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# Effect of Pyrolysis Temperature and Time on Properties of Palm Kernel Shell-Based Biochar

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**Abstract.** Pyrolysis is a thermal decomposition of biomass occurring in the absence of oxygen. Biochar (solid), bio-oil (liquid) and biogas (gas) are the typical products from pyrolysis of biomass. This endothermic process produced biochar with high carbon content. During pyrolysis, the material is heated up from ambient to a peak temperature and remains for a defined residence time. Therefore, the pyrolysis peak temperature and the residence time are the key parameters for pyrolysis. Studies on the effect of these parameters on the biochar characteristics and the pyrolysis products composition are numerous. However, there are limited findings of these parameters with palm kernel shell (PKS) as the biomass. This study focusses on the effect of the pyrolysis temperature and residence time of PKS on the yield of biochar produced and the biochar physio-chemical properties. The results showed that biochar yield decreased as the peak temperature and residence time increased. This finding is consistent with the findings by other researchers. However, those factors do not have distinct influence on biochar's carbon content as found in other study which the peak temperature has the bigger impact instead of residence time. The effect of peak temperature or residence time on grindability; i.e. particle size of biochar after wet ball milled is insignificant. Smaller size of biochar may improve its function as reinforcing filler. As a conclusion, the optimum setup of pyrolysis is needed for a balance production in yield and biochar's properties. It is recommended to produce biochar at higher peak temperature and shorter residence time to increase the total production. Additional analysis e.g. physical testing on the final polymer product can be used to investigate the effect of pyrolysis peak temperature and residence time.

## 1. Introduction

Outstanding physical and mechanical properties made plenty different type of composites based on polymer matrix available on the market [1]. The interest on carbon nanotubes and graphene as fillers in polymers has increased [2]–[7]. However, reduction in the cost of production and the cost of filler are important towards commercialization. Attention has been given to composites derived from environmental-friendly materials. Areas such as Malaysia [8] has abundance source of biomass i.e., palm kernel shells (PKS) produced from palm oil mill. It has potential to be utilize for new applications [9]–[12].

Pyrolysis is a major thermal decomposition process to convert biomass into three main products; biochar (solid), bio-oil (liquid) and biogas (gas) [13]–[15]. The biomass is heated up from ambient to a set peak temperature and remained for a defined residence time during the pyrolysis process in the absence of oxygen [16]. Biochar can be used as alternative filler since it is carbon rich.

The pyrolysis temperature and the residence time play a role in the yield and governing the physio-chemical properties of the biochar. Increasing pyrolysis temperature is expected to give



lower biochar yield [17] while the residence time has no significant effect [18]. For proximate analysis especially on ash and fixed carbon content, pyrolysis temperature has remarkable impact compared to time [19]. Hydrogen/carbon (H/C) and oxygen/carbon (O/C) ratio based on determined C, H, nitrogen (N), sulphur (S) and O from ultimate analysis showed decreasing trend as the pyrolysis temperature increased [20]. Changes on pH value of biochar substantially influenced by pyrolysis temperature with time has statistically non-significant impact [21].

Studies showed that the biochar particle size affects its interaction with the rubber as well as the rheological properties of the biochar dispersion [22-23]. Thus, the grindability of the biochar is crucial and the grindability depends on the pyrolysis parameters [24-25]. Apart from the pyrolysis parameters, the biochar particle size is limited by temperature, loading, rotational speed and others on wet ball milling technique [26]–[28]. This study focuses on the effect of pyrolysis temperature and the pyrolysis residence time on the physico-chemical properties of PKS biochar and its grindability; i.e. particle size after wet ball milling as well as its dispersion rheological properties.

## 2. Experimental

### 2.1. Material

PKS as the raw biomass was used for pyrolysis process. It is the waste shell after removal of the nut in palm oil mill. PKS was collected from Palm Oil Mill Technology Centre (POMTEC), Malaysia. For each pyrolysis process, 20 kg of PKS was sieved to remove sand, dirt and stones before dried at 105°C for 24 hours to reduce the moisture content.

