EFFECT OF HYDROGEN PEROXIDE AS AN OXIDANT FOR THE WET TORREFACTION OF PALM KERNEL SHELL

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Abstract

Hydrogen peroxide (H_2O_2) is a green oxidant for hydrothermal treatment of biomass. In this research, the effect of hydrogen peroxide (H_2O_2) for the wet torrefaction of palm kernel shell (PKS) was studied. H_2O_2 can give extra intensity to reaction severity during the wet torrefaction process. The effect of H_2O_2 dosages from 0.0 M to 1.0 M at 200 °C was investigated. The mass yield of torrified PKS varied from 59.8 wt. % to 50.6 wt. % as H_2O_2 dosage increased. The trends of greater fixed carbon content, higher ash content, and lower moisture content were similar for torrified PKS treated with and without H_2O_2, as compared to raw PKS. The FTIR analysis revealed an increase in the breakdown of lignocellulosic components with torrefaction severity in the torrified PKS. The average HHV was 21.62 MJ/kg for different H_2O_2 dosages. Overall, the findings demonstrated that H_2O_2 did not make a substantial contribution to further enhancing the solid fuel properties. However, a higher degradation of cellulose and lignin components to liquid was achieved during the wet torrefaction process.

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1.0 INTRODUCTION

The rapid rise in energy demand excites the growth of renewable energy resources like biomass, wind, and solar energy. Biomass is greatly utilised among renewable energy resources and could account for up to 12% of global consumption (Krysanova *et al.,* 2019). However, low heating value, bulk density, high moisture content, and poor grindability (Specific energy consumption for grinding) offer significant limitations to the practical usage of biomass as a fuel source. These drawbacks result in higher costs of handling, transportation, and storage of biomass fuels. The pre-treatment process known as torrefaction is suggested to address these limitations of biomass. Torrefaction upgrades biomass into energy-dense solid fuels with improved properties like higher heating value, lower moisture content, and much better grindability than raw biomass (Ullah *et al.,* 2021).

Wet torrefaction (WT) can be described as a conversion process in a hydrothermal medium or hot compressed water at temperatures ranging from 180 °C to 260 °C (He *et al.,* 2018). At the threshold of the critical point, the characteristics of liquid water undergo notable changes such as the density and viscosity of hot compressed water (HCW) decrease, resulting in an increased mass transfer of chemical compounds (Phuang *et al.,* 2021). The enhanced transport properties of HCW expedite reactions, making it an outstanding medium for WT (Bach & Skreiberg, 2016). In addition, water improves its ability to dissolve organic compounds, makes it an exceptional reaction medium for facilitating reactions (Cortes-Clerget *et al.,* 2021).

Wet torrefaction is inspired by the concept of hydrothermal carbonisation (HTC), introduced by the German Nobel laureate, Friedrich Bergius (Bach & Skreiberg, 2016). Although WT is somehow similar to HTC, they are notably distinct from one another. WT is employed to produce solid biomass fuels with enhanced properties as feedstock for combustion, gasification,

and pyrolysis; whereas HTC is applied to synthesise carbonaceous char with higher carbon content to apply as energy storage, fertilisers, and activated carbon (He *et al.,* 2018). Operating parameters such as reaction temperature, reaction time, water-to-biomass ratio, and catalyst amount influence the effectiveness of WT in improving the properties of biomass-derived fuel.

Soh *et al.* studied the effect of temperature and residence time of wet torrefaction on the yield and inorganic content of two biomass. They reported that the wet torrified mass yield of empty fruit bunches (EFB) and oil palm trunks (OPT) decreased from 80.50 wt% to 62.89 wt% and from 64.58 wt% to 51.34 wt% respectively with increasing temperature from 180 °C to 240 °C. The energy density of EFB and OPT increased from 1.037 to 1.171 and from 1.070 to 1.147 respectively with increasing temperatures (Soh *et al.,* 2021). Moreover, Soh *et al.* reported that the torrified mass yield of EFB and OPT reduced 69.88 wt% to 62.89 wt% and from 62.47 wt% to 51.34 wt% respectively with elevated residence time from 2 to 3 h. (Soh *et al.,* 2021). Nevertheless, the influence of residence time on mass yield is not as significant compared to that of reaction temperature. Furthermore, Gan *et al.* studied the effect of temperature, water-to-biomass ratio, and residence time of WT on palm kernel shell whereas Phuang *et al.* studied the effect of temperature and water-to-biomass ratio of WT on yard waste. Both their studies revealed that the effect of the water-to-biomass ratio is rather insignificant (Gan *et al.,* 2019; Phuang *et al.,* 2021).

