Effect of Particle Size and Temperature on Pyrolysis of Palm Kernel Shell

Khairunnisa Kamarul Zaman[1], Vekes Balasundram[2], Norazana Ibrahim[3]*, Mohammad Dinie Muhaimin Samsudin[4], Rafiziana Md. Kasmani[5], Mohd. Kamaruddin Abd Hamid[6], Hasrinah Hasbullah[7]

[1]*Energy Management Group, Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia (UTM), 81310 UTM Johor Bahru, Johor, Malaysia.*
[2]*Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia (UTM),*
81310 UTM Johor Bahru, Johor, Malaysia.
*Corresponding author E-mail: norazana@utm.my

Abstract

Pyrolysis is a viable solution to curb the issue of growing lignocellulosic waste in the world through conversion to potential biofuel and bio-based chemicals. This study focused on the effect of biomass particle size on the feedstock characterisation, biomass ash content, thermal behaviour and pyrolysis products yield. The particle size ranges studied were <0.355, 0.355 to 0.710. 0.710 to 1.00 and 1.00 to 2.00 mm. Thermal behaviour was analysed using thermogravimetric analyser, and pyrolysis experiments were conducted in a fixed-bed pyrolyzer. TGA results show smaller particle size maximum temperature shifted to a lower temperature. From ashing, the results indicated that ash content is the highest at the smallest particle size, <0.355mm (2.8 wt.%). The gaseous yield was the highest in dpA (<0.355 mm) at a temperature of 600°C. The highest pyrolysis oil yield (50.1 wt.%) occurred at 400°C from dpA (<0.355mm). The highest char yield (33.70 wt.%) occurred at 400°C obtained from the largest particle size, dpD (1-2mm).

Keywords: *Ash content; palm kernel shell; particle size; pyrolysis; temperature.*

1. Introduction

Due to rapid population growth, more waste has been generated. This includes lignocellulosic waste such as agricultural residues, dedicated energy crops and woody materials. The resources represent sustainable and low-cost feedstocks that can be converted into valuable products on a large scale, reducing the world's dependency on fossil-based industrial products. A lignocellulosic material consists of three main components (cellulose, hemicellulose and lignin), a small fraction of inorganic materials and extractives. More interests have been shown in valorising these components towards producing a variety of additional high-value end-uses such as pellets and bio-based chemicals. In Malaysia, palm oil plantation alone is expected to generate about 100 million dry tonnes of solid biomass by 2020 [1]. It clearly shows a higher value-added opportunity for the nation to invest in biomass technology.

The conversion of biomass to biofuel can be made through three pathways namely thermochemical, biochemical and physical processes. Among the three, thermochemical pathways offer opportunities for rapid and efficient processing of diverse feedstocks into fuels, chemicals and power [2]. The advantages relative to biochemical and physical methods include greater feedstock flexibility, faster reaction rates and ability to produce a diverse selection of products. However, through selection of biomass, one of the main issues is the presence of inorganic metals (sodium, potassium, calcium, magnesium) which can be found inside biomass ash. The elements are reported as detrimental to thermochemical processes by causing slagging, fouling and corrosion to the reactors

[3]. In pyrolysis, alkali and alkaline earth metals (Na, K, Mg, Ca) display catalytic activity which alters the chemical composition of the pyrolysis oil, increase in char yield and maximum degradation temperature shifted to a lower temperature [4]. Pyrolysis oil upgrading using commercial catalyst was also hindered by the deactivation of the catalyst due to its poisoning effect on the active sites on its surface [5].

The biomass ash which contains the inorganic metals present in two types, introduced and physiological ash [6]. Introduced ash is originated from dust, dirt, rocks and other forms or inorganic contaminations occurred during the harvest and collection process. While physiological ash is the existing minerals within the plant's tissues. The ash contains macronutrients (magnesium, potassium), essential micronutrients (zinc, iron, chloride) and non-essential beneficial elements (sodium, silicon). Different lignocellulosic materials and anatomical parts (leaves, roots, shells) have different concentration of minerals, and they are not uniformly distributed throughout the plant. It was reported that wood biomass has the lowest ash content (<1%) while agricultural residues are grouped among the highest ash concentration (1-20%) [7]. Low ash biomass is often categorised as high-value feedstocks. Different biomass also has different elemental concentration. For example, rice straw is high in silica while driftwood is high in calcium [8], [9].