### 2.2. Pyrolysis process

A multi-mode pyrolysis machine, Biochar Experimenter's Kit (BEK) from All Power Labs (APL) was used for pyrolysis process to produce biochar as the main product. After drying, 17 kg of PKS biomass was fed into the BEK. A combination of propane gas and compressed air were used to ignite the flame in the burner during start-up. The heat energy does indirect heating to the PKS biomass from ambient; 25°C to the desired temperature; 400 or 500°C and maintained at a set residence time; 30, 45, 60 or 75 minutes. After the temperature was above 100°C, the pyrolysis sustained by burning of produced biogas without propane gas support. The pyrolysis products; biochar and bio-oil were weighed to obtain the yield using the equation below where  $W_{BC/BO}$  is weight of biochar or bio-oil (kg) and  $W_{RP}$  is weight of raw PKS (kg).

$$\text{Yield}_{BC/BO}(\text{wt. \%}) = \frac{W_{BC/BO}}{W_{RP}} \times 100\%$$

### 2.3. Physico-chemical characterization

Prior to the physico-chemical characterisation, the PKS biochar was ground using Golden Bull SY-10 grinder and sieved to the size of 105 µm. Ground biochar undergo pH analysis used modified dilution of 1:20 biochar: deionized water (w:v) with 90 minutes in a shaker for equilibrium [29] using a calibrated BP3001 Trans Instruments pH meter. Proximate analysis was done using thermogravimetric analyser Leco TGA 701 according to ASTM D5142 and ultimate analysis using CHNS analyser Leco 628 according to ASTM D5373. Oxygen content calculated using equation below. The raw PKS biomass was characterized using the same methods.

$$O(\text{wt. \%}) = 100 - C(\text{wt. \%}) - H(\text{wt. \%}) - N(\text{wt. \%}) - S(\text{wt. \%}) - \text{Ash}(\text{wt. \%})$$

#### 2.4. Wet ball milling

Only biochar from pyrolysis temperature of 400 and 500°C with pyrolysis time of 30 and 60 minutes were chosen to proceed with wet ball milling process. Deionized water was mixed with the biochar to produce 50 wt.% of biochar dispersion. Mill jar of 2.5 liters capacity was used with alumina grinding ball media and biochar dispersion occupied 60% of the total volume. The mill jar positioned horizontally on a pair of rods on the mill machine. The ball milling process was run at 50 rpm for 24 hours.

#### 2.5. Particle size analysis

After ball milling, the biochar's particle size was analyzed using particle size analyzer Malvern Mastersizer 2000. The stirrer speed was set at 1500 rpm. The system was clean using distilled water until laser level reach minimum 76%. The biochar dispersion was put into the dispersion cuvette until laser obscuration level reached 5%. Before measurement was done, sonication was made for 30 seconds.

#### 2.6. Scanning electron microscopy morphological analysis

Morphology analysis on the particle size of PKS biochar before and after ball milling were done using scanning electron microscopy (SEM) Hitachi SU-3500 Microscope. The biochar mounted on a 12 mm aluminium sample holder (stub) using carbon double-sided tape for adhesion.

#### 2.7. Rheological properties analysis

Steady state experiment was done on the 50 wt.% of biochar dispersion using Anton Paar MCR 302 rheometer. The shear rate studied was 0 to 1000 s<sup>-1</sup> with frequency fixed at 1 Hz. Cone and plate setup were used with temperature set at 25°C. The biochar dispersion was pre-sheared for 2 minutes followed by rest for 10 minutes and continued with shear for another 2 minutes.

### 3. Results and Discussion

#### 3.1. Analysis of PKS

Table 1 showed volatile content of raw PKS is the highest from the proximate analysis. The pyrolysis process is intended to remove this volatile matter to increase its grindability in the later stage. The carbon content is the highest from the ultimate analysis. This carbon is the important part of reinforcement with rubber particles.

