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# Properties of Torrefied Palm Kernel Shell via Microwave Irradiation

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Additional information is available at the end of the chapter

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## Abstract

This study describes the characteristic and thermal properties of torrefied palm kernel shell (PKS) by microwave irradiation pretreatment. The microwave power level (200, 300, 450, and 600 W) and processing time (4, 8, and 12 min) were used in this study. The pretreated samples were analyzed for mass and energy yield, calorific value, proximate and elemental composition, and thermal decomposition. Results showed that the characteristic of pretreated PKS was enhanced by increasing the microwave power level and processing the time. The oxygen content and O/C ratio of torrefied PKS were reduced by increasing the microwave power level. The carbon content of pretreated PKS, which was closed to the untreated MB coal properties with comparable calorific value, was obtained. The microwave power level of 450 W and processing time of 8 min were suitable to upgrade the PKS to a respectable quality feedstock. Thus, it can be concluded that the alteration in physical, chemical, and thermal properties of torrefied PKS discovered the potential of this feedstock to be applied in subsequent thermochemical conversion such as pyrolysis and gasification.

**Keywords:** pretreatment, torrefaction, microwave irradiation, palm kernel shell, gasification

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## 1. Introduction

In recent years, the increasing emission of CO<sub>2</sub>, SO<sub>x</sub>, and NO<sub>x</sub> 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

a 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 is difficult to achieve due to the increase in energy demand that had caused the shortage supply and reduction of coal [3]. Consequently, one of the approaches is to utilize the biomass in thermochemical conversion such as pyrolysis, liquefaction, and gasification. The traditional use of biomass has been restricted to cooking and heating purposes, which has affected adverse impacts such as land degradation and desertification. However, the current use of biomass with a high-quality energy carrier transformed from raw biomass for electricity and heat production can substantially reduce emissions from the conventional power plants. This ability to convert raw biomass into convenient energy carriers increases the interest on biomass use for energy purpose, especially the lignocellulosic biomass [4].

Biomass is one of the capable renewable energy sources and is applied as solid, liquid, and gas fuels [5]. The biomass is an appealing concern worldwide, because of its nonedible characteristic, carbon neutrality, and relative abundance. Moreover, the rising worries about the effects of CO<sub>2</sub> emissions from fossil fuels call for sustainable energy sources, such as biomass [6]. In Malaysia, oil palm residues are considered to be the most plentiful biomass and the greatest prospects for fuel generation. Malaysia produces about 47% of the world's palm oil source and can be reflected as one of the world's largest producers of palm oil. Therefore, Malaysia creates huge quantity of oil palm biomass including palm kernel shell (PKS), oil palm trunks, oil palm fronds, empty fruit bunches, and fibers as residues from harvesting and processing activities [7]. The PKS as one of the residues from oil palm industry generated about 4.19 MnT in 2016 [8]. Therefore, PKSs appear to have prominent capacities to become an alternative source of energy for the country.

However, the utilization of biomass, which is a renewable and environmental friendly resource during thermal conversion, imposed several problems. The untreated biomass has the drawbacks as follows:

- i. Low energy content
- ii. High moisture and oxygenated compound
- iii. Hygroscopic behavior
- iv. Poor grindability

Likewise, it is reasonably challenging for straight application of untreated PKS as raw material for fuel production such as gasification or pyrolysis. Typically, the palm plantations and their processing plants are located in rural areas. Thus, the untreated PKS is opened to fungal attack and biodegradation through storage and transportation. The high moisture content also can interrupt the thermal conversion process for energy production [9]. The low energy density of PKS, normally 18 MJ/kg, with high moisture content typically around 10 wt.% as a result of its hygroscopic character, is a weakness of biomass [10–12]. As shown by the previous researcher [13–15], highly oxygenated biomass with high O/C ratio will lower the gasification efficiency in contrast with low O/C feedstock such as coal. Consequently, these properties of the untreated PKS were associated with several problems in biomass thermal

conversion such as in gasification. As a result, prior to gasification, it might be attractive to transform the biomass characteristics.

A pretreatment method prior to thermal conversion is required in direction to reduce some of the aforementioned problems. Thus, torrefaction pretreatment appears to be an effective route. The thermal pretreatment or torrefaction at low temperature between 200 and 300°C, which operated in the nonappearance of oxygen, upgraded the untreated feedstock to more value feedstock. Nitrogen is generally used as carrier gas to provide a nonoxidizing atmosphere in most laboratory tests. Since torrefaction is conducted at conditions similar to those of pyrolysis that usually takes place between 350 and 650°C, torrefaction has also been known as mild pyrolysis [16]. The pretreated biomass has high calorific value and carbon fraction with low moisture content and O/C ratio compared to the untreated or original material. The energy value of pretreated material will increase with increasing carbon fraction and calorific value [17].

The previous studies have also shown other advantages of this torrefaction pretreatment, such as it improves feedstock hydrophobicity, homogeneity, and grindability [4, 18]. Satpathy et al. [19] found that the torrefied wheat and barley straw are more hydrophobic and the moisture uptake is reduced by 61–68% under suitable torrefaction condition. Torrefaction of marula seeds and blue gum improves the higher heating value and energy content of the biomass. The weight loss also increases when the torrefaction temperature increases due to moisture removal and hemicellulose breakdown, which produce  $H_2O$ ,  $CO$ ,  $CO_2$ , and other hydrocarbons [20].

Torrefaction temperature is one of the important parameters in torrefaction pretreatment [4]. Ibrahim et al. [21] found that the lower temperature and shorter residence time were the best treatment to achieve good physical properties with a relatively high energy yield. When treated at these conditions, the softwood mixture had the highest energy (95%), followed by the hardwood mixture (80%), then willow (79%), and finally eucalyptus (75%). Increasing the severity of the torrefaction conditions greatly improved the physical characteristics of the torrefied biomass, in terms of grindability properties and hydrophobicity. The optimum temperatures were reliant on raw material, and consequently, the effects specify that careful optimization is necessary for all feedstock types to increase the advantages of torrefaction at the same time preserving an adequate energy yield. As pretreatment conditions became more severe between temperature of 250 and 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 [22]. By increasing the torrefaction temperature, the weight loss increased and bulk density decreased. The torrefied wood samples improved solid fuel property with high fuel ratio, which are close to lignite coal [23]. Mamvura et al. [20] found that the nonoxidative conditions with low heating rates and shorter residence time resulted in the best torrefied biomass. The increase in HHV together with increase in energy density for torrefied marula seeds during investigation intended that it is potential to co-conversion with coal making it a promising biomass source. Therefore, the pretreated or torrefied biomass, which has been improved in energy density, hydrophobicity, and grindability, overcomes the weakness of untreated biomass and is then driven to be applied in thermochemical conversion [4, 16].