Chen *et al.* studied premixed dry spent coffee grounds (SCGs) with H_2O_2 and taken for dry torrefaction to improve HHVs of torrified biomass without extra energy input. They found that pretreatment with 18% H_2O_2 solution had a 7.8 % higher carbon content and 6.5 % higher HHV compared to the unpretreated one (Chen *et al.,* 2022). At higher operating conditions, H_2O_2 is decomposed into hydrogen cations (H^+) and perhydroxyl anion (HO_2-). HO_2- ion contacts with another peroxide molecule and forms free radicals like the hydroxyl ($HO^•$) and peryhdroxyl ($HO_2^•$) radicals. Perhydroxyl and water are formed from the reaction of the hydroxyl radicals ($HO^•$) and more peroxide molecules until all peroxide is converted into water. As a result, free radicals like $HO^•$ and $HO_2^•$ contribute to organic matter decomposition (Torres *et al.,* 2014). Therefore, the fuel properties of torrified biomass can be further improved through the utilisation of hydrogen peroxide (H_2O_2) as an oxidant during the biomass pre-treatment process. As of now, there is no literature reporting the application of oxidants to the WT process. Further investigation regarding the significance of varying dosages of H_2O_2 in the WT process will be addressed in this study. In this research, the authors hypothesised that the addition of H_2O_2 would provide higher severity in reaction than the corresponding temperature and pressure.

Palm kernel shell (PKS) is produced abundantly from the palm oil industry and therefore can be utilised as the raw material for wet torrefaction (WT). According to Gan *et al.,* the optimal temperature range for wet torrefaction under energy-efficient conditions should be between 180 °C to 220 °C (Gan *et al.,* 2019). Therefore, in the current research, the effects of H_2O_2 on the WT process were investigated using different dosages (0.0 M to 1.0 M) of H_2O_2 solution at a constant temperature of 200 °C with a residence time of 20 min and a biomass-to-water ratio of 0.15. These parameters were selected based on Gan *et al.*'s study. Raw and torrified PKS samples were analysed for thermogravimetry, proximate and ultimate analysis, HHV, and Fourier-Transform Infrared Spectroscopy (FTIR) whereas the liquid samples were analysed by pH and FTIR.

2.0 EXPERIMENTAL METHODOLOGY

2.1 Sample Preparation

The feedstock utilised in this research was PKS, which was procured from the Seri Ulu Langat Palm Oil Mill, located in Dengkil, Malaysia. The PKS was dried in an oven for 16 h at 75 °C.

2.2 Wet Torrefaction Experiments

The wet torrefaction of PKS was performed using a stainless-steel 1L high-pressure reactor autoclave (Model A 2335, Amar Equipment Pvt. Ltd.) capable of withstanding a maximum pressure of 350 bar and a temperature of 500 °C. Approximately 15 g of the PKS sample was placed into the reactor with a suitable amount of distilled water according to the H_2O_2 dosage. The autoclave and reactor vessel were firmly sealed with clamp bolts to prevent leakage during WT. A thermocouple was inserted to monitor the reaction temperature, while the sampling and vent ports were secured to enable pressure build-up in the reactor during the experiment. The mixture was continuously stirred at a rate of 107 rpm throughout the process. An automatic proportional integral derivative-controlled 2250-watt ceramic heater was then activated to increase the reactor temperature to the predetermined value. The pressure and temperature inside the reactor were recorded at 3-minute intervals until the desired temperature was reached. Once the desired temperature was reached, it was maintained for 20 min. The heater and stirrer were turned off after the experiment, and the reactor was allowed to cool down to ambient temperature, with the torrified biomass slurry left inside. The reactor vessel was then removed, and the slurry product was poured into a clean container. The reactor vessel was rinsed repeatedly with distilled water to collect all materials that had adhered to the reactor wall. The slurry products, which contained both solid and liquid products, were filtered and filtered through vacuum filtration and solid products were dried in an oven for 24 h at 103 °C. The torrified biomass was stored in a zipper storage bag at room temperature. The filtrate (liquid product) was measured for its volume and stored in a bottle in the fridge before further analysis.

The raw PKS sample and the H_2O_2-aided torrified PKS samples were labelled as raw PKS and TB $_{xxx}$, respectively. For instance, TB $_{0.000}$ represents torrified biomass without the use of H_2O_2 whilst TB $_{0.004}$ means torrified biomass with 0.004 M of H_2O_2.

To study the impact of oxidant-aiding wet torrefaction on PKS, the physicochemical properties of PKS before and after wet torrefaction at various H_2O_2 dosages were evaluated. By knowing the mass of raw and wet-torrified PKS before and after each run, the mass yield can be obtained using equation (1). Also, by knowing the volume of liquid feed and the volume

of the filtrate obtained after each run, the liquid yield can be calculated using equation (2).

$$\text{Mass yield (\%)} = \frac{m_{\text{solid torrefied PKS}}}{m_{\text{raw PKS}}} \times 100\% \quad (1)$$

$$\text{Liquid yield (\%)} = \frac{\text{volume of filtrate}}{\text{volume of liquid feed}} \times 100\% \quad (2)$$