**Table 1.** Proximate and ultimate analysis of PKS

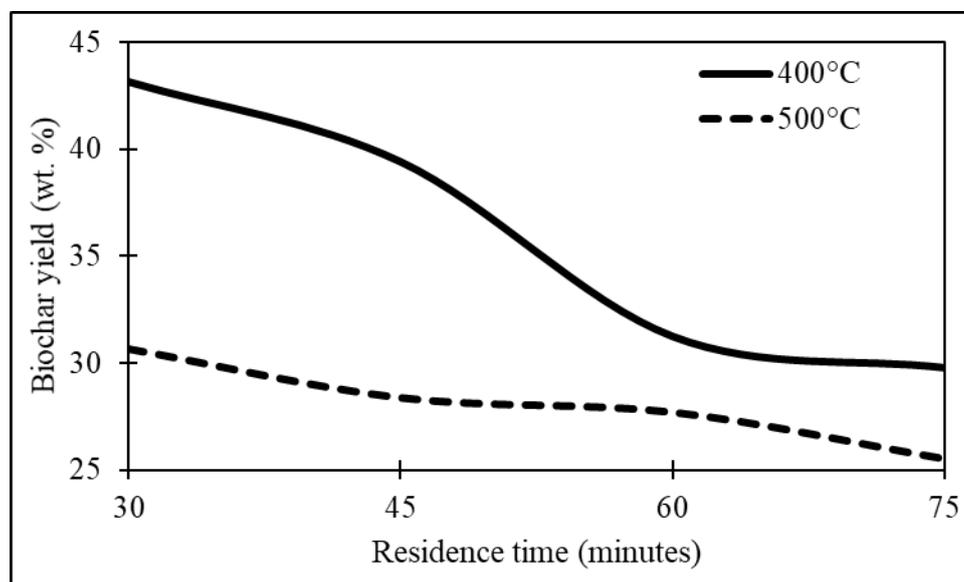
| Proximate analysis | Value (wt.%) | Ultimate analysis   | Value (wt.%)     |
|--------------------|--------------|---------------------|------------------|
| Moisture content   | 4.86         | Carbon              | 48.7             |
| Volatile content   | 70.74        | Hydrogen            | 6.21             |
| Fixed carbon       | 22.23        | Nitrogen            | 0.057            |
| Ash content        | 2.17         | Sulphur             | <sup>a</sup> BDL |
|                    |              | <sup>b</sup> Oxygen | 45.06            |

<sup>a</sup>Below detectable limit

<sup>b</sup>By difference

### 3.2. Yield of PKS biochar

Fig. 1 showed the yield of PKS biochar after pyrolysis process. 25% increase in pyrolysis temperature from 400 to 500°C had decreased the biochar yield from 43.13% to 30.69% with 12.44% in difference. For pyrolysis temperature of 400°C, the pyrolysis time need to be increased for 150% from 30 to 75 minutes to have biochar yield decreased with 13.3% difference. For temperature of 500°C, increasing the time for 150% will only decrease the biochar yield with 5.19% difference. As reported by Titiladunayo and co-workers [30], decreased in biochar yield with the increasing of pyrolysis temperature is due to more volatile matter were released. Increasing pyrolysis time across the same pyrolysis temperature also has the same effect but only at lower pyrolysis temperature because higher temperature predominantly alters the biochar's internal structure and surface [31].



**Fig. 1.** Yield of PKS biochar at different pyrolysis temperature and residence time.

### 3.3. Fixed carbon, ash, moisture and volatile content

There is no significant difference on the moisture and ash content as the pyrolysis temperature or time increased. At fixed pyrolysis temperature of 500°C, both volatile matter and fixed carbon content has no significant difference across pyrolysis time of 30 to 75 minutes. However, for pyrolysis temperature of 400°C, it took 100% increase in pyrolysis time or 25% increase in pyrolysis temperature to have volatile matter and fixed carbon content of below 20% and above 70% respectively. This results are in agreement with Ronsse and co-workers' findings as the pyrolysis temperature has greater impact on the volatile matter and fixed carbon content compared to time because of devolatilization reaction is developing more carbon [19].