Most of the biomass torrefactions applied the conventional electric heater, while there is an alternative technology designated microwave irradiation. Microwave technology has expanded remarkable importance in the thermochemical pretreatment of waste materials, including biomass, waste cooking oil, scrap tires, and others. Innovative fields are being exposed in which microwave can be applied as an alternative source of heating. The application of microwave in waste treatment originated about two decades ago. Therefore, it can be considered at an early stage of enlargement [24]. Microwave irradiation is an electromagnetic irradiation in the range of wavelengths from 0.01 to 1 m and the equivalent frequency range of 0.3–300 GHz. Normally, the microwave reactors for chemical synthesis and all domestic microwave ovens operate at 2.45 GHz frequency, which corresponds to a wavelength of 12.25 cm. Microwave irradiation has attracted much attention in recent years due to the advantages associated with dielectric heating effects. Microwave dielectrics are known as a material, which absorbs microwave irradiation; thus, microwave heating is called dielectric heating [25]. The pretreatment using microwave irradiation is an effective method for upgrading the biomass [26]. Unlike conventional heating technique in which heat gradually enters into samples over normal heat transfer mechanisms (convection, conduction, and radiation) [27], microwave irradiation employs electromagnetic energy to produce heat, which can enter deep into samples, permitting heating to initiate volumetrically [28]. Microwave irradiation has many advantages such as:

- i. Noncontact heating
- ii. Energy transfer instead of heat transfer
- iii. Rapid heating
- iv. Selective material heating
- v. Volumetric heating
- vi. Quick start-up and stopping
- vii. Heating from the interior of the material body [25, 29]

Wang et al. [30] utilized microwave irradiation to upgrade the properties of rice husk and sugarcane residues by varying different parameters, including microwave power level and processing time. They found that the suitable microwave power levels are proposed to be set between 250 and 300 W for the torrefaction of these two agricultural wastes. Also, with appropriate processing time, the caloric value is able to increase 26% for rice husk and 57% for sugarcane residue. Huang et al. [31] found that higher microwave power levels contributed to higher heating rate and reaction temperature and therefore produced the torrefied biomass with higher heating value and lower H/C and O/C ratios. The torrefied biomass or biochar probably substitutes coal due to high heating value and fuel ratio as well as low atomic H/C and O/C ratios. The microwave torrefaction of *Leucaena* produced thermally stable biochar compared with sewage sludge at lower microwave power levels, which means that the microwave heating performance of *Leucaena* is better. Compared with conventional torrefaction, mass and energy yields of microwave torrefaction were lower, which might be attributable to the further severe reaction accomplished by microwave irradiation [32].



Consequently, more research is required to entirely understand the characteristic of torrefied biomass using microwave irradiation prior to further thermochemical conversion. It is also necessary to understand the thermal decomposition of torrefied biomass during pyrolysis in thermogravimetric analyzer (TGA) since, in the thermal conversion studies, the beginning stage involves the feedstock devolatilization. Therefore, in this study, the PKS was initially torrefied in microwave, and the properties of torrefied PKS were explored. Subsequently, the thermal decomposition and behavior of torrefied PKS during pyrolysis process using TGA were examined.

## 2. Method

### 2.1. Materials

PKS as a biomass sample was obtained from United Oil Palm Mill Sdn. Bhd., Nibong Tebal, Penang, Malaysia. The PKS is produced from the shell/kernel separator. The PKS sample was crushed and sieved through progressively finer screen to obtain particle sizes in the range of 200–400  $\mu\text{m}$ . The untreated PKS sample was dried in an oven at 105°C for 24 h for rendering moisture-free and finally stored in an air-tight container until the experiments and analyses were carried out. The pre-drying is needed to avoid further biodegradation of the sample through storage since the moisture mass fraction of the raw PKS is relatively high [33]. Moreover, the pre-drying is used to simulate the industrial practice of sun-drying the materials before storage [6].

### 2.2. Torrefaction experiment

The torrefaction experiment was carried out in a domestic microwave oven (Samsung) with technical specifications of ~240 V and 50 Hz and a maximum power of 800 W. The microwave output power levels of 200, 300, 450, and 600 W were used in this study. The untreated PKS of 5 g was put in the sample crucible placed at the center of the microwave oven. Then, the nitrogen gas at a flow rate of 50 mL/min was purged in the reaction compartment to retain the inert atmosphere condition. After 10 min purging, the microwave system was turned on, and the microwave output power level was selected with respective processing time of 4, 8, and 12 min. The inert atmosphere condition was continued during the microwave irradiation. The power supply was turned off, and the nitrogen gas flow was stopped after the set processing time was achieved. The final temperature of the pretreated PKS was measured using infrared thermometer immediately after the pretreatment process. The final weight of pretreated PKS was measured once it reached the room temperature. The experiment under all of the studied parameters was repeated to confirm the measurement quality and repeatability of the achieved results.

### 2.3. Calculation of solid conversion, mass yield, and energy yield

The solid conversion ( $X_s$ ), mass yield ( $Y_m$ ), and energy yield ( $Y_e$ ) of the pretreated samples were calculated according to Eqs. (1)–(3), respectively:

$$X_s = (M_u - M_p) / M_u \quad (1)$$

$$Y_m = (M_p / M_u) \times 100 \quad (2)$$

$$Y_e = Y_m \times (CV_p / CV_u) \quad (3)$$

where  $M$  is the mass of sample,  $CV$  is the calorific value, the subscript  $u$  means the value of untreated sample, and the subscript  $p$  means the value of pretreated sample.

## 2.4. Sample analyses

The physical and chemical characteristics of the untreated and pretreated samples were analyzed. The elemental composition of the sample was examined using elemental analyzer CHNS-O Flash 2000. The elemental composition examines the carbon (C), hydrogen (H), nitrogen (N), and sulfur (S) contents. The oxygen content was analyzed by the difference of total mass content. The sample of 2 mg was weighted and encapsulated into a tin capsule. The sample was placed in the sample loading chamber. During the analysis, the sample was dropped into a furnace held at 1000°C. At the same time the sample drops into the furnace, a dose of oxygen is released into the furnace. The sample was combusted by the heated oxygen-rich environment. The products of elemental analysis are  $CO_2$ ,  $H_2O$ ,  $NO_x$ , and  $SO_x$ . These gases, which were carried through the system by the helium carrier, will be swept through the oxidation tube packed with copper sticks (which removes oxygen), to complete the conversion to  $SO_2$ . These gases are passed through four infrared detectors of C, H, N, and S, and the results were displayed as weight percent of C, H, N, and S.

The proximate analysis that analyzed the moisture, volatile matter, ash, and fixed carbon content was carried out using a Mettler Toledo thermogravimetric analyzer (TGA) according to the standards of the American Society for Testing and Materials (ASTM). For each analysis, about 10 mg of sample was weighted using a microbalance and placed in a ceramic crucible. Next, this crucible was positioned in the furnace where the analysis was performed. The programmed TGA began by applying the heating rate of 20°C/min to heat the furnace from room temperature until the temperature reaches 950°C with a flow of an inert purified nitrogen gas at 100 mL/min. Then, the same heating rate was applied to increase the furnace temperature to 1300°C, and the gas being flowed at this combustion stage was changed to purified air. The trend of weight loss was recorded by thermogravimetry (TG) and derivative thermogravimetry (DTG). The data analysis was calculated based on weight loss procedure by the TGA software.

The Leco AC-350 bomb calorimeter was used to determine the calorific value (CV). The calorific value of a sample is determined by burning the sample in a controlled environment. The heat released by combustion is proportional to the calorific value of the substance. In the AC-350 bomb calorimeter, the weighed sample to be examined was located in a combustion vessel, which contains high-pressure atmospheric environment. The combustion vessel was surrounded by water and the sample is ignited. Succeeding that, the change in water temperature between pre-fire

and post-fire was processed by the computer. The result was then being corrected for the length of fuse wire. The result, which is the calorific value, is then being shown on the display screen.

