-1)	Vibration characteristics	300°C			400°C			500°C		
		60min	90min	120min	60min	90min	120min	60min	90min	120min
3400-3200	O-H stretching	3252.94	3204.69	3279.74	3380	3309	3280	-	-	-
1740-1700	C=O stretching	1718.41	1715.51	-	-	-	-	-	-	-
1650-1550	N-H bend	1567.18	1559.47	1544.57	1614.9	1614.9	1611.5	1608.1	1608.1	1614.7
1470-1430	Methyl C-H asymmetric	1455.60	-	-	1442.5	1456.5	1431.5	-	-	-
1310-1250	C-O stretching	1233.84	1258.22	1280.97	-	-	-	-	-	-
1090-1020	Primary amine of C-C stretch	-	1076.03	1068.61	1082.08	1084.58	1083.71	1087.83	1087	1077.5
1100-1000	Si-O-Si antisym stretch	1015.45	1022.77	1011.77	1089	1090	1092.5	1095	1093.72	1099.3
1000-625	C=C bending	834.80	987.08	967.25	802.93	801.95	801.23	803.19	804.03	798.67

3.2. Surface Morphology

Figure 4 indicates that initially, the raw rice husk does not exhibit any pores. This can be attributed to the presence of tissue that has not undergone devolatilization and the incomplete development of pores.

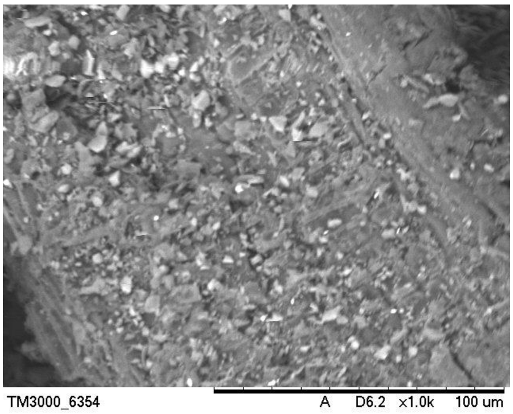
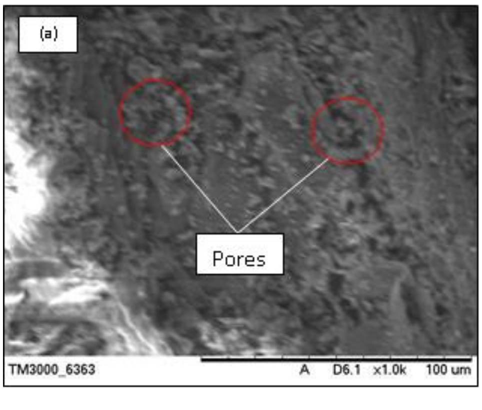
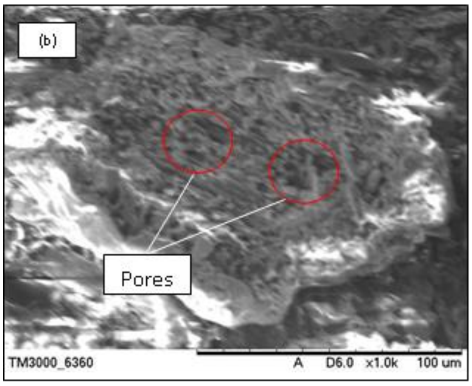


Figure 4. SEM image for raw rice husk at 1000x magnification.

The surface of raw rice husk appears congested, rigid, and densely formed due to its layered structure and the compact nature of the outermost layer called the hull. Despite its compactness, the surface of raw rice husks appears rough and uneven due to densely packed plant cells, fibrous structures, and lignocellulosic materials.

The SEM image of rice husk biochar in Figure 5 reveals the presence of dark regions, indicating pore spaces within the particles. When heated to 500°C for pyrolysis, rice husk biochar transforms into a honeycomb-like structure with interconnected cylindrical holes and larger holes, resulting in large pores on the surface. At lower temperatures of 300°C and 400°C (Figure 5(a) & 5(b)), the biochar surface exhibits irregular globular shapes and numerous small-sized pores. These changes in morphology are attributed to the loss of volatile organic compounds during the pyrolysis process, which leads to increased porosity in rice husk biochar (Asadi et al., 2021).





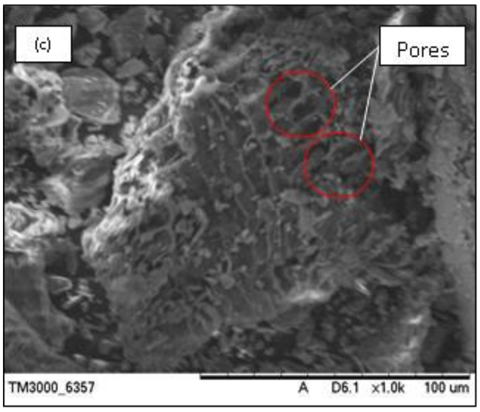


Figure 5. SEM image of rice husk biochar (1000x magnification) with various pyrolysis conditions (a) 300°C, 60 min, (b) 400°C, 90 min and (c) 500°C, 120 min.