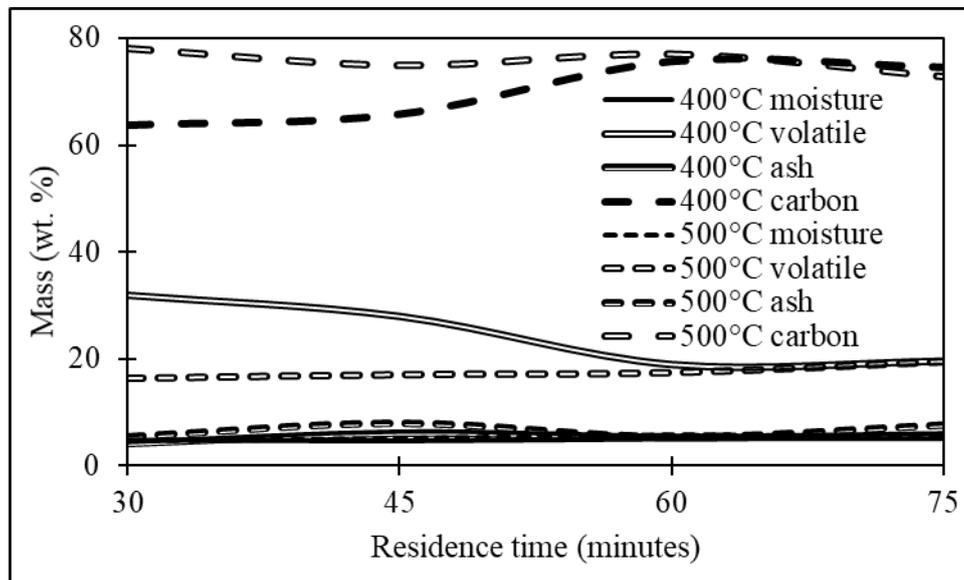


Fig. 2. Proximate analysis of PKS biochar.

#### 3.4. C, H, N, S and O content

The C, H, N, S and O content from ultimate analysis were used to obtain H/C and O/C ratio as shown in Van Krevelen of Fig. 3. PKS biochar produced from pyrolysis parameters of 400°C at 30 minutes and 400°C at 45 minutes lies outside of maximum H/C ratio of 0.7. Those biochars did not meet the standard by Initial Biochar Initiative (IBI). All PKS biochars produced using temperature of 500°C positioned within the IBI standard in the Van Krevelen diagram. The pyrolysis temperature has significant impact to reduce H/C and O/C ratio compared to pyrolysis time due to better deoxygenation and dehydration as pyrolysis temperature increases [32].

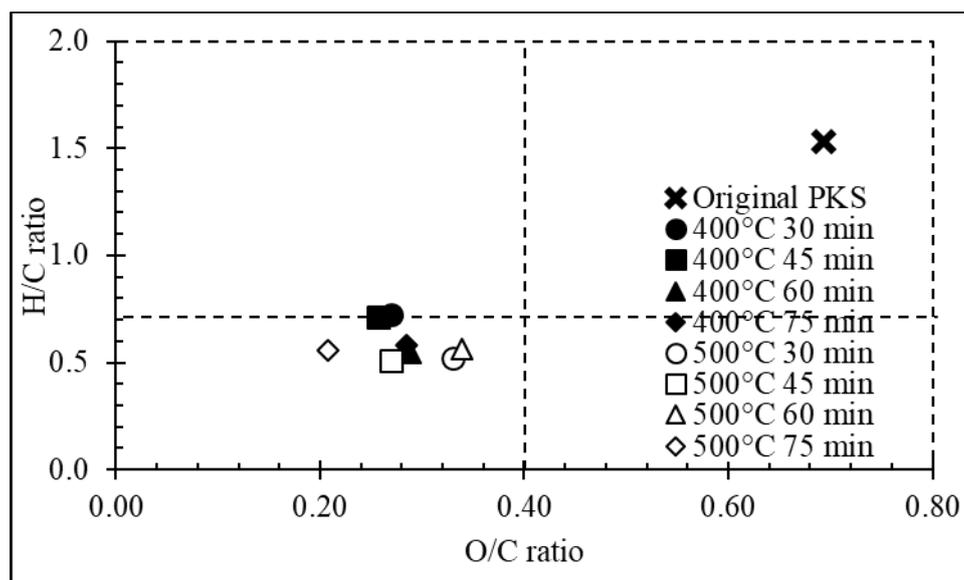
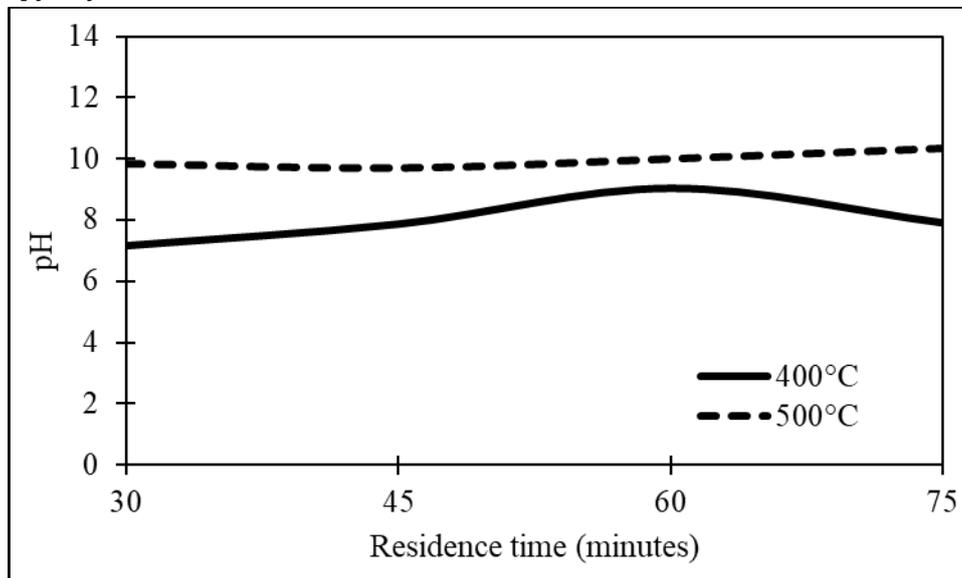