The Fourier-transform infrared (FTIR) spectra were recorded using a Perkin Elmer FTIR spectrophotometer. The spectral region from 4000 to 400  $\text{cm}^{-1}$  was investigated. This spectrometer has a spectral resolution of 0.5  $\text{cm}^{-1}$  standard with an accuracy in its higher wavelength of 0.01–3000  $\text{cm}^{-1}$ . The resulting spectrum represents the sample absorption, following in its molecular fingerprint, due to its own functional groups. The FTIR spectra provide a quick qualitative technique that uses the standard IR spectra to identify the functional groups of the sample. The fundamental properties of the untreated PKS are summarized in **Table 1**.

## 2.5. Thermal decomposition using TGA

The thermal decomposition of the untreated and pretreated PKS was discovered by pyrolysis using a Mettler Toledo TGA/DSC 1 STAR<sup>e</sup> System. TGA provides a rapid method for determining the temperature-assisted decomposition profile of a sample and the kinetics of its thermal decomposition. A sample weight of 20 mg was inserted into 90  $\mu\text{L}$  ceramic crucible. The pyrolysis temperature was raised from room temperature to 900°C. The experiments were conducted under heating rates of 10°C/min. The high-purity nitrogen with flow rate of 50 mL/min was used as a carrier gas to ensure the inert atmosphere during the pyrolysis

Properties	Value
Elemental analysis (wt. %)	
Carbon	47.67
Hydrogen	5.52
Nitrogen	0.39
Sulphur	0
Oxygen <sup>a</sup>	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
<sup>a</sup> Calculated by different.	

**Table 1.** Properties of untreated PKS.

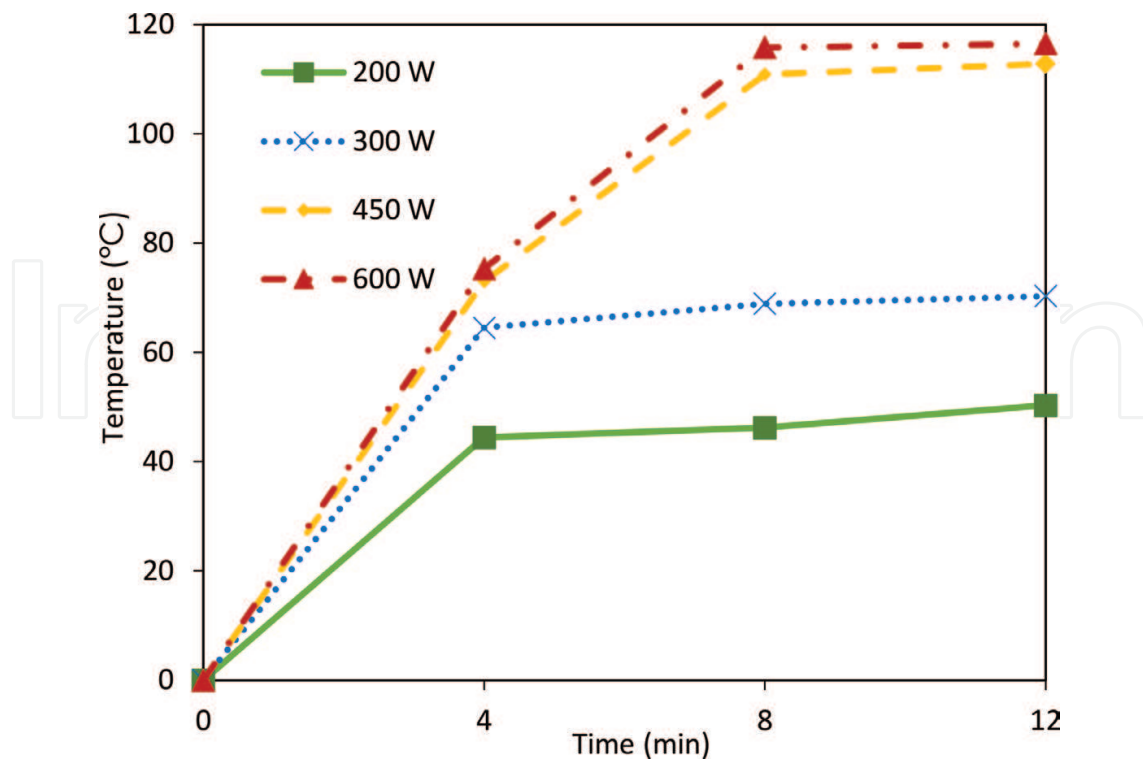


process. The decomposition of the sample was analyzed using the TG curve, which showed the mass loss versus temperature and time curves of TGA experiment [34]. Also, the DTG curves, representing the rate of weight loss with the increasing temperature, indicated the determination of the decomposition and thermal characteristics of untreated and pretreated samples. Each untreated and pretreated sample was pyrolyzed at least twice. However, additional duplications were carried out where some inconsistencies were observed.

### 3. Results and discussion

#### 3.1. Temperature profiles of torrefied PKS

**Figure 1** shows the temperature profiles of torrefied PKS at different processing time and microwave power levels. It shows that higher microwave power level contributed to increase the final temperature and heating rate. The torrefied PKS demonstrated increasing the final temperature and heating rate of 50.2–470.4°C and 12.6–117.6°C/min, respectively, when the microwave power level increased from 200 to 600 W in the first 4 min. These temperature profiles increased much steadily after about 4–8 min processing time. Conversely the temperature increment is not significant after 8–12 min processing time regardless the microwave power level. Therefore, higher processing time above 8 min was not necessary to upgrade the PKS. The microwave power level at 600 W with 4 min processing time was not suitable for upgrading the PKS, where it reached high heating rate of 117.5°C/min as the torrefaction requires heating rate equal or below 50°C/min [31].



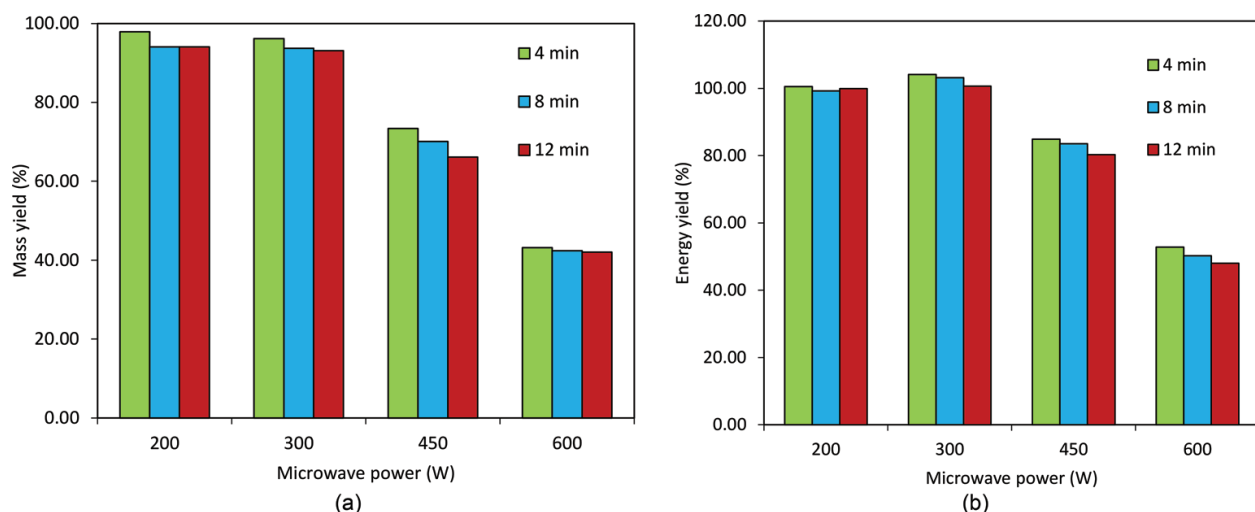
**Figure 1.** Temperature profile of torrefied PKS at various processing time and microwave power levels.