The temperature expansion during biochar production improves pore characteristics (Yaashikaa et al., 2020). In contrast, small-sized pores (50µm) at lower pyrolysis temperatures are present due to the incomplete decomposition of organic components such as lignin and cellulose derivatives. The release of volatile compounds such as silicon dioxide (SiO_2) from the rice husk during pyrolysis can also lead to the formation of small-sized pores, as these volatiles accumulate within the biochar matrix at lower temperatures (Rashid & Duta., 2020).

3.3. Characterization of Commercial Biochar

Commercial biochar is a type of charcoal produced using pyrolysis and inert gas, such as nitrogen. Figure 6 and Table 2 show the FTIR spectrum of commercial biochar, indicating the presence of different functional groups. Peaks at 3240.24 cm^{-1} suggest organic O-H stretching, potentially due to retained water or hydroxyl groups. Both commercial biochar and rice husk biochar exhibit an N-H bend. The presence of a peak at 1472.95 cm^{-1} indicates the existence of organic compounds with methyl groups.

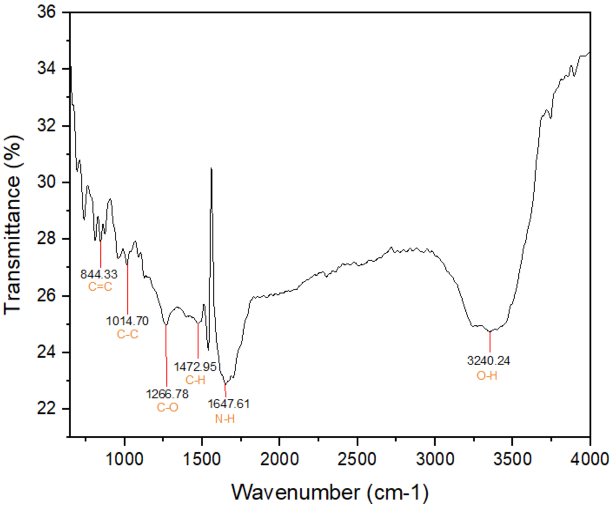


Figure 6. FTIR spectrum of commercial biochar.

Table 2 Functional groups observed in commercial biochar sample

Wave number	Functional group
3240.24cm^{-1}	O-H stretch, strong appearance
1647.61cm^{-1}	N-H bend
1472.95cm^{-1}	Methyl C-H asymmetric
1266.78cm^{-1}	C-O stretching
1014.70cm^{-1}	The primary amine of C-C stretch
844.33cm^{-1}	C=C bending, strong appearance, alkene

The peak around 1266.78 cm^{-1} suggests C-O stretching vibrations in commercial biochar compared to rice husk biochar produced at high pyrolysis temperatures. The transmission peak at 1014.70 cm^{-1} suggests the presence of aromatic compounds with C-C stretching.

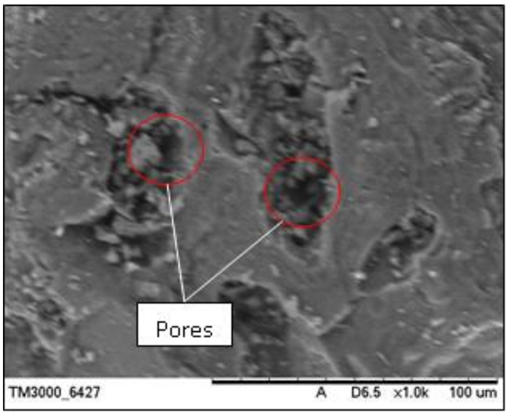


Figure 7. SEM image of commercial biochar at 1000x magnification.

Figure 7 shows pores in the structure as well as white spots that are scattered throughout the surface. The pores on the surface of the commercial biochar are less in number but greater in size. These observations are related to the pyrolysis's release of volatile substances, especially the breakdown of the lignin component, which results in a rough texture (Ma et al., 2016). The use of higher temperatures during the pyrolysis process may cause the commercial biochar's greater porosity when compared to rice husk biochar. The formation of pores in biochar is additionally enhanced by the rise in temperature, which leads to better pore characteristics.

High temperatures during pyrolysis lead to the breakdown of complex organic compounds present in the biomass, such as cellulose, hemicellulose, and lignin. The thermal decomposition of these materials releases gases, leaving behind a carbon-rich structure. This process contributes to the development of a porous network within the biochar. The increase in temperature induces structural changes in the biomass, leading to the development of an expanded, porous structure. The chemical reactions that occur during pyrolysis at higher temperatures can promote the formation of micropores, mesopores, and macropores, contributing to an overall improvement in pore characteristics.

4. CONCLUSION

This study investigated the effects of the pyrolysis process on rice husk to produce porous biochar for soil amendment. Different temperatures, residence times, and heating rates were used in the slow pyrolysis process. The enhancement of pore characteristics in biochar with increasing temperature during pyrolysis is a result of various processes, including thermal decomposition, and structural changes. Lower temperatures resulted in the presence of various bonds and compounds, while at higher temperatures, some of these peaks diminished. Additionally, as the temperature increased, indicated the larger pores in the biochar structure. The biochar's pore structure enhanced water retention and plant accessibility in the soil. The study also found that using a double crucible method without nitrogen-inert gas produced rice husk biochar similar to commercial biochar.

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