Fig. 3. Van Krevelen of PKS biochar at different pyrolysis temperature and residence time.

### 3.5. pH of biochar

Fig. 4 shows the effect of pyrolysis temperature and pyrolysis residence time on the biochar's pH. The pH of biochar from pyrolysis temperature of 400°C is consistently lower than those of 500°C within the pyrolysis residence time studied.

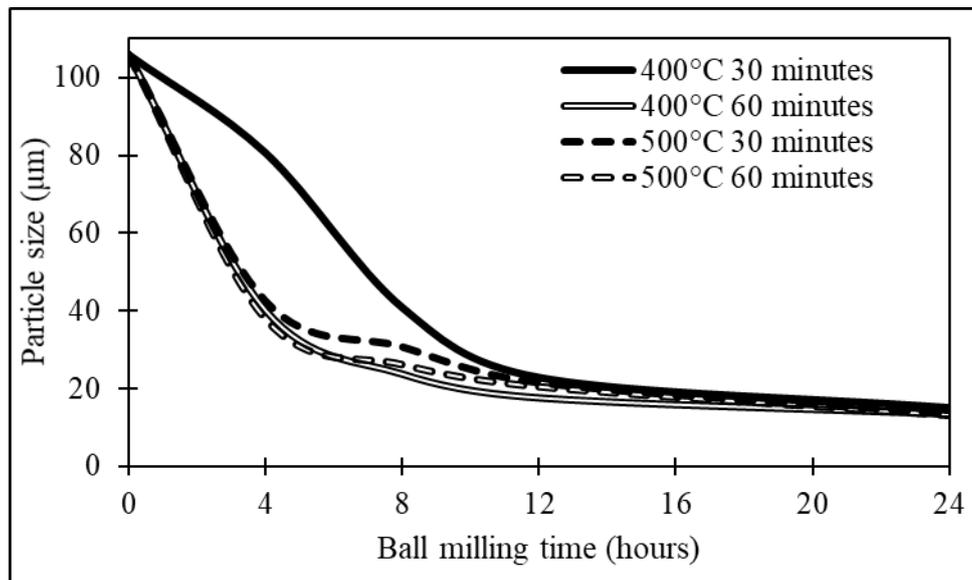


**Fig. 4.** pH of PKS biochar obtained from different pyrolysis temperature and residence time.

To produce biochar with pH at around 10, a 25% increase in pyrolysis temperature from 400 to 500°C is needed. However, 150% increase in pyrolysis time from 30 to 75 minutes still unable to produce biochar with pH at around 10. This showed pyrolysis temperature has greater impact on pH of produced biochar compared to pyrolysis time. Increasing pyrolysis temperature will increase the pH of produced biochar as it will lead to higher ash content. Higher ash content in biomass produced biochar with higher pH value. This also depends on the characteristics of the raw biomass [33].

