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Characterization on Morphological and Bonding Behavior of Torrefied Biochar from Oil Palm Empty Fruit Bunch

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Abstract

This study is purposely generated to investigate the torrefaction process effects on surface morphology as well as bonding behavior of oil palm empty fruit bunch (OPEFB) to become torrefied OPEFB biochar as a potential renewable energy source. The analyses of morphology as well as the bonding behavior have been investigated using scanning electron microscope (SEM) and Fourier transformation infrared spectroscopy (FTIR). Moreover, both surface morphology and bonding behavior of the torrefied OPEFB biochar is significantly influenced by the degradation of the lignocellulose, hemicellulose, cellulose and lignin. SEM images showed the surface morphology of OPEFB after undergo torrefaction by which it was completely decomposed by initiating pores while the structure become flattened with almost left sharp edge compared to the raw OPEFB. The changes of presence functional groups before and after the torrefaction process were observed under certain wavelength which were C=O (1750-1680 cm^{-1}), N-H (3500-3100 cm^{-1}) and C-N (1350-1000 cm^{-1}). These functional groups determined the changes of functional groups as well as the wavelength whereby the degradation of hemicellulose, cellulose and lignin take place. The longer torrefaction process, biochar started to rupture due to longer period of thermochemical reaction process, and the FTIR spectrum proved that the weak bonds had diminished at this condition.

Keywords: *bonding behavior, oil palm empty fruit bunch, surface morphology, torrefaction*

1. Introduction

The fact that the energy sources like non-renewable energy especially fossil fuels is depleting day by day and environmental chaos brought by it such as acid rain, emission of greenhouse gases (GHGs) and global warming has led to public awareness towards a cleaner source of energy production using renewable energy sources. According to [1]-[2], constituents of renewable energy are solar, hydro, wind, geothermal and biomass. These energies could be an alternative to current non-renewable energy production which is more dependent on fossil fuel to cater the rise of energy demand. Among the entire alternative available, biomass present as one of the potential for energy regeneration purposes due to its abundance availability parallel to Malaysia as agricultural country.

In Malaysia, there abundance of agricultural crops such as oil palm residue, paddy residue, wood residue, coconut residue, and rubber residue [3]-[4]. During harvesting, some residues are left over on the field, for example OPEFB. These agricultural residues can be applied as alternative energy to substitute to fossil fuel and to solve the problem of energy crisis as well [5].

In producing energy from biomass sources, they need to undergo conversion process. Thermochemical as one of the biomass energy conversion process that converts biomass feedstock into gas, liquid or solid under controlled temperature and oxygen with a higher energy

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dense that makes it easier to transport and have a convenient combustion characteristic. Torrefaction or mild pyrolysis is the latest thermal treatment that gathered attention of researchers for its satisfactory results with different agricultural and forestry biomass [6].

Therefore, by taking torrefaction process as an advantage, this study seeks to examine the torrefaction effect on the morphology and bonding behavior of torrefied OPEFB biochar from mild to severe holding temperature conditions ranging from 200 to 300°C with 30, 60 and 90 minutes of residence time. It has been examined the morphology reaction conditions, bonding properties and potential product yield from the torrefied OPEFB biochar through SEM and FTIR. The technique was a simple, timely and reliable approach widely applied to simulate and examine the thermochemical biomass conversion processes such as torrefaction in the literature.

2. Materials and Methods

2.1. Sample Preparation

The raw OPEFB which contained lignocelluloses, oil and water was soaked into fresh water until became thoroughly wet for a certain period in order to remove the residual oil. Then, it was torn apart to lose the fibrous strands, then was washed with tap water, cleaned, sorted and dried for 24 hours under the sunlight. To minimize the moisture, it was then oven-dried at constant temperature at 80±5°C for 1 hour.

The OPEFB fibre was cut into length of approximately 3mm in order to get a better quality fibre before further treatment. The dried OPEFB fiber was grinding using domestic blender before undergoing screening using auto sieve shaker machine into three different sizes which were 250, 500 and 750µm. The purpose of grinding and screening was to obtain a desired sample scales without any contamination.

2.2. Torrefaction Process

Torrefaction process was conducted in an electrical furnace (muffle furnace of WiseTherm). The holding temperature was set at 300°C without the O_2, with varied residence time of 30, 60 and 90 minutes.

2.3. Sample Analyses

The morphological of the torrefied OPEFB biochar and raw OPEFB samples were conducted using SEM model JEOL JSM 6400 LV which was operated at 15kV. To examine the BET surface area of the torrefied OPEFB biochar, a quantachrome autosorb-1surface analyzer was used for better porosity measurement. The FTIR that takes place for bonding behavior had been done using Perkin–Elmer Spectrum (Perkin Elmer) aided by OMNIC software from Thermofisher Scientific. The wavelength that had been analyzed was from 4000-1500cm^{-1}.

