Torrefaction of palm kernel shell using conventional and microwave irradiation pretreatment

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Abstract. This study describes the properties of torrefied palm kernel shell (PKS) by conventional and microwave irradiation (MI) pretreatment. In conventional pretreatment, the untreated PKS was torrefied using fixed bed reactor at temperature of 210, 230, 250, 270 and 290 °C for 60 min of holding time. In MI pretreatment, the untreated PKS was irradiated with microwave power of 200, 300, 450 and 600 W for 8 min of holding time. The torrefied samples were analysed for mass and energy yield, energy density, calorific value and proximate and ultimate analysis. The results showed that, the properties of torrefied samples were improved with increasing torrefaction temperature and microwave power. The mass and energy yield, moisture, volatile matter and oxygen content of torrefied PKS decreased, whereas, the calorific value, energy density and carbon content increased with increasing torrefaction temperature and microwave power. The torrefaction temperature of 270 °C and microwave power of 450 W were appropriate to upgrade the PKS properties. Therefore, the change in properties of torrefied PKS revealed the potential of applying pretreatment prior to further thermal conversion such as pyrolysis and gasification.

1. Introduction

In recent years, the increasing emission of CO2, SOx and NOx has become a concern on the utilization of the world energy [1]. In the midst of limited availability of fossil fuels and high level of air pollution, energy efficient technologies are gaining importance and gasification being highly efficient technology, has received significant attention [2]. Currently, coal is the main feedstock in gasification and is expected to be applied as the energy resource for many decades ahead. However, this direction difficult to achieve due to the increasing in energy demand that had caused the shortage supply and reducing of coal [3]. Consequently, one of the approaches is to utilize the biomass in thermochemical conversion.

The utilization of biomass which is a renewable and environmental friendly resource during gasification imposed several problems. Untreated biomass has relatively low energy, high moisture and oxygenated compound, hygroscopic behavior and poor grindability [4], [5]. Accordingly, the pretreated or torrefied biomass which has been improved in energy density, hydrophobicity and
grindability overcome the weakness of untreated biomass, then driven to be applied in thermochemical conversion [6], [7].

Conventionally, the thermal pretreatment or torrefaction work at low temperature between 200-300 °C which operated in the absence of oxygen, upgraded the untreated feedstock to more valuable feedstock. The torrefied biomass has high calorific value and carbon fraction with low moisture content and O/C ratio compared to the original material. The energy value of torrefied material will increase with increasing the carbon content and calorific value [8]. As pretreatment conditions became more severe between temperature of 250 to 300 °C, this led to a more qualified and energy-dense solid fuel with higher fixed carbon content, increased calorific values and reduced hydrogen and oxygen contents [9]. Most biomass torrefaction applied conventional electric heater, while there is an alternative technology designated microwave irradiation (MI).

The pretreatment using MI is an alternative method for upgrading the biomass [10]. Unlike conventional heating technique in which heat gradually enters into samples over normal heat transfer mechanisms (convection, conduction, and radiation) [11], MI employs electromagnetic energy to produce heat which can enter deep into samples, permitting heating to initiate volumetrically [12]. MI has many advantages such as: (i) non-contact heating, (ii) energy transfer instead of heat transfer, (iii) rapid heating, (iv) selective material heating, (v) volumetric heating, (vi) quick start-up and stopping, and (vii) heating from the interior of the material body [13], [14]. Consequently, more research is required to entirely understand the characteristic of torrefied biomass using MI prior to further thermochemical conversion.

Thus, this study intentions to explore the properties of torrefied PKS using the two pretreatment methods (conventional and MI).

2. Methodology

2.1. Materials
PKS as a biomass sample was obtained from United Oil Palm Mill Sdn. Bhd., Nibong Tebal, Penang, Malaysia. PKS sample was crushed and sieved through progressively finer screen to obtain particle sizes in the range of 200 to 400 µm. The untreated PKS sample was dried in an oven at 105 °C for 2 h for rendering moisture free and finally stored in an air-tight container until the experiments and analyses were carried out.

2.2. Conventional pretreatment
The conventional pretreatment of PKS was carried out using a vertical fixed bed reactor with an internal diameter of 60 mm and height of 300 mm at an ambient pressure. An electric furnace surrounding the reactor was used to heat the reactor. Approximately 5 g of sample was weighed and positioned inside the reactor. Then, the reactor was flushed with nitrogen gas for 15 min before experiment. A nitrogen flow rate of 0.5 L/min was remained constant to create an inert atmosphere inside the reactor. Next, the temperature of the reactor was increased to the pretreatment temperature (210, 230, 250, 270 and 290 °C) at a constant heating rate of 10 °C/min. The untreated samples were treated for 60 min holding time at each pretreatment temperature. When the heating process has completed, the heater was turned off and the reactor was left to cool to the ambient temperature. The final weight of pretreated sample was measured once it reached at room temperature. Then, the sample was kept in a sealed container for further analyses.
2.3. Microwave irradiation pretreatment