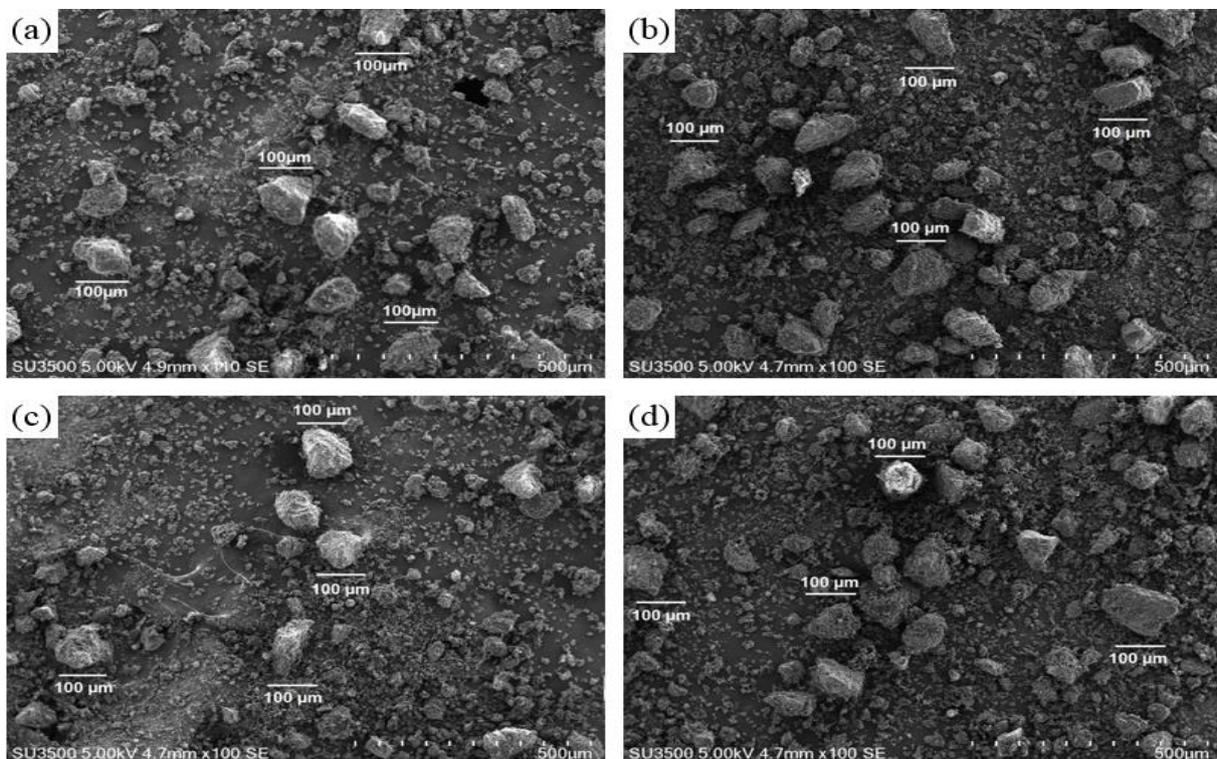
### 3.6. Particle size of wet ball milled biochar

From Fig. 5, PKS biochar produced from pyrolysis temperature of 400°C requires 100% increase in pyrolysis time to have particle size comparable to biochar from temperature of 500°C prior to 12 hours of wet ball milling. This showed pyrolysis temperature has more influence on grindability of biochar compared to pyrolysis time for ball milling lesser than 12 hours. After 12 hours of ball milling until 24 hours, no significant difference was observed on particle size of all biochars. There is significant improvement on grindability between raw biomass and biochar but there is minimal improvement with biochars produced at different pyrolysis temperature [23].