### 3.2. Mass and energy yield of torrefied PKS

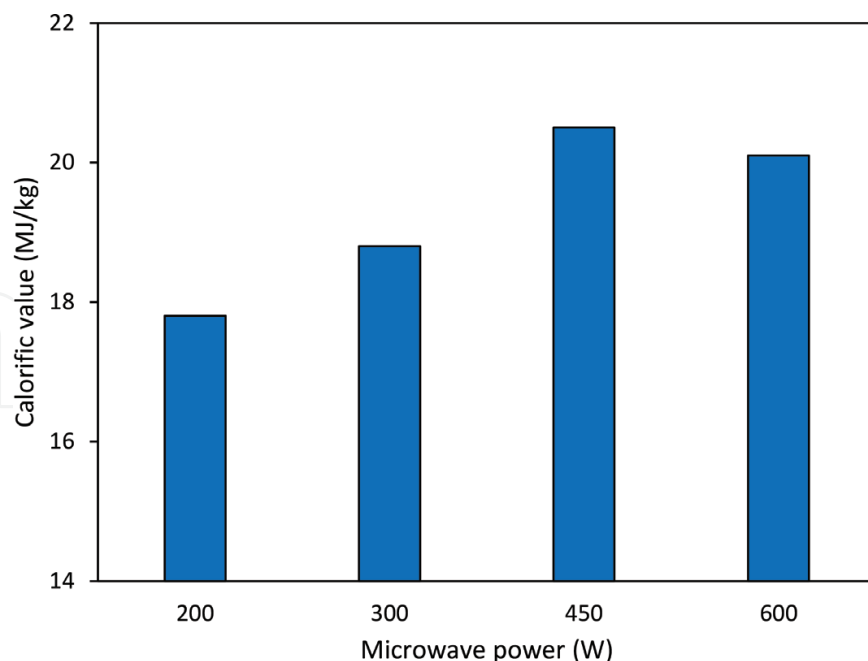
**Figure 2(a)** and **(b)** represents the mass and energy yield of torrefied PKS, respectively. It can be seen that the microwave pretreatment decreased the mass and energy yield of torrefied PKS while applying higher microwave power at certain reaction time. For example, the mass yields of torrefied PKS for 4 min were 97.9, 96.1, 73.3, and 43.2%, while the energy yields were 100.5, 104.1, 84.9, and 52.8% at 200, 300, 450, and 600 W, respectively. The high mass and energy yield at 200 and 300 W were influenced from low reactivity at low microwave power level. While at moderate power level of 450 W, the mass and energy yield were reduced reasonably to 70.1 and 83.5%, respectively, at 8 min processing time. However, at a microwave power level of 600 W, the mass and energy yield extensively reduced toward 43.7 and 52.8%, respectively, at processing time of 4 min, because of the severe reaction at the high microwave power level. At the higher reaction temperatures, which also increase microwave power level, the volatilization reaction of biomass might become a predominant reaction during the pretreatment process. As a result, the mass and energy yield of biomass would be reduced. At operating condition of 450 W and 8 min, more than 70% of mass and 80% of energy have been remained in the torrefied PKS. This phenomenon should be due to the carbonization and volatilization reactions of biomass, which would take place at the same time during the pretreatment process.

### 3.3. Calorific value (CV) of torrefied PKS

The CV is one of the main parameters for fuels to be used in subsequent thermal conversion. **Figure 3** shows the CV of torrefied PKS at different microwave power levels for 8 min processing time. The CV of untreated PKS was 18.2 MJ/kg. At the microwave power level of 450 W, the torrefied PKS had the highest CV of 20.5 MJ/kg, which was 12.6% higher than untreated PKS. Commonly, higher microwave power level contributed to higher CV of pretreated feedstock. However, when the microwave power level increased from 450 to 600 W, the CV of



**Figure 2.** (a) Mass yield of torrefied PKS at various microwave power and processing time, (b) Energy yield of torrefied PKS at various microwave power and processing time.



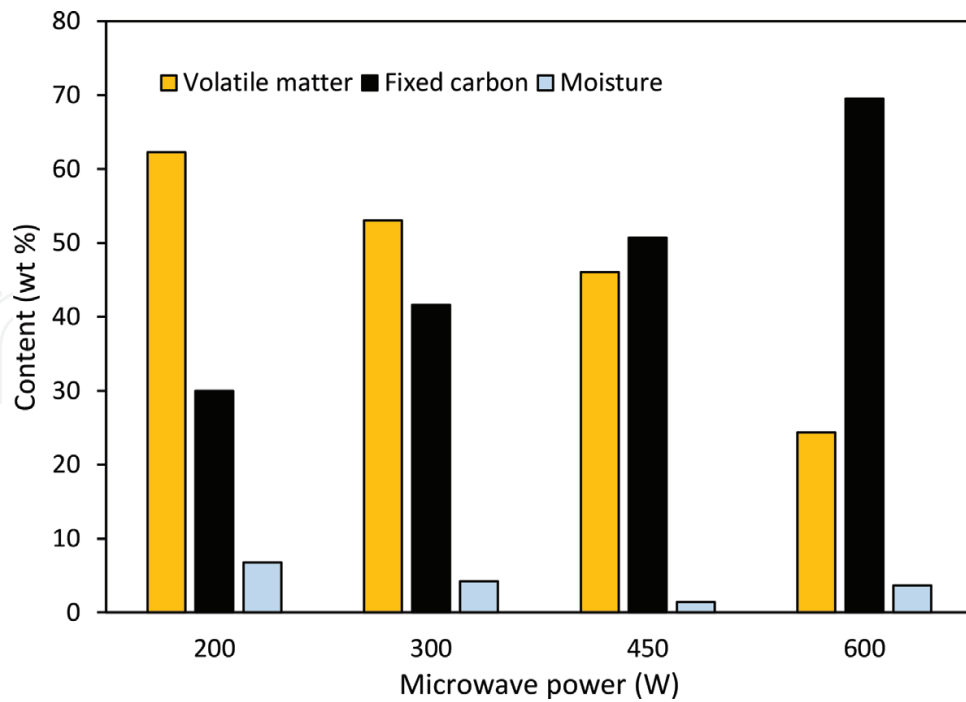
**Figure 3.** Calorific value of torrefied PKS at various microwave power with 8 min processing time.

torrefied PKS decreased. This may infer that when the reaction temperature is over 400°C due to higher microwave power levels (referring to **Figure 2(b)**), the fixed carbon content of biomass reduced resulting in the decrease of calorific value of torrefied PKS.