2.3 Characterisation of Raw and Wet-Torrified Palm Kernel Shell

The proximate analysis of raw and torrified samples was analysed in a thermogravimetric analyser (TGA−DSC1, Mettler Toledo). 10 mg of the samples were heated fro m room temperature to 110 °C at a constant heating rate of 10 °C/min with a nitrogen flow rate of 20 mL/min. The temperature was maintained at 110 °C for 10 min. Subsequently, the samples were subjected to a constant heating rate of 10 °C/min and heated from 110 °C to 900 °C, following which they were maintained at 900 °C for 5 minutes. This was followed by the replacement of nitrogen with oxygen, with an oxygen flow rate of 20 mL/min, and the sample was kept at a constant temperature of 900 °C for an additional 10 minutes. The weight loss until 110 °C and the weight loss from 110 °C to 900 °C were regarded as moisture content (MC) and volatile matter (VM), respectively. In addition, the moisture and ash contents of biomass samples were determined manually to validate the results. In order to obtain the moisture content, 1 g of the sample was dried in an oven at 105 °C for 16 h and then allowed to cool in a desiccator with the use of silica gel as the drying agent. For the ash content, 1 g of the sample was ignited in an ashing furnace at 575 °C for 3 h and then allowed to cool in a desiccator with the use of silica gel as the drying agent. The fixed carbon (FC) can then be calculated using equation (3).

TB $_{0.050}$, TB $_{0.500}$, and TB $_{1.000}$ as samples were identified for their ultimate analysis as weight percentages (wt. %) of carbon, hydrogen, nitrogen, and sulphur in PKS using a CHNS elemental analyser (vario MACRO cube, Elementar), whilst the weight percentage of oxygen was calculated using equation (4).

$$\text{FC (\%)} = 100 - \text{MC(\%)} - \text{VM(\%)} - \text{AC(\%)} \quad (3)$$

$$\text{O (\%)} = 100 - \text{C(\%)} - \text{H(\%)} - \text{N(\%)} - \text{S(\%)} - \text{AC(\%)} \quad (4)$$

TB $_{0.004}$, TB $_{0.050}$, TB $_{0.100}$, TB $_{0.500}$, and TB $_{1.000}$ samples were sent to Universiti Teknologi PETRONAS, Perak for higher heating values (HHV) evaluation. Also, the fuel ratio (FR), combustibility index (CI), and volatile ignitability (VI) were calculated using equations (5), (6), and (7), respectively (Allouzi *et al.,* 2023).

$$\text{FR} = \frac{\text{FC}_{\text{dry basis}}}{\text{VM}_{\text{dry basis}}} \quad (5)$$

$$\text{CI (MJ/kg)} = \text{HHV}_{\text{dry basis}} \times (115 - \text{AC}_{\text{dry basis}}) \times \frac{1}{105\text{FR}} \quad (6)$$

$$\text{VI (MJ/kg)} = \frac{\text{HHV}_{\text{dry basis}} - 0.338\text{FC}_{\text{dry basis}}}{\text{VM}_{\text{dry basis}} - \text{FC}_{\text{dry basis}}} \quad (7)$$

Raw PKS, TB $_{0.004}$, TB $_{0.500}$, and TB $_{1.000}$ samples were assessed for their chemical changes in molecular bonding and functional groups using the Fourier transform infrared spectroscopy (FTIR, Spectrum RXI Perkin-Elmer) with attenuated total reflection (ATR) detector. Before scanning, the ATR diamond region was cleaned with acetone to ensure cleanliness. Samples were then placed in contact with the diamond crystal of the ATR device. The FTIR analyses for samples were run in the spectral range of 400 − 4000 cm^{-1} at a room temperature of 25 °C by reading an average of 8 scans with a resolution of 2 cm^{-1}.

3.0 RESULTS AND DISCUSSION

3.1 Wet Torrefaction Process and Products Yields

The primary objective of wet torrefaction process is to break down the complex polymer structures in biomass into shorter chains with lower molecular weights, thereby improving its fuel properties. In this research, H_2O_2 was shown to have a perceptible effect on the mass yield of torrified PKS, as shown in Table 1. The mass yield decreased with the increase in H_2O_2 dosage, especially while 1.0 M of H_2O_2 was used. This phenomenon could be attributed to the breakdown of hemicellulose and the partial decomposition of lignin and cellulose. As H_2O_2 dosage increased, there was an extra mass loss resulting from the complete disintegration of hemicellulose and further decomposition of lignin and cellulose. This determined that the incorporation of H_2O_2 has a substantial impact on the mass yield of torrified biomass. This also suggested that the addition of H_2O_2 during WT resulted in a lower mass yield even without raising the reaction temperature. The previous study conducted by Gan *et al.* revealed that the mass yield of PKS that underwent WT at 200 °C was 59.15 ± 0.72 wt. %, whilst that at 235 °C was 51.22 wt. % (Gan *et al.,* 2019). Furthermore, another research by Ameen *et al.* showed that the mass yield of palm shells that underwent HTC at 300 °C was 54.5 % (Ameen *et al.,* 2022).