3. Results and Discussion

3.1. Morphological Characterization of Torrefied OPEFB Biochar

Fig. 1 shows SEM images of raw and torrefied OPEFB biochar samples at 300°C, at various residence times. Fig. 1(a) illustrated the surface structure of raw OPEFB fibre at magnification of ×250 with an insert magnification at ×1500. The raw OPEFB fibre possessed a rigid surface with matrix layer like wax covering the entire fibre surface. This layer plays an important role to protect the plants as to counter the water loss like most plants do. From the SEM images observed, the cell walls of this biomass are thick, resulting in a high level of coarseness and rigidity.

The torrefied OPEFB biochar as observed in Fig. 1(b) with 30 minutes of residence time shows that the resulted biochar had less rigid surface and some physical changes occurred. Rough fibre surface is clearly seen due to the pretreatment process. Another observation revealed from the SEM images of the torrefied OPEFB biochar is the existence of pores on the fibre surface as presented in the Fig. 1(b) insert. In [7] had reported this is because the strand formation is an indication that the structure has been loosened up due to delignification. Since lignin acts as glue and often referred to as the plant cell wall adhesive, thus when delignification process occurred, the bonding between cellulose strands loosened.

Torrefaction for 60 minutes of residence time as in Fig. 1(c) shows that the physical changes of torrefied OPEFB biochar had smoother fibre surface and bigger porosity as the residence time increases due to pretreatment process. The torrefaction process of torrefied OPEFB biochar is therefore important to expand the structure and make it more digestive and increase the conversion degree as well [8].

Meanwhile, torrefaction for 90 minutes of residence time for torrefied OPEFB biochar is shown in Fig. 1(d). The physical changes can be seen clearly in both Fig. 1(d) and the insert. The surface structure of the torrefied OPEFB biochar ruptured and the coarseness increase. This is due to the cell wall breakdown. Thus, the porosity of the torrefied OPEFB biochar decreases due to the thermochemical conversion.

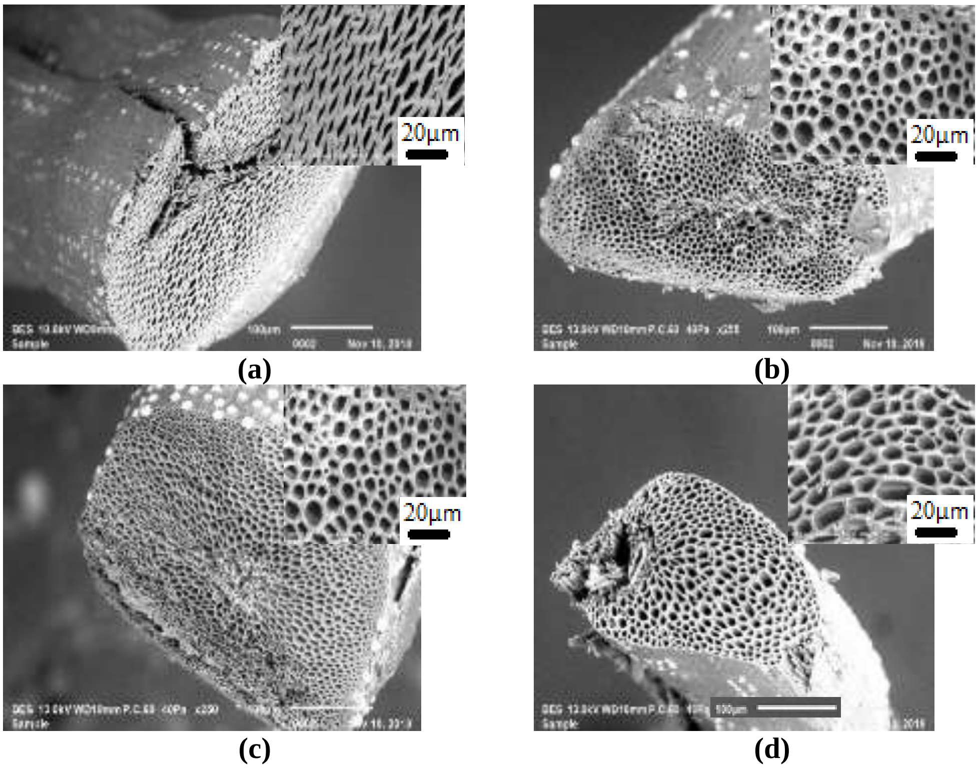

Fig. 1: SEM images of raw and torrefied OPEFB biochar surface structure with magnifications of ×250 and insert of ×1500 on (a) raw OPEFB, (b) torrefied OPEFB biochar at 300°C, 30 minutes, (c) torrefied OPEFB biochar at 300°C, 60 minutes, and (d) torrefied OPEFB biochar at 300°C, 90 minutes

3.2. Bonding Behavior Torrefied OPEFB Biochar

Fig. 2 shows the IR spectrums of raw OPEFB fiber and torrefied OPEFB biochar at 300°C and various residence times. In the Fig. 2, there are inorganic phosphate, alkynes and aliphatic hydrocarbons presence where C=O and C-O identified on raw OPEFB fiber. There may also be bands due to associated water molecules around 3400 and 1640cm-1. However, a strong bond absorption is identified at 3212.66cm-1 where O-H stretching presence. The hydrogen bonding of cellulose OH groups is actually the product of three hydrogen-bonds together of: 1) hydrogen bond of 2-OH and O-6, 2) hydrogen bond of 3-OH and O-5, 3) hydrogen bond of 6-OH and O-3.