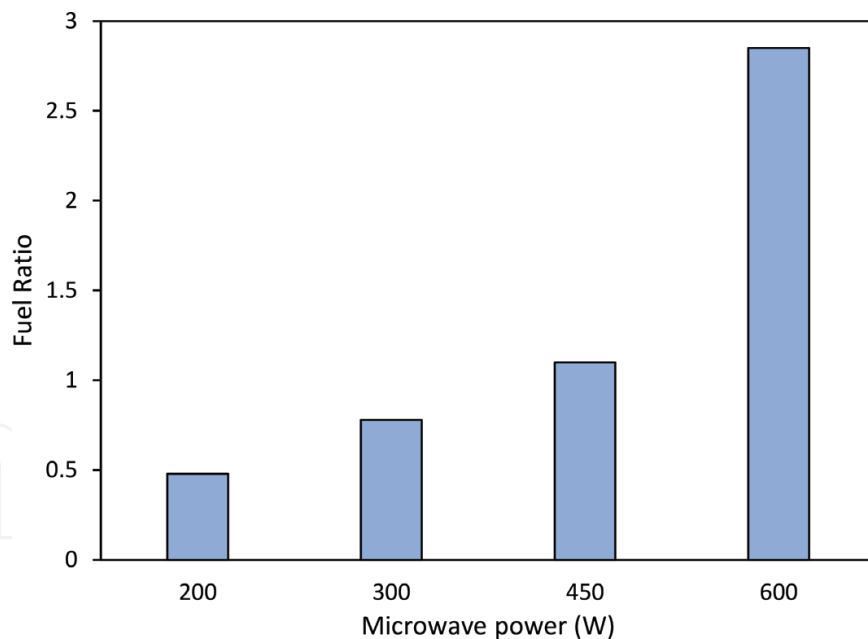
### 3.4. Proximate analysis of torrefied PKS

The torrefied PKS at 8 min processing time was chosen for proximate analysis. **Figure 4** shows the effect of microwave power level on moisture, volatile matter, and fixed carbon, respectively, of torrefied PKS. Generally, it can be seen that the moisture content and volatile matter decreased with increasing microwave power, in comparison to the untreated PKS. The results showed the characteristics of the torrefied PKS were altered due to high moisture content of untreated sample and its ability in absorbing microwave radiation. However, the fixed carbon of the torrefied PKS increased, with increasing microwave power level. The fixed carbon of the pretreated sample noticeably increased, representing a modification in quantity of energy per unit mass, which is related to the calorific value. Moreover, the decrease in volatile matter and moisture was observed. Since, the microwave pretreatment increases the carbon content, the fuel ratio of the irradiated samples eventually increased. This phenomenon was due to drying, volatilization, and decomposition of biomass feedstock during the pretreatment at higher microwave power.

The ratio of fixed carbon to volatile matter content, which is the fuel ratio, can indicate the accurate feedstock for thermal conversion. The fuel ratios of torrefied PKS at different microwave power levels with 8 min processing time are presented in **Figure 5**. After microwave pretreatment, the fuel ratios of pretreated materials significantly increased with increasing microwave power level. The fuel ratios of torrefied PKS increased from 0.48 to 2.85 when the microwave power levels increased from 200 to 600 W. The fuel ratio of 1.1 for pretreated PKS at 450 W is comparable with typical fuel ratio of bituminous coal, which is around 1.0–2.5 [35].



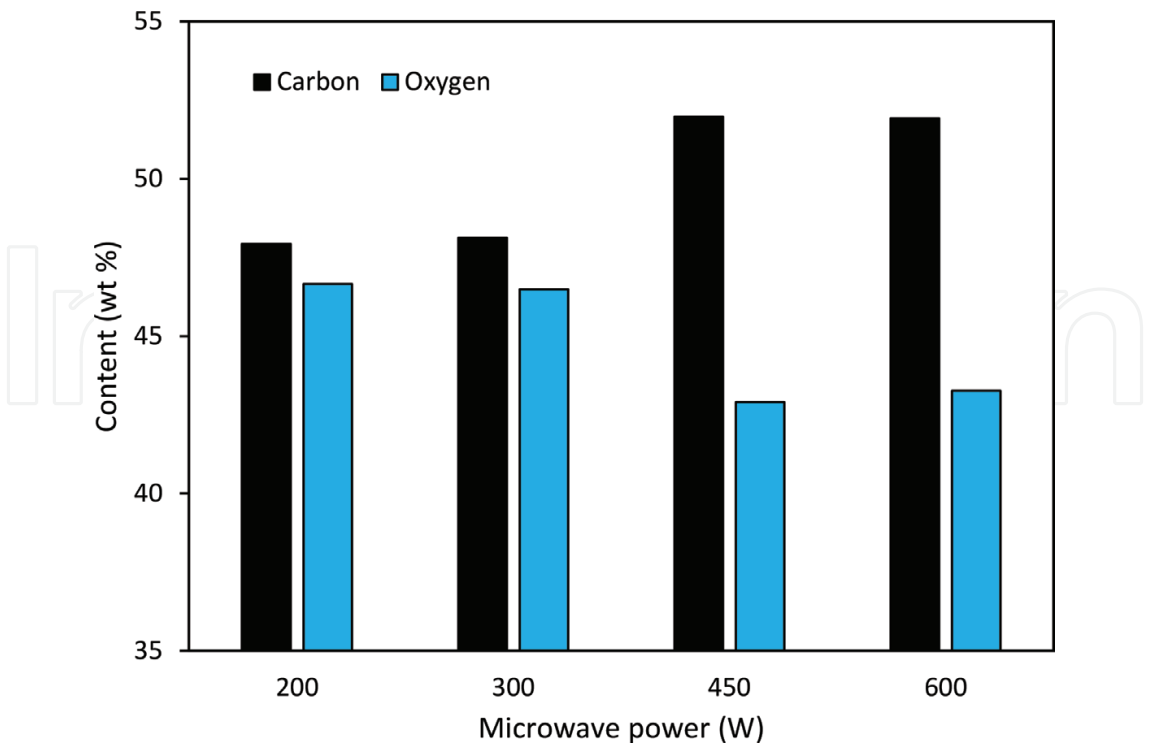
**Figure 4.** Volatile matter, fixed carbon and moisture content of torrefied PKS at various microwave power level with 8 min processing time.