Table 1: Product yield and liquid yield for torrified PKS

Sample	Mass Yield (wt. %)	Liquid Yield (wt. %)	Pressure (bar)
TB $_{0.000}$	59.80	63.00	13
TB $_{0.004}$	59.76	83.00	13
TB $_{0.050}$	59.30	87.00	13
TB $_{0.100}$	58.87	85.00	11
TB $_{0.500}$	56.60	83.00	15
TB $_{1.000}$	50.60	79.00	15

He *et al.* reported that the order of decomposition rate for wet torrefaction processes above 200 °C can be ranked as with hemicellulose being the most reactive, followed by cellulose and lignin being the least reactive component (He *et al.,* 2018). According to Gan *et al.* and Phuang *et al.,* the ideal temperature range for efficient fuel production is between 180 and 220 °C (Gan *et al.,* 2019); (Phuang *et al.,* 2021). This is to avoid operating at high pressures, which would lead to increased capital and operating costs, as well as higher energy demands.

Table 2: Proximate analysis, ultimate analysis, and fuel properties of raw and torrified PKS

Sample	raw PKS	TB $_{0.000}$	TB $_{0.004}$	TB $_{0.050}$	TB $_{0.100}$	TB $_{0.500}$	TB $_{1.000}$
Proximate Analysis (wt. %)							
MC	7.9	3.6	4.6	5.1	4.2	3.7	2.7
VM	65.0	56.9	53.9	55.1	56.8	55.0	58.4
AC	0.9	1.1	1.0	1.0	1.1	1.4	1.6
FC	26.2	38.4	40.5	38.8	37.8	39.8	37.3
Ultimate Analysis (wt. %)							
C	47.9	53.5	-	53.6	-	54.6	55.1
H	6.1	5.8	-	5.8	-	5.7	5.5
N	0.52	0.50	-	0.34	-	0.35	0.34
S	0.22	0.07	-	0.38	-	0.17	0.15
O	40.7	36.7	-	38.9	-	37.7	37.3
H/C ratio	1.53	1.3	-	1.29	-	1.25	1.19
O/C ratio	0.64	0.51	-	0.54	-	0.52	0.51
Fuel Properties (MJ/kg)							
HHV	18.9	22.6	22.5	21.5	21.2	22.0	21.8
FR	0.40	0.64	0.75	0.70	0.67	0.72	0.64
CI	55.4	37.7	34.1	35.0	36.0	34.1	37.9
VI	0.30	0.57	0.74	0.58	0.49	0.62	0.46

'-' not analysed

Since the primary focus of this study was on the effect of H_2O_2 dosage on WT, the temperature was kept constant at 200 °C.

Moreover, the influence of various H_2O_2 dosages on the operating pressure during the wet torrefaction process was insignificant, possibly due to the dominant effect of liquid feed on the pressure. This revealed that the employment of H_2O_2 did not increase the operating pressure, which is desirable as a higher operating pressure often leads to higher operational risks at the industrial level. It could be concluded that the addition of H_2O_2 can achieve a similar outcome in terms of reducing the mass yield without the need to raise the reaction temperature, which would otherwise incur higher capital costs.

On the other hand, the incorporation of H_2O_2 during the WT process resulted in a higher liquid yield compared to that without H_2O_2. This may be attributed to the elevated decomposition rate of biomass with increasing reaction severity, which aligned with the findings reported for HTC (Nizamuddin *et al.,* 2015). Another study conducted by Kumar *et al.* suggested that the bio-oil yield increased during the hydrothermal liquefaction (HTL) process from 44 wt. % to 46 wt. % while employing H_2O_2 in an inert (N_2) condition (Kumar *et al.,* 2021). It could be deduced that the incorporation of H_2O_2 during the WT process led to a higher liquid yield but the effect of varying H_2O_2 dosages was found to be insignificant. Further investigation is required to analyse the influence of H_2O_2 dosage on the quality of biomass composition using various analysis methods.

3.2 Physicochemical Properties of Raw and Wet-Torrified Palm Kernel Shell

3.2.1 Proximate and Ultimate Analyses

The result of the proximate analysis at different H_2O_2 dosages is shown in Table 2. The moisture content of H_2O_2-aided torrified PKS was significantly lower than that of raw PKS, suggesting that the hydrophilic property of PKS declined (Stirling *et al.,* 2018). Besides, H_2O_2-aided torrified PKS exhibited a lower volatile matter content compared to raw PKS, resulting in fuel properties that more closely resemble coal (Bach & Skreiberg, 2016). The use of a higher H_2O_2 dosage in WT led to a higher ash content in PKS. As a result, H_2O_2-aided torrified PKS samples had higher ash content than raw PKS, which is consistent with the reported findings that employed H_2O_2 for dry torrefaction (Chen *et al.,* 2022). This may be linked to the breaking of hydrogen-carbon bonds, which leads to a higher retention of ash content in the biomass (Phuang *et al.,* 2021a). Additionally, all torrified samples had significantly higher fixed carbon content than untreated PKS, which is a preferred fuel attribute. Nevertheless, the moisture, volatile matter, ash, and fixed carbon contents of H_2O_2-aided torrified PKS were found to be similar to those of TB $_{0.000}$, indicating that the addition of H_2O_2 did not contribute significantly to further enhancing the fuel characteristics of PKS.