In the study of biomass combustion, ash content was proven to correlate with the feedstock's particle size. Studies on the effect of particle size on potassium enrichment on woody biomass ash for combustion process was reported by Maeda [10]. They stated that the potassium content in the ash decreased as the biomass ash's mass median diameter increased. Research on sugarcane trash to improve the feedstock quality also reported that there were varia-

tions in the results of ash content with different particle size where a higher concentration of mineral impurities was found in smaller particles (<0.25mm)[11]. Conversion efficiency was also reported to improve by reducing ash content [6]. In their study, the ash was successfully separated using particle size and anatomical fractionation methods where the selections can minimise the need for more expensive ash reduction treatments.

In combustion studies, the particle size is an important parameter to determine the selection of biomass feedstock to avoid fouling of combustion reactor [12], [13]. Pyrolysis, on the other hand, has fewer issues with fouling and slagging as it has low alkali metals, silicon and chlorine emissions compared to gasification and combustion [9]. However, knowledge of the ash chemistry for pyrolysis process is essential to understand how it affects the thermal behaviour, pyrolysis product yield and the product compositions. Sodium, potassium, calcium and magnesium are the primary inorganic metals naturally present in biomass which have been causing unwanted catalytic reactions during the pyrolysis process. These metals are known as alkali and alkaline earth metals (AAEM). In pyrolysis, researchers who reported on the effect of AAEM often ignored how it is related to one of the process parameters in pyrolysis, the particle size [14], [15]. However, this parameter has been covered intensively in combustion and gasification studies based on the published data available in the literature [16], [17]. In pyrolysis study, the experimental evidence on this topic shall provide a better understanding in biomass selection based on particle size which in turn could reduce the cost of post pretreatment of biomass feedstock to reduce the inorganic metals through acid leaching or water washing. Therefore, in assessing pyrolysis product yield, the study would have been more relevant if the effects of AAEM is considered thoroughly when selecting particle size as a variable as it has been reported to affect the heating rate of pyrolysis process [18], [19].

In studying the particle size as a pyrolysis parameter, previously reported data showed a lot of contradictions, especially on the pyrolysis oil yield. For instance, Aysu [10] conducted a pyrolysis experiment at 500°C to four different particle size range from 0.15mm to 0.85mm. Results showed a small increase (2.19%) in oil yield as the particle size decreases. Pyrolysis of durian shell by Tan [20] however, reported a contradiction where the results showed a reduction in oil yield as the particle size decreases. The experiment was done in a drop type fixed-bed pyrolyser at 550°C with particle size ranges from <0.5 to 5mm. However, both authors concluded the particle size effect is insignificant to pyrolysis process based on the yield differences they obtained from the experiments.

Previous experiments were done on various types of biomass also showed inconsistent trends. For instance, pyrolysis of safflower seed, waste paper, rapeseed, hazelnut and Chinese tallow tree showed a graph of increasing trend and followed by a decrease in terms of pyrolysis oil yield as the particle size increases [21]–[25]. It shows that the maximum oil yield occurred at intermediates particle size. However, we must take note that the pyrolysis was done at different temperature and particle size range for each analysis mentioned. As such, it is difficult to compare on the effect of particle size due to the difference in temperature, pyrolyser and type of biomass. Plus, previous researchers failed to conduct experiments at a various temperature to see the trend and instead to analyse the results based on a single pyrolysis temperature only. Therefore, it is difficult to see the overall pattern of the result.

In the thermogravimetric analysis, Chouchene [26] reported that particle size has a significant effect on thermal degradation of olive solid's waste using the thermogravimetric analyser. Smaller particle size showed the highest mass loss rate during volatilisation step and released a high quantity of volatile matters. However, Bridgeman [27] reported that all these effects were due to the catalytic effect of metal contents as different particle sizes have different metal concentrations.