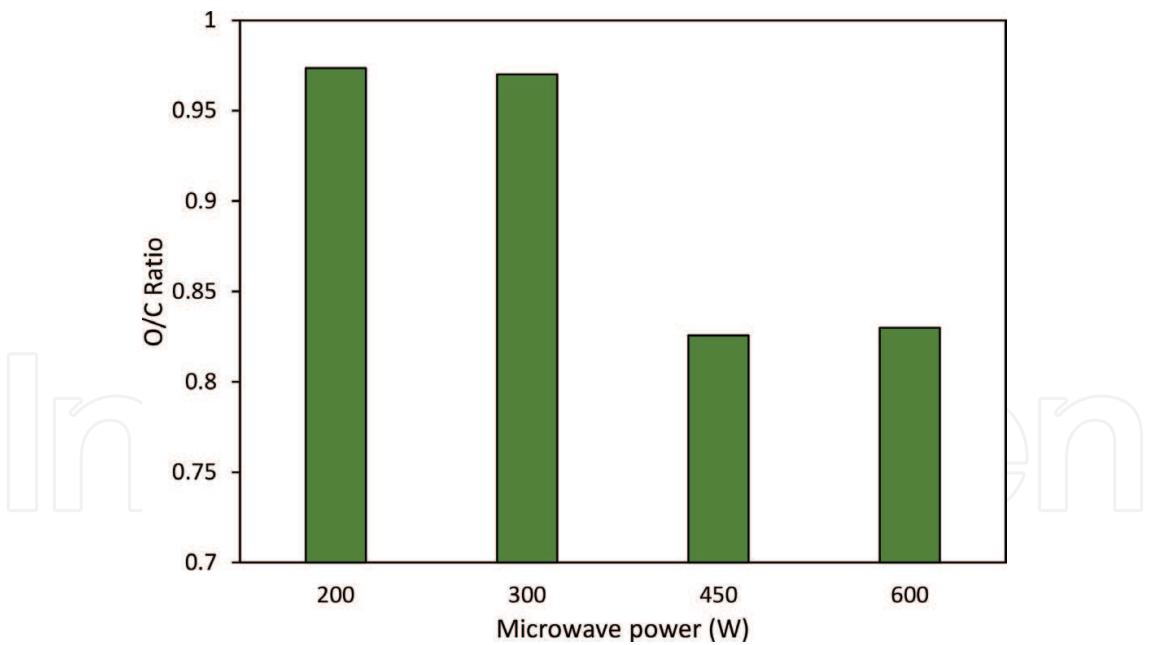
**Figure 5.** Fuel ratio of torrefied PKS at various microwave power with 8 min processing time.

### 3.5. Carbon and oxygen content of torrefied PKS

The torrefied PKS at 8 min processing time was chosen for ultimate analysis (carbon and oxygen content). **Figure 6** shows the effect of microwave power level on carbon and oxygen content of pretreated PKS. In general, the results indicate that oxygen decreased and carbon increased with the increase in microwave power level. The oxygen was reduced up to 43%



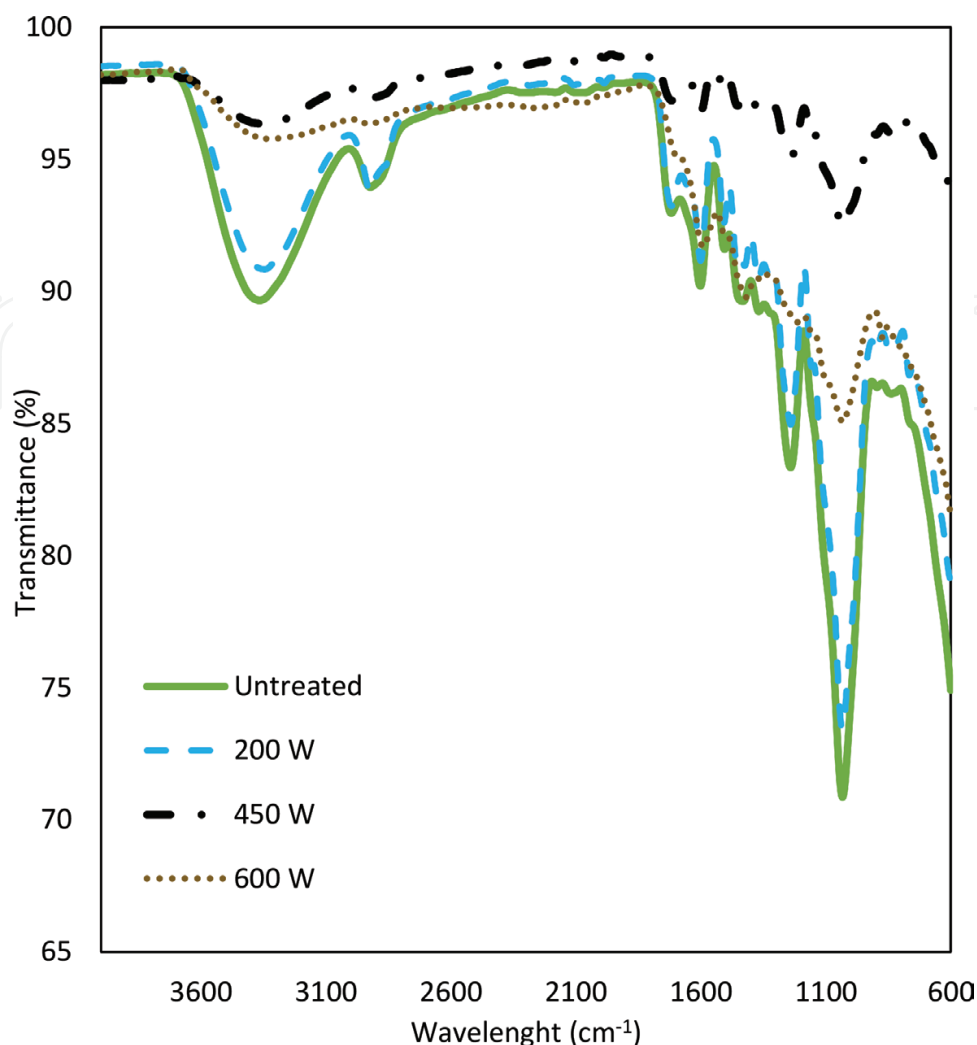
**Figure 6.** Carbon and oxygen content of torrefied PKS at various microwave power with 8 min processing time.



**Figure 7.** O/C ratio of torrefied PKS at various microwave power with 8 min processing time.

of pretreated PKS. On the contrary, carbon was increased up to 52 and 62% for torrefied PKS at the highest microwave power level of 600 W. The decrease in oxygen contents was generally attributable to the destruction of the hydroxyl group ( $-OH$ ) in PKS during pretreatment, which consequently produced solid hydrophobic fuel. Eventually, by removing oxygen using microwave irradiation method, the energy density of the torrefied PKS increased.





**Figure 8.** FTIR spectra of the untreated and pretreated PKS.

Due to the decomposition and elimination of volatile matter during pretreatment process, the oxygen mass fraction of the pretreated products will be lowered. Therefore, as illustrated in **Figure 7**, the O/C ratio of all torrefied samples was lower than that the untreated sample. As the microwave power level increased, the O/C ratio of torrefied PKS is gradually reduced as more volatile matter is being released as a result of the continuous decomposition process. The reduction of the atomic ratios also indicates the measures of conversion efficiency and oxidation degree of pretreated products [16].