Typically, solid fuels with a low O/C ratio are associated with reduced water vapour formation, smoke emission, and energy loss during combustion (Yang *et al.,* 2017). Torrified biomass with a high oxygen content has a lower heating value and is considered a mediocre fuel as a consequence of the high flue gas emissions during the following thermochemical process. Thus, solid fuels with low oxygen content and a low O/C atomic ratio are preferred as they exhibit coal-like behaviour (Tumuluru, 2016).

TB $_{0.050}$ had a carbon content of 53.6 wt. % and the carbon content in TB $_{1.000}$ was increased to 55.1 wt. %. In contrast, the weight percentages of hydrogen and oxygen decreased as the H_2O_2 dosage increased, as shown in Table 2. Gan *et al.* reported that the O/C and H/C atomic ratios for PKS that went through WT at 200 °C were 0.51 and 1.30, respectively (Gan *et al.,* 2019). The incorporation of H_2O_2 during the WT process

led to a similar O/C atomic ratio but a lower H/C atomic ratio. These changes were likely due to the increase in dehydration and decarboxylation reactions that happened during WT (Nizamuddin *et al.,* 2015). The sulphur content reduced with increasing H_2O_2 dosage implied that fewer sulphur oxides are likely to form during combustion. In contrast, the differences in nitrogen content were insignificant. It could be inferred that the addition of H_2O_2 contributed to a slight reduction of the O/C atomic ratio. Reduction in the H/C ratio was not favoured. The current result showed that the addition of H_2O_2 did not enhance hydrogenation.

Furthermore, the thermogravimetric (TG) curves and its derivative (DTG) curves for raw PKS, TB $_{0.004}$, TB $_{0.500}$, and TB $_{1.000}$ were displayed in Figure 1 and Figure 2. Thermal decomposition of PKS happened in three zones, namely the dehydration zone, the devolatilisation zone, and the char decomposition zone (Phuang *et al.,* 2021). The dehydration stage took place from 25 °C to 130 °C, ascribed to the decrease in moisture level in the samples due to the process of evaporation and drying. During the devolatilisation stage, which occurred between 130 °C and 450 °C, a significant weight loss was spotted mainly brought about by the volatilisation of cellulose and hemicellulose. While for the char decomposition stage that ranges from 450 °C to 800 °C, lignin, and other strongly bonded compounds decomposed slowly and contributed to the remaining weight loss.

As shown by the DTG curves in Figure 2, the point where the most significant mass loss can be identified. The first zone of the DTG curve (<130 °C) exhibited a minor weight loss in the samples, occurring at a temperature of approximately 60 °C and 110 °C for raw PKS and H_2O_2-aided torrified PKS, respectively, attributed to the removal of moisture and some light volatile compounds (Nizamuddin *et al.,* 2018). This could be attributed to the fact that the H_2O_2-aided torrified PKS contained mainly equilibrium moisture content and therefore the delay in weight loss.

The second stage of the DTG curve (130 – 450 °C) emerges from the thermal breakdown of cellulose and hemicellulose. As shown in Figure 2, a single peak accompanied by two smaller peaks was detected. The first small peak was observed at 281 °C for raw PKS because of the thermal breakdown of hemicellulose as hemicellulose is extremely reactive at temperatures above 200 °C (Aslam *et al.,* 2019). Conversely, a much smaller peak was seen for TB $_{0.004}$, TB $_{0.500}$, and TB $_{1.000}$, showing that much of the hemicellulose was removed after the H_2O_2-aided WT process (He *et al.,* 2018). Since the peak of hemicellulose was detected at a lower temperature, it was indicative that the thermal stability of hemicellulose, cellulose, and lignin increased in ascending order. This could be proven that hemicellulose is the least thermally stable among the three constituents (Phuang *et al.,* 2021).