For the IR spectrum band of torrefaction at 300°C, 30 minutes of residence time, the alkynes

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monosubstituded groups and started to diminish. The C=O also presence at 300°C torrefied OPEFB biochar at the strong band centered from peak 1698 to 3212cm-1 which appears as one band and multiple bands.

The IR spectrum band of torrefaction at 300°C, 60 minutes of residence time shows that only alumino silicate observed at peak 1534.48cm-1 with C=O stretch and aliphatic carboxylic acid presence at 3195.60cm-1. Carboxylic acids normally exist in a dimeric form with very strong hydrogen bonds between the carbonyl and hydroxyl groups. This association results in the very broad, unusual -OH stretching absorption.

On the torrefaction at 300°C, 90 minutes of residence time, the IR spectrum shows that only alumino silicates can be identified at peaks 1704.38 and 3077.44cm-1 where N-H stretching and C=O, respectively. This means that the other peaks with the weak bonds had been diminished, particularly by the longer heating time.

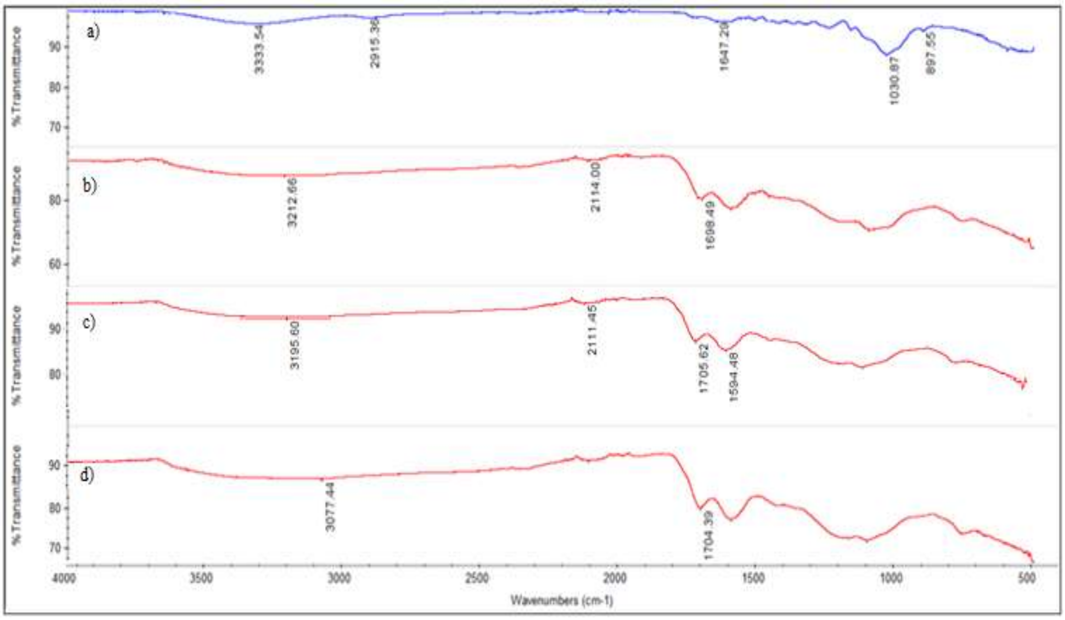

Fig. 2: FTIR spectrum band of (a) raw OPEFB, (b) torrefied OPEFB biochar at 300°C, 30 minutes, (c) torrefied OPEFB biochar at 300°C, 60 minutes, and (d) torrefied OPEFB biochar at 300°C, 90 minutes

4. Conclusion

The characterizations of torrefied OPEFB biochar have been done on surface morphology and bonding behavior. Both surface morphology and bonding behavior of the torrefied OPEFB biochar was impact of the degradation of the lignocellulose, hemicellulose, cellulose and lignin. From all the torrefied OPEFB biochar produced in this study, biochar at 300°C and 60 minutes of residence time showed the high porosity while at 90 minutes of torrefaction process, the surface structure of the biochar portrayed that it started to rupture due to longer period of thermochemical reaction process, and the FTIR spectrum proved that the weak bonds had diminished at this condition.

Acknowledgments

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