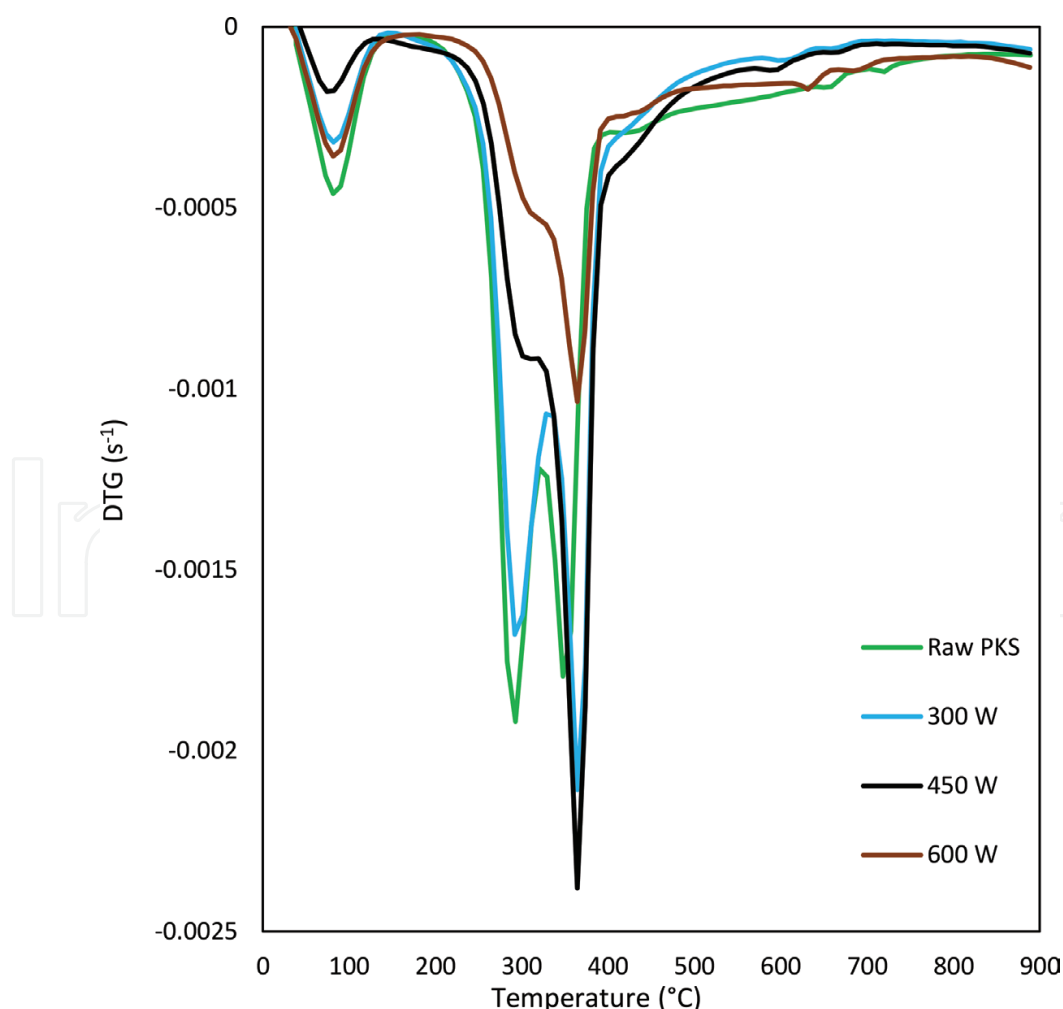
### 3.6. Functional group analysis of torrefied PKS

The torrefied PKS at 8 min processing time with microwave power of 200, 300, 450, and 600 W were chosen for functional group analysis. The chemical structure difference of untreated and pretreated PKS at various microwave power level was characterized using FTIR as shown in **Figure 8**. The FTIR spectra of untreated and pretreated PKS are similar in shape, but the intensity of the peaks is different. A broad peak at  $3400\text{ cm}^{-1}$  for untreated PKS was associated to the hydroxyl group ( $-\text{OH}$ ). These  $-\text{OH}$  groups exist with alcohols and phenols. The  $-\text{OH}$  peaks were

remarkably decreased with the increase of the microwave power. The peaks at  $2920$  and  $2880\text{ cm}^{-1}$  indicated aliphatic methylene groups. The peak intensity of pretreated PKS was smaller than raw PKS at higher microwave power of  $450$  and  $600\text{ W}$ . The carbonyl group ( $\text{C}=\text{O}$ ) bonds were observed at  $1750\text{ cm}^{-1}$  corresponding to various acids, aldehydes, and ketones, which were formed by decomposition of cellulose and hemicellulose. The peak was smaller at higher torrefaction temperature, which was linked with breakdown of hemicellulose. Peaks at  $1550\text{ cm}^{-1}$  present alkenes of  $\text{C}=\text{C}$  stretching. The most concentrated peaks were observed in the range of  $1500\text{--}1000\text{ cm}^{-1}$  and assigned to  $\text{C}=\text{O}$  stretching and  $\text{O-H}$  deformation at organic compounds containing oxygen (alcohols, phenols, and ethers). Aromatic groups are represented by peak  $790\text{ cm}^{-1}$  for PKS.

### 3.7. Thermal decomposition of torrefied PKS

The torrefied PKS at  $8\text{ min}$  processing time with microwave power of  $300$ ,  $450$ , and  $600\text{ W}$  were chosen for thermal decomposition in TGA. The analysis of pretreated sample at  $200\text{ W}$  was not chosen because its characteristic was similar with the untreated sample as discussed in the earlier section. The DTG curve of untreated and pretreated PKS is presented in **Figure 9**. The untreated and pretreated PKS showed three noticeable peaks existed in the DTG curve.



**Figure 9.** DTG curve of the untreated and pretreated PKS.

The main DTG peak at temperature range of 50–130°C indicated the moisture removal of the samples. The second DTG peak is located at 292 and 347°C, which referred to the maximum decomposition rate of hemicellulose and cellulose, respectively. After pretreated at microwave power level of 300 W, the peak was at 292°C and decreased slightly. However, the peak at 292°C moved to higher temperature at 373°C and significantly increased in the peak height. When the microwave power was increased to 450 and 600 W, the peak at 292 disappeared. Although the peak at 292°C moved to higher temperature at 373°C and significantly increased the peak height when pretreated at 450 W, there was a reduction in peak height after pretreated at 600 W. It is obvious that the second peak disappearance represents the hemicellulose lost at higher microwave power level at 450 W and above, whereas the third peak showed the cellulose retained, but the intensity was different. It is inferred that partial part of the cellulose and lignin remains and is not decomposed by the torrefaction using microwave irradiation [30].

## 4. Conclusions

This study presents the properties of torrefied PKS using thermal pretreatment via microwave irradiation. The torrefied PKS underwent physical and chemical modifications, which include mass reduction, rise in energy content, and change in chemical compositions. The increase in microwave power level showed the significant effect, which decreased the mass and energy yield of torrefied PKS. As the microwave power level increased, the moisture, volatile mater, oxygen content, and O/C ratio decreased. Among the microwave power-level variation studies, the carbon content and calorific value were enhanced to 55.94% and 21.20 MJ/kg, respectively, at microwave power of 450 W. The peak intensity of oxygenated functional group was reduced with the increase of the microwave power as presented in FTIR spectra. The TGA analysis has correlated the thermal decomposition with hemicellulose, cellulose, and lignin in torrefied PKS. The research can be concluded that the PKS can be upgraded via MI pretreatment to a value-added feedstock at microwave power of 450 W with processing time of 8 min. Thus, the torrefied PKS has the prospective to be applied in thermochemical conversion such pyrolysis, liquefaction, and gasification or co-conversion with coal.