The second small peak in the devolatilisation zone was observed at 360 °C, which lies within the range of 300 °C to 400 °C where the cellulose degradation took place (Cichosz & Masek, 2020). The intensity of this peak diminished as the H_2O_2 dosage increased, indicating the partial removal of cellulose at higher H_2O_2 dosages. The similarity in peak positions

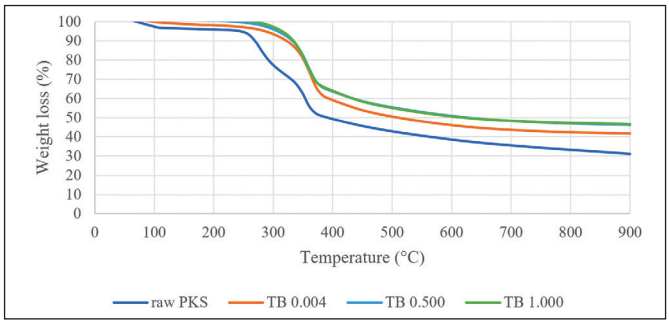

Figure 1: TGA curves for raw and torrified samples with different H_2O_2 dosages

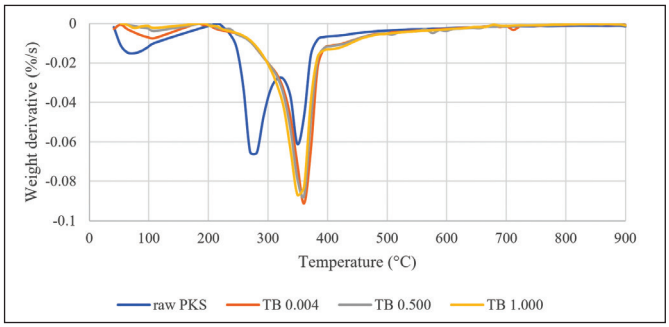

Figure 2: DTG curves for raw and torrified samples with different H_2O_2 dosages

among the torrified samples indicated that the H_2O_2-aided WT process did not significantly alter the structural characteristics of cellulose. The thermal decomposition of lignin was characterised by a smooth region over a broad temperature range of 380 – 500 °C. In addition, a minor peak identified at around 508 °C and 580 °C for TB $_{0.500}$ were attributed to the thermal decomposition of some cellulose and mostly lignin whilst a small peak was spotted at approximately 700 °C for TB $_{1.000}$ corresponded to the secondary or complete disintegration of lignin (Phuang *et al.,* 2021).

3.2.2 Fuel Properties

Gan *et al.* reported that the higher heating value (HHV) of PKS that underwent WT at 200 °C was 22.57 ± 0.08 MJ/kg. As shown in Table 2, the HHVs of torrified PKS were found to be relatively similar across different H_2O_2 dosages. This suggested that the thermal degradation rate of the H_2O_2-aided torrified PKS samples remained consistent, even with the varying dosages of H_2O_2 used. Therefore, the torrified PKS with different H_2O_2 dosages exhibited comparable HHVs, which could be attributed to similar thermal stability (Arpia *et al.,* 2021). The findings implied that the effect of varying H_2O_2 dosages on HHV was found to be insignificant at higher levels. However, the presence of H_2O_2 gave better results in terms of FR.

The fuel ratio (FR), typically expressed as the ratio of fixed carbon to volatile matter, is widely used for classifying coals as it provides theoretical insights into combustion efficiency. According to Table 2, it was observed that the fuel ratio was significantly higher in torrified PKS compared to raw PKS. However, the difference in fuel ratio between torrified PKS treated with and without H_2O_2 was minor. A high fuel ratio resulted in reduced smoke formation and limited emissions

during burning, which ultimately improved the fuel quality. In general, biomass has a low fuel ratio, but this ratio was increased to between 0.64 and 0.75 through WT, indicating an improved fuel quality. The high fuel ratio in torrified PKS was attributed to the increased fixed carbon content and reduced volatile matter, resulting in stable and complete combustion (Allouzi *et al.,* 2023).

The combustibility index (CI) usually refers to the fire and combustion behaviour of materials. The CI value decreased from raw PKS to torrified PKS, suggesting an improvement in PKS quality through the WT process. Nevertheless, the difference in CI value between wet torrified PKS with and without the use of H_2O_2 was insignificant. This indicated that the addition of H_2O_2 during the WT process did not further improve the compatibility of the torrified PKS for mixed combustion with coal (Allouzi *et al.,* 2023).

Moreover, the volatility index (VI) typically indicates the total energy content of the fuel yielded by the volatile elements by assuming that the fixed carbon in the fuel consists solely of pure carbon. The VI value increased by 2 times, but this increment was insufficient as beyond 10 times increment is required for a coal-like fuel (Allouzi *et al.,* 2023).