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2.4. Sample analyses

The mass yield ($Y_m$), energy yield ($Y_e$) and energy density, ($Y_d$) of the pretreated samples were calculated according to Eq. (1), (2) and (3), respectively.

$$Y_m = \left( \frac{M}{M_u} \right) \times 100$$  \hspace{1cm} (1)

$$Y_e = Y_m \times \left( \frac{CV}{CV_u} \right)$$  \hspace{1cm} (2)

$$Y_d = \frac{Y_e}{Y_m}$$  \hspace{1cm} (3)

where, $M$ is the mass of sample, $CV$ is the calorific value, the subscript $u$ means the value of untreated PKS, the subscript $t$ means the value of torrefied PKS.

The physical and chemical characteristics of the untreated and pretreated samples were analysed. The elemental composition of the sample was examined using elemental analyser CHNS-O Flash 2000. The proximate analysis which analysed the moisture, volatile matter, ash and fixed carbon content was carried out using a Mettler Toledo thermogravimetric analyser (TGA). The Leco AC-350 bomb calorimeter was used to determine the calorific value (CV). The fourier transform infrared (FTIR) spectra was recorded using a Perkin Elmer FTIR Spectrophotometer. The fundamental properties of the untreated PKS are summarized in Table 1.
Table 1. Properties of untreated PKS.

| Properties                        | Value  |
|-----------------------------------|--------|
| Elemental analysis (wt. %)         |        |
| Carbon                            | 47.67  |
| Hydrogen                          | 5.52   |
| Nitrogen                          | 0.39   |
| Sulphur                           | 0      |
| Oxygen                            | 46.42  |
| Proximate analysis (wt. %)         |        |
| Moisture                          | 10.60  |
| Volatile matter                   | 77.54  |
| Fixed carbon                      | 10.95  |
| Ash                               | 0.91   |
| Calorific value (MJ/kg)           | 18.20  |

*By difference*

3. Results and discussion

3.1 Mass and energy properties

The mass and energy properties of torrefied PKS via conventional and microwave irradiation (MI) pretreatment at various temperatures and power level, respectively, is shown in Table 2. Both conventional and MI pretreatment showed decreasing of mass and energy yield with increasing pretreatment temperature and microwave power. While, the energy density increased with increasing pretreatment temperature and microwave power.

The mass yield ranges from 87.7 to 64.4 % and 94.1 to 42.4 % for conventional and MI pretreatment, respectively. The high mass yield at temperature of 210 °C and microwave power of 200 W was considered due to the loss of moisture [15]. The torrefied PKS showed mass yield of less than 80 % when it were heated at temperature of 250 °C to 290 °C and irradiated at microwave power of 450 to 600 W. This was due to volatiles released i.e. hemicellulose and some short-chain lignin compounds during torrefaction [16], [17]. Several researchers confirmed that the hemicelluloses is the major decomposition fraction of torrefaction [18]–[20].

The energy yield of torrefied PKS was drastically reduced to 75 % at pretreatment temperature of 290 °C and microwave power of 600 W. This observation is mainly due to the additional decomposition of hemicellulose and cellulose [21]. Consequently, more than 80 % of energy yield was able to be reserved at the pretreatment temperature of 270 °C and microwave power of 450 W. Therefore, conventional pretreatment at 290 °C MI pretreatment at microwave power of 600 W is not suggested in order to avoid extremely loss of energy yields, where, the volatilization reaction of biomass might become a predominant reaction during the pretreatment process.

The energy density increased by factors of 1.16 and 1.18 at the maximum pretreatment temperature of 290 °C and microwave power of 600 W, respectively. The energy density increased significantly at
pretreatment temperature of 270 °C and microwave power of 450 W. Therefore, these parameters can be considered as the optimal condition with the concerns of desired energy density and yield.

3.2. Proximate analysis

Table 3 shows the effect of pretreatment temperature and microwave power on proximate analysis and calorific value of torrefied PKS. Generally, it can be seen that the moisture content decreased with increasing pretreatment temperature and microwave power. The results indicated the characteristics of the torrefied PKS were altered due to high moisture content of untreated PKS and its ability in absorbing heat and microwave irradiation.

Moreover, the decreased in volatile matter was observed with increasing the pretreatment temperature and microwave power. This phenomenon was due to drying, volatilization, and decomposition of biomass feedstock during the pretreatment of PKS at higher temperature and microwave power. The torrefied PKS showed huge reduction of volatile matter with decreased to 40 % and 24 % with increasing pretreatment temperature to 290 °C and microwave power to 600 W. The hemicelluloses content in PKS are easy to degrade during torrefaction process. These results on the extensive volatile matter reduction were comparable to the work published by Uemura et. al., [22], Matali et. al [9] and Sabil et al. [23] in the study of empty fruit bunch, woody biomass and oil palm frond, respectively.