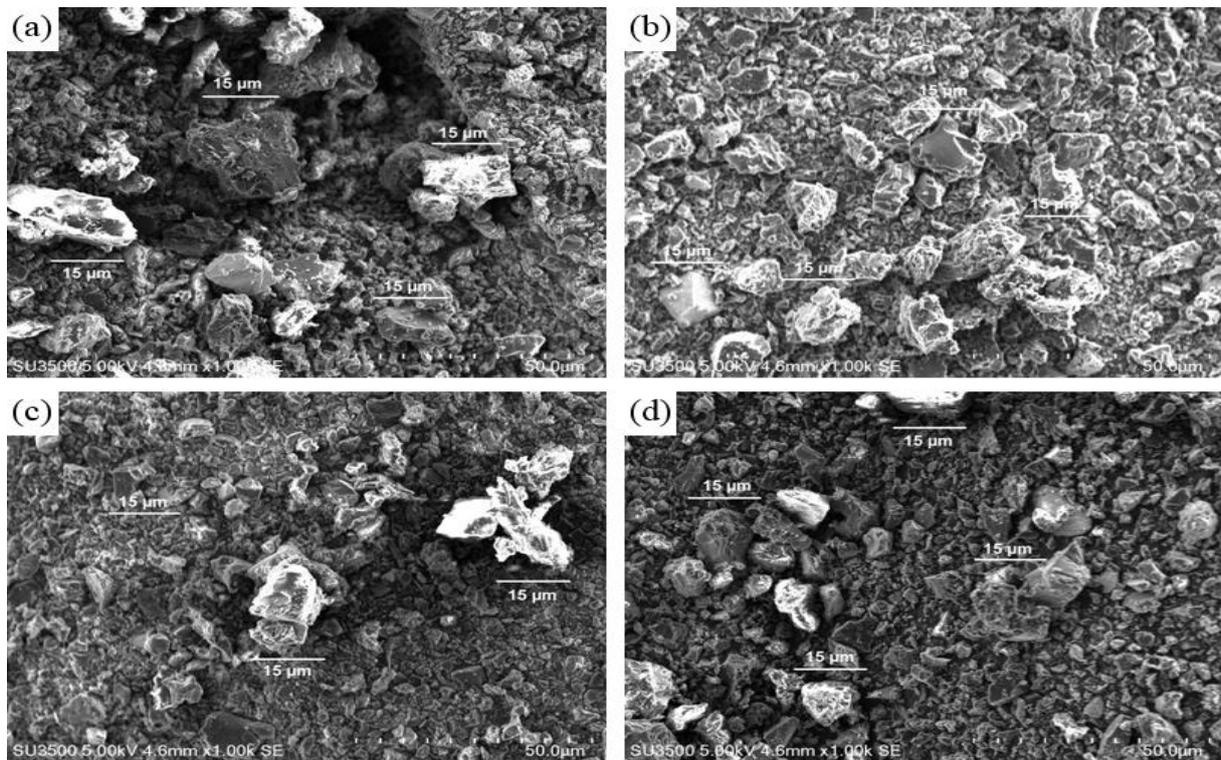


**Fig. 5.** Particle size of PKS biochar during wet ball milling measured using Mastersizer 2000.

Fig. 6 shows PKS biochar before wet ball milling process while Fig. 7 shows PKS biochar after 24 hours of wet ball milling. The morphological images showed in both Fig. 6 and Fig. 7 is in agreement with the biochar size measured using Mastersizer 2000. Before ball milled, the particle size was at 105 µm and between 13-15 µm after ball milled for 24 hours.



**Fig. 6.** PKS biochar before ball milling at <math><105\ \mu\text{m}</math>. (a) 400°C; 30 minutes (b) 400°C; 60 minutes (c) 500°C; 30 minutes (d) 500°C; 60 minutes.



**Fig. 7.** PKS biochar after ball milling at 13 - 15  $\mu\text{m}$ . (a) 400°C; 30 minutes (b) 400°C; 60 minutes (c) 500°C; 30 minutes (d) 500°C; 60 minutes.

### 3.7. Rheological properties of biochar dispersion

Shear stress against shear rate results is shown in Fig. 8 while viscosity against shear rate results is shown in Fig. 9. From the results it showed that there is no clear influence of the pyrolysis temperature or residence time on the steady state rheological properties. However, it is noticeable that all biochar dispersion exhibit shear-thinning behaviour. Addition of biochar dispersion into other suspension such as natural rubber latex would lead to poor mixing thus, this rheology study is important to investigate the flow behaviour of PKS biochar dispersion due to its characteristic flocculated nature [34], [35].