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## Conflict of interest

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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## References

- [1] Emami Taba L, Irfan MF, Wan Daud WAM, Chakrabarti MH. The effect of temperature on various parameters in coal, biomass and CO-gasification: A review. *Renewable and Sustainable Energy Reviews*. 2012;**16**(8):5584-5596
- [2] Heidenreich S, Foscolo PU. New concepts in biomass gasification. *Progress in Energy and Combustion Science*. 2015;**46**:72-95
- [3] Mohr SH, Wang J, Ellem G, Ward J, Giurco D. Projection of world fossil fuels by country. *Fuel*. 2015;**141**:120-135
- [4] Nhuchhen D, Basu P, Acharya B. A comprehensive review on biomass torrefaction. *International Journal of Renewable Energy & Biofuels*. 2014;**2014**:1-56
- [5] Uemura Y, Omar WN, Tsutsui T, Yusup SB, Bt S. Torrefaction of oil palm wastes. *Fuel*. 2011;**90**(8):2585-2591
- [6] Sabil KM, Aziz MA, Lal B, Uemura Y. Effects of torrefaction on the physiochemical properties of oil palm empty fruit bunches, mesocarp fiber and kernel shell. *Biomass and Bioenergy*. 2013;**56**:351-360
- [7] Atnaw SM, Sulaiman SA, Yusup S. Syngas production from downdraft gasification of oil palm fronds. *Energy*. 2013;**61**:491-501
- [8] Ahmad Kushairi D. Malaysian oil palm industry performance 2016 and prospects for 2017. In: *Palm Oil Economic Review & Outlook Seminar 2017*. 2017. p. 6
- [9] Sabil KM, Aziz MA, Lal B, Uemura Y. Synthetic indicator on the severity of torrefaction of oil palm biomass residues through mass loss measurement. *Applied Energy*. 2013;**111**:821-826
- [10] Brar JS, Singh K, Wang J, Kumar S. Cogasification of coal and biomass: A review. *International Journal of Forestry Research*. 2012;**2012**:1-10

- [11] Ahmad R, Hamidin N, Ali UFM, Abidin CZA. Characterization of bio-oil from palm kernel shell pyrolysis. *Journal of Mechanical Engineering Science*. 2014;**7**(1):1134-1140
- [12] Ahmad R, Ismail K, Ishak MAM, Kasim NN, Abidin CZA. Pretreatment of palm kernel shell by torrefaction for co-gasification. In: 4th IET Clean Energy and Technology Conference (CEAT 2016). 2016. pp. 1-6
- [13] Chang ACC, Chang H-F, Lin F-J, Lin K-H, Chen C-H. Biomass gasification for hydrogen production. *International Journal of Hydrogen Energy*. 2011;**36**(21):14252-14260
- [14] Howaniec N, Smoliński A. Effect of fuel blend composition on the efficiency of hydrogen-rich gas production in co-gasification of coal and biomass. *Fuel*. 2014;**128**:442-450
- [15] Ahmad R, Azlan M, Ishak M, Kasim NN, Ismail K. Effect of different pretreatments on palm kernel shell and low-rank coal during co-gasification. *Progress in Petrochemical Science*. 2018;**2**(2):1-7
- [16] Chen WH, Peng J, Bi XT. A state-of-the-art review of biomass torrefaction, densification and applications. *Renewable and Sustainable Energy Reviews*. 2015;**44**:847-866
- [17] Asadullah M, Adi AM, Suhada N, Malek NH, Saringat MI, Azdarpour A. Optimization of palm kernel shell torrefaction to produce energy densified bio-coal. *Energy Conversion and Management*. 2014;**88**:1086-1093
- [18] Nam H, Capareda S. Experimental investigation of torrefaction of two agricultural wastes of different composition using RSM (response surface methodology). *Energy*. 2015;**91**:507-516
- [19] Satpathy SK, Tabil LG, Meda V, Naik SN, Prasad R. Torrefaction of wheat and barley straw after microwave heating. *Fuel*. 2014;**124**:269-278
- [20] Mamvura TA, Pahla G, Muzenda E. Torrefaction of waste biomass for application in energy production in South Africa. *South African Journal of Chemical Engineering*. 2018;**25**:1-12
- [21] Ibrahim RHH, Darvell LI, Jones JM, Williams A. Physicochemical characterisation of torrefied biomass. *Journal of Analytical and Applied Pyrolysis*. 2013;**103**:21-30
- [22] Matali S, Rahman NA, Idris SS, Yaacob N, Alias AB. Lignocellulosic biomass solid fuel properties enhancement via torrefaction. *Procedia Engineering*. 2016;**148**:671-678
- [23] Wang P, Howard BH. Impact of thermal pretreatment temperatures on woody biomass chemical composition, physical properties and microstructure. *Energies*. 2018;**11**(1):1-20
- [24] Salema AA, Ani FN. Microwave-assisted pyrolysis of oil palm shell biomass using an overhead stirrer. *Journal of Analytical and Applied Pyrolysis*. 2012;**96**:162-172
- [25] Motasemi F, Afzal MT. A review on the microwave-assisted pyrolysis technique. *Renewable and Sustainable Energy Reviews*. 2013;**28**:317-330
- [26] Tahmasebi A, Yu J, Han Y, Li X. A study of chemical structure changes of Chinese lignite during fluidized-bed drying in nitrogen and air. *Fuel Processing Technology*. 2012;**101**:85-93



- [27] Pickles CA, Gao F, Kelebek S. Microwave drying of a low-rank sub-bituminous coal. *Minerals Engineering*. 2014;**62**:31-42
- [28] Kingman SW, Rowson NA. Microwave treatment of minerals—A review. *Minerals Engineering*. 1998;**11**(11):1081-1087
- [29] Binner E, Lester E, Kingman S, Dodds C, Robinson J. A review of microwave coal processing. *The Journal of Microwave Power and Electromagnetic Energy*. 2014;**48**(1):35-60
- [30] Wang MJ, Huang YF, Chiueh PT, Kuan WH, Lo SL. Microwave-induced torrefaction of rice husk and sugarcane residues. *Energy*. 2012;**37**(1):177-184
- [31] Huang YF, Chen WR, Chiueh PT, Kuan WH, Lo SL. Microwave torrefaction of rice straw and pennisetum. *Bioresource Technology*. 2012;**123**:1-7
- [32] Huang Y, Sung H, Chiueh P, Lo S. Microwave torrefaction of sewage sludge and leucaena. *Journal of the Taiwan Institute of Chemical Engineers*. 2017;**70**:236-243
- [33] Sukiran MA, Abnisa F, Wan Daud WMA, Abu Bakar N, Loh SK. A review of torrefaction of oil palm solid wastes for biofuel production. *Energy Conversion and Management*. 2017;**149**:101-120
- [34] Vuthaluru HB. Investigations into the pyrolytic behaviour of coal/biomass blends using thermogravimetric analysis. *Bioresource Technology*. 2004;**92**:187-195
- [35] Sutcu H. Pyrolysis by thermogravimetric analysis of blends of peat with coals of different characteristics and biomass. *Journal of the Chinese Institute of Chemical Engineers*. 2007;**38**(3-4):245-249