The fixed carbon of the torrefied PKS increased, with increasing pretreatment temperature and microwave power. The fixed carbon of the pretreated samples increased more than 50 % at the highest pretreatment temperature of 290 °C and microwave power of 600 W with comparison to the untreated PKS. The effect of pretreatment condition was more noticeable at pretreatment temperature of 270 °C and above and at microwave power of 450 W and above, due to hemicelluloses and cellulose decomposition of PKS. From mild to severe pretreatment temperature range of 250 to 290 °C and microwave power range of 450 to 600 W, the PKS sample decomposed completely into volatile and char product [9]. The torrefied PKS with high fixed carbon content is suitable to be blended with coal in co-gasification process due to energy enhancement in the biomass.

Table 3: Proximate and ultimate analysis of torrefied PKS.

| Properties          | Conventional | Microwave Irradiation |
|---------------------|--------------|-----------------------|
|                     | Pretreatment temperature, °C | Microwave power, W |
|                     | 210 230 250 270 290 | 200 300 450 600 |
| Proximate analysis (wt. %) |               |                       |
| M                   | 2.4          | 3.4 2.4 1.6 2.0       | 6.8 4.2 1.4 3.7 |
| VM                  | 52.2         | 50.8 48.9 47.0 39.3   | 62.3 53.0 46.1 24.4 |
| FC                  | 44.4         | 44.4 47.5 49.1 56.2   | 30.0 41.6 50.7 69.5 |
| A                   | 1.0          | 1.5 1.2 2.3 2.6       | 0.9 1.1 1.7 2.4 |
| CV (MJ/kg)          | 19.6         | 21.1 20.5 20.9 21.2   | 17.8 18.8 20.5 20.1 |
| Ultimate analysis (wt. %) |               |                       |
| C                   | 48.4         | 49.6 50.1 52.3 55.9   | 47.9 48.1 52.0 51.9 |
| H                   | 5.1          | 4.7 4.5 4.0 3.7       | 5.4 5.4 5.1 4.8 |
| N                   | 0.8          | 0.8 0.9 0.9 0.9       | 0.0 0.1 0.1 0.1 |
| O                   | 45.7         | 44.8 44.5 42.8 39.5   | 46.7 46.5 42.9 43.3 |

Note: M = moisture, VM = volatile matter, FC = fixed carbon, A = ash, CV = calorific value, C = carbon, H = hydrogen, N = nitrogen, O = oxygen (by different)

The increasing of fixed carbon on torrefied PKS representing a modification in quantity of energy per unit mass which related to the calorific value. The calorific value is one of the important parameters for fuels to be used in subsequent thermal conversion. The torrefied PKS at pretreatment temperature of 290 °C had the highest calorific value of 21.2 MJ/kg which was 16.5 % higher than untreated PKS. At microwave power of 450 W, the torrefied PKS had the highest calorific value of
20.5 MJ/kg which was 12.6 % higher than untreated PKS. Commonly, higher pretreatment temperature and microwave power contributed to higher calorific value of torrefied biomass.

3.3. Ultimate analysis
The ultimate analyses of torrefied PKS and preheated MB samples are displayed in Table 3. In general, the results indicate that oxygen and hydrogen content decreased with carbon content increased with increasing in pretreatment temperature and microwave power. The oxygen content reduced to 39.46 % at pretreatment temperature of 290 °C. While, using MI, the oxygen content only reduced to 42.92 % at microwave power of 450 W. The carbon content increased to 55.94 % and 51.93 % with conventional and MI pretreatment, respectively at the highest operating condition. The decreased in hydrogen and oxygen contents due to the destruction of hydroxyl group (-OH) in PKS during pretreatment, which consequently produced solid hydrophobic fuel [24], [25]. Eventually, by removing oxygen using thermal pretreatment method, the energy density of the torrefied PKS increased.

4. Conclusion
This study presents the characterization of torrefied PKS using conventional and MI pretreatment. The increased in pretreatment temperature and microwave power showed the significant effect which decreased the mass and energy yield, moisture, volatile matter and oxygen and hydrogen content of torrefied PKS. While, the energy density, fixed carbon, carbon content and calorific value were increased with increasing the pretreatment temperature and microwave power. The torrefied PKS showed a comparable value with appropriate characteristics at pretreatment temperature of 270 °C and microwave power of 450 W. Therefore, the untreated PKS can be upgrade via conventional and MI pretreatment which improved the quality of untreated biomass. Thus, it has the potential to be applied as an upgraded renewable fuel in other thermal conversion or co-conversion such as pyrolysis and gasification.

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