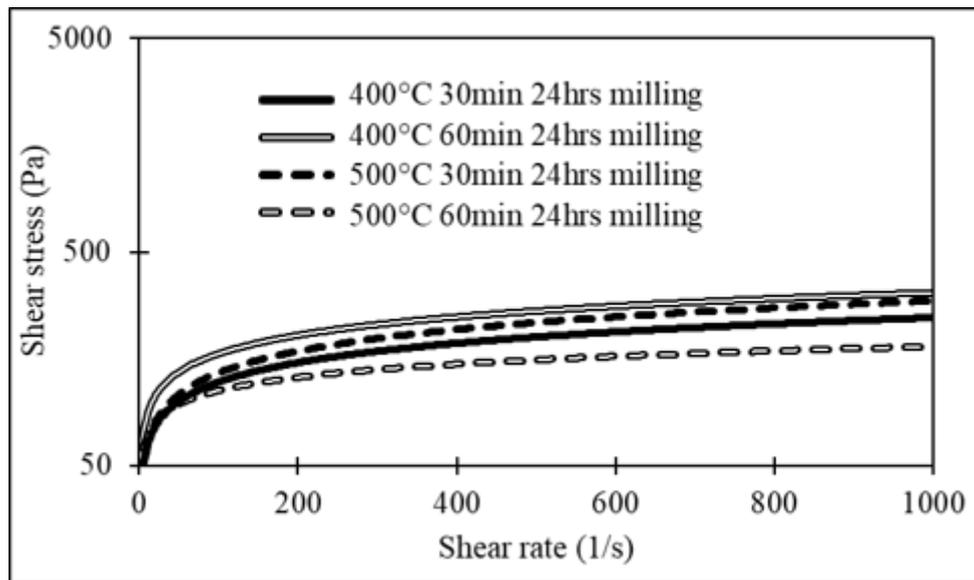


Fig. 8. Shear stress against shear rate of PKS biochar dispersion.

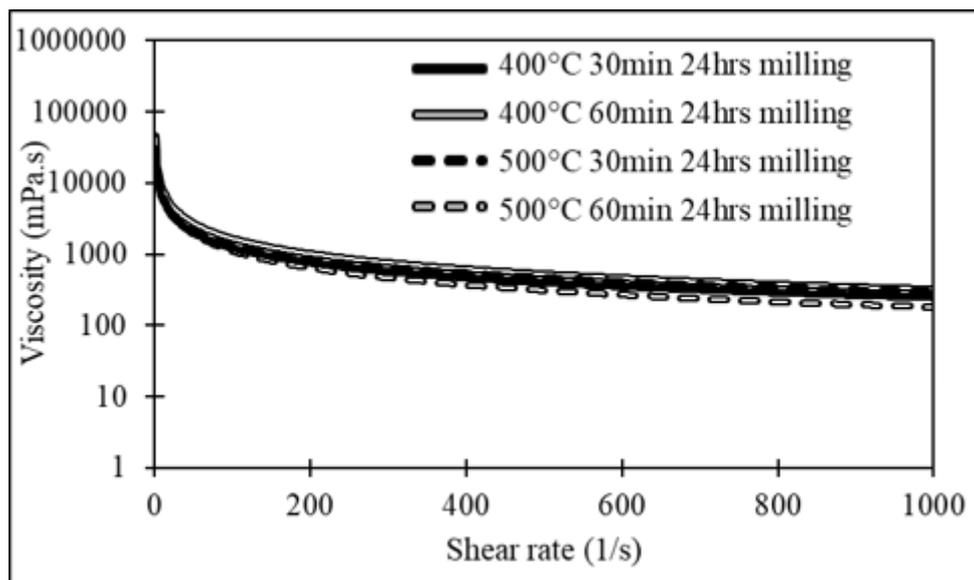


Fig. 9. Viscosity against shear rate of PKS biochar dispersion.

#### 4. Conclusion

Pyrolysis parameters such as temperature and time affects the biochar yield. Higher temperature and longer time give lower yield of biochar. Other properties that are decreasing as the pyrolysis temperature and time increased are volatile matter content, moisture content, H/C and O/C ratio. In contrast, pH value, fixed carbon content and carbon content increased as the pyrolysis temperature and time increased. Increasing pyrolysis temperature and time also improved grindability of biochar prior to 12 hours of wet ball milling. However, no clear effect on the rheological properties of biochar dispersion as the pyrolysis temperature and time increased. Based on the results, it can be concluded that the pyrolysis temperature has greater impact on the biochar physico-chemical characteristics compared to pyrolysis time and subsequently affect the grindability.

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