3.2.3 Fourier-Transform Infrared Spectroscopy Analysis (FTIR)

The FTIR spectra in Figure 3 portrayed the functional groups present in the samples. They exhibited some similarities in their absorbance peaks, but there were significant molecular changes. The broad transmittance peak at 3300 cm^{-1} corresponded to the stretching vibration of O−H due to intra- and intermolecular hydrogen bonds, a distinctive feature of crystalline cellulose. The decrease in peak intensity at TB $_{0.500}$ and TB $_{1.000}$ indicated that H_2O_2-aided torrified PKS samples have fewer sites for hydrogen bonding, presumably due to the degradation of hemicellulose and cellulose (Gan *et al.,* 2019). Elimination of this hydroxyl group was beneficial as it improved the hydrophobic nature of the biomass (Zhang *et al.,* 2019). The peaks at 2931 and 2843 cm^{-1} were attributed to the stretching vibration of C-H of alkanes in hemicellulose and cellulose (Wang *et al.,* 2018). The decline in the intensity of these bands indicated the elimination of aliphatic −CH2 groups (Kumar Mishra & Mohanty, 2020). The peak at approximately 1725 cm^{-1} was solely detected in raw PKS. It signified the stretching vibrations of C=O in the carboxylic acids of hemicellulose. The lack of this peak in TB $_{0.004}$, TB $_{0.500}$, and TB $_{1.000}$ implied the complete elimination of the hemicellulose ester group (Pérez-Limiñana *et al.,* 2022), as a result of deacetylation with the aid of H_2O_2 during WT. Hemicellulose has less thermal stability as compared to cellulose and lignin. The thermal stability of torrified biomass increased as H_2O_2 amount increased as shown in TGA analysis in Figure 1.

The reduction in carboxylic acid groups was accompanied by a corresponding increase in the relative amount of lignin, as revealed by the peaks at 1685 and 1600 cm^{-1}. These peaks represented the stretching vibrations of C=O and C=C, which could be carboxyl groups, aldehydes, esters, ketones, and aromatic structures that are present in lignin (Ullah *et al.,* 2021). The strengthened absorption of C=O with 0.004 M H_2O_2 reaction was attributed to the greater abundance of lignin in H_2O_2-aided torrified PKS samples, which also resulted high amount of fixed carbon and fuel ratio (FR). The peaks at 1450 and 1428 cm^{-1} corresponded to the C≡C bond, which confirmed the presence of the alkyne group (Kumar Mishra & Mohanty, 2020), which the dominance of lignin in torrified samples and therefore improvement in fuel properties. The peak at 1269 cm^{-1} was attributed to the stretching vibration of C-O for guaiacyl and syringyl groups in lignin (Phuang *et al.,* 2021a). The peak intensity measured in this study was almost similar to the previous results reported by Gan *et al.* (Gan *et al.,* 2019). This revealed that the aid of H_2O_2 during WT had a mild influence on lignin decomposition.

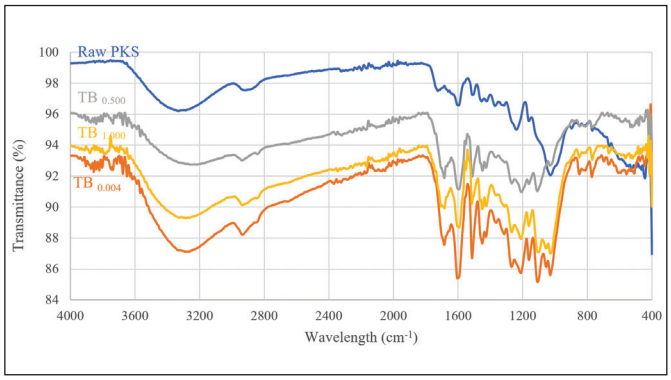

Figure 3: FTIR spectra of raw and wet-torrified PKS

The band observed at approximately 1162 cm^{-1} corresponded to the antisymmetric stretching vibrations of C−O−C glycosidic linkages in both hemicellulose and cellulose. A significant decrease in absorbance was observed in H_2O_2-aided torrified PKS, compared to raw PKS, indicating the significant loss of cellulose fractions. The peak intensity observed in this study was higher for TB $_{0.004}$, possibly because of the removal of hemicellulose and cellulose at higher concentrations of H_2O_2. The intensified peaks could also be a result of some degree of degradation that may have occurred (Phuang *et al.,* 2021a). Furthermore, the peaks observed at approximately 1071 cm^{-1} in raw PKS and 1031 cm^{-1} in H_2O_2-aided torrified PKS, indicating the vibrations of aliphatic C−O−C and C−OH in alcohol, primarily originating from cellulose (Wang *et al.,* 2018). Lastly, the peak discovered at 771 cm^{-1} symbolised mono and polycyclic aromatic groups owing to O-H bending vibrations (Kumar Mishra & Mohanty, 2020). In short, H_2O_2-aided torrified PKS samples showed increasing aromatic characteristics, owing to their removal at higher H_2O_2 concentrations.

3.3 Characterisation of Liquid Produced from Wet Torrefaction

3.3.1 pH

The pH for liquid produced from WT is shown in Table 3. Increasing the H_2O_2 dosages led to decreases in the pH of the liquid produced. The decrease in pH was indicative of increased acidity in the liquid, possibly due to the degradation of lignin. Therefore, the liquid samples produced at higher H_2O_2 dosages exhibited higher levels of acidity than those produced with lower H_2O_2 dosages. The acidity in the liquid was mainly because

Table 3: pH for liquid produced from WT

H_2O_2 Dosage (M)	pH
0.004	3.3
0.050	3.2
0.100	3.2
0.500	3.0
1.000	2.8

organic acids, such as formic and acetic acids are present, which are breakdown products of hemicellulose. However, the presence of these acids may result in liquid instability and equipment corrosion (Chong *et al.,* 2019). However, an increase in the acidity of liquid samples for the increase in H_2O_2 dosage showed that further cracking happens, and more acids would be formed.

3.3.2 Fourier-Transform Infrared Spectroscopy Analysis (FTIR)

The FTIR spectra in Figure 4 illustrates the functional groups present in the liquid samples. Although they shared some similarities in their absorbance peaks, significant molecular changes were observed. The wide transmittance peak at 3300 cm^{-1} manifested the stretching vibration of O−H and implied the presence of phenols, organic acids, aromatics, and water impurities in WT liquid samples (Kumar Mishra & Mohanty, 2020). The peak intensity increased as the H_2O_2 dosage increased, which can be related with the increase in organic acids. An increase in acidity as the increase in H_2O_2 dosage was noticed in section 3.3.1. A peak at 1635 cm^{-1} is observed, which was attributed to C=C stretching vibration, indicating the presence of alkenes and aromatic compounds in liquid samples as more lignin degradation occurred (Kumar Mishra & Mohanty, 2020). The presence of aliphatic and aromatic compounds in the liquid samples was confirmed by the peak detected at 607 cm^{-1}, which corresponded to the bending vibrations of O-H in mono and polycyclic aromatic groups (Kumar Mishra & Mohanty, 2020). This peak showed the presence of more lignin degraded components in the liquid. The product yield and characterisation studies revealed that the presence of H_2O_2 in a small amount made a negligible change in the torrified biomass. However, as the concentration of H_2O_2 increased significantly, more severity in the reaction happened, which did not improve solid fuel properties, instead the cellulose or lignin degradation into liquid components happened.

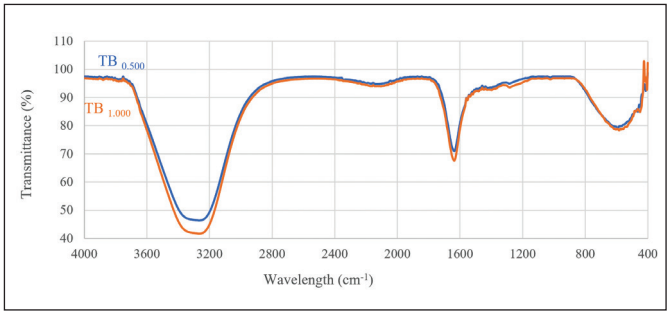

Figure 4: FTIR spectra of liquid produced

4.0 CONCLUSION

Palm kernel shell (PKS) exhibits promising potential as a sustainable and high-quality renewable energy resource. In this research, wet torrefaction of PKS was performed with the aid of H_2O_2 to enhance its fuel properties without raising the reaction temperature. The mass yield of PKS decreased from 59.8 wt. % to 50.6 ± 0.3 wt. % with elevated H_2O_2 dosages, indicating the disintegration of hemicellulose and cellulose during wet torrefaction. The trends of greater fixed carbon content, higher ash content, and lower moisture content as compared to raw PKS. However, these properties were similar for torrified PKS treated with and without H_2O_2, implying that the addition of H_2O_2 did not contribute significantly to further enhancing the fuel characteristics of PKS. The FTIR analysis revealed an increase in the breakdown of lignocellulosic components with torrefaction severity in the torrified PKS. The CHNS elemental analysis demonstrated an enhancement in the fuel properties of PKS through an increase in carbon content from 53.6 wt. % to 55.1 wt. %, a decrease in oxygen content from 38.9 wt. % to 37.3 wt. %, and a reduction in the O/C atomic ratio from 0.54 to 0.51 with increased H_2O_2 dosages, making the solid fuel more analogous to coal. Overall, the findings demonstrate that H_2O_2 did not make a substantial contribution for further enhancing the solid fuel properties during the wet torrefaction process. ■

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- **Poh Lae Ooi**: Writing – original draft, validation, methodology, data collection, formal analysis
- **Rui Hong Teoh**: Validation, methodology, data collection, formal analysis
- **Lai Yee Lee**: Writing – review & editing, formal analysis
- **Suyin Gan**: Writing – review & editing, formal analysis
- **Revathi Raviadaran**: Methodology, investigation
- **Sona R. Moharir**: Methodology, formal analysis
- **Suchithra Thangalazhy-Gopakumar**: Writing – review & editing, validation

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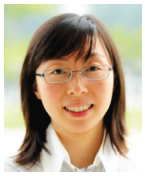

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