Previous reported data showed a knowledge gap in finding the relations between AAEM and particle size in the field of biomass pyrolysis at different pyrolysis process conditions. Therefore, this work aims to conduct a thorough study on the effect of biomass particle size on pyrolysis product yields by experimenting at a broader range of pyrolysis temperature. The effect of particle size was also focused on the ash content and thermal behaviour through thermogravimetric study using palm kernel shell as the biomass feedstock. The analysis was conducted by varying the particle size and pyrolysis temperature. To our knowledge, this parameter has not been considered thoroughly to this date, and previously reported data were mostly focused on analysing at only one constant temperature to see the effect of particle size in a fixed-bed pyrolyzer. As such, there is still lack of comprehensive data to investigate the effect of particle size and pyrolysis product distribution with regards to biomass pyrolysis.

2. Materials and Method

2.1. Feedstock Characterization

The palm kernel shell (PKS) used in this study was collected from Kempas Palm Oil Mill in Melaka, Malaysia. The feedstocks were dried under the sun to reduce moisture content and crushed using a high-speed crushing machine mounted with a 2mm screen sieve (Brand: Branco; Model: RT-20). Feedstocks were then separated into four different size fractions by sieving through Endecotts woven wire stainless steel sieve which measurement and inspection are based on ASTM E11. The Endecotts mesh size of sieves used was 355µm, 710µm and 1.00mm. The prepared particle sizes were as follows: dpA (<355 µm), dpB (355 - 710µm), dpC (710µm - 1.00mm) and dpD (1.00-2.00mm). All sample size was characterised by proximate analysis for the volatile matter, moisture and fixed carbon value via thermogravimetric analyser (TGA) (Mettler Toledo TGA/SDTA851, USA) according to American Society for Testing and Materials (ASTM D-3172). Prior to analysis, the biomass feedstocks were sun-dry for one day followed by one-hour oven-dry at 105°C. The heating rate was set constant at 20°C/min for the drying step from room temperature to 700°C. Nitrogen gas was supplied continuously at a flow rate of 100ml/min as the furnace medium. Results were interpreted using the method described in [28]. The ultimate analysis was done to obtain the value of C, H, N, O and S using an elemental analyser (Elementar, Thermo Scientific). Ash content was determined by complete combustion using AOAC 942.05 17th Edition while elemental analysis was done using Inductively coupled plasma-optical emission spectroscopy (ICP-OES) from Thermo Scientific Model ICP6000 using Method AOAC 968.08 17th Edition. The hemicellulose, cellulose and lignin content of palm kernel shell was based on the literature [29]. The high heating value (HHV) of biomass fuel was estimated using empirical correlations [30].

2.1. Pyrolysis Experiment

Pyrolysis of PKS was performed in a lab scale fixed-bed reactor under atmospheric pressure as shown in schematic diagram in Fig. 1. Around 10.00 ± 0.50g of biomass was loaded into the reactor, and the residual air was purged out using nitrogen gas which was supplied continuously during the analysis (flow rate: 50ml/min). The reactor furnace was heated until it reached the target temperature (450°C, 500°C, 550°C, 600°C). The PKS was loaded in the furnace when it reached the target temperature which was displayed on the temperature panel. The temperature drop was between 20-35°C and reached the exact temperature of analysis within 3-4 minutes. The heating was maintained for 30 minutes for all samples to ensure all condensable vapour were collected. Biomass bed temperature was taken as the pyrolysis temperature, and the thermocouple indicated the skin temperature of the reactor. The vapor was condensed, and the pyrolysis oil was collected.
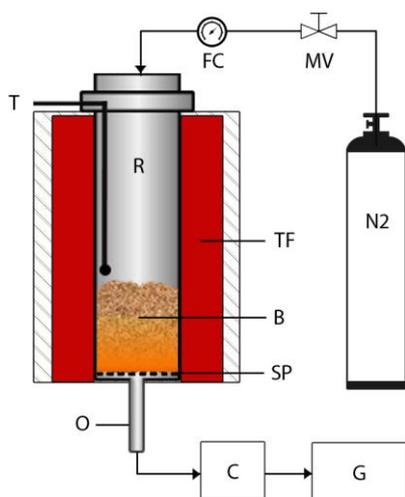
Fig. 1: Schematic diagram of the lab scale fixed-bed pyrolyzer: TF = tubular furnace, T = thermocouple, R = fixed-bed reactor, O = outlet, C = condenser, G = gas collector, N2 = nitrogen gas, FC = flow controller, MV = manual valve, B = biomass, SP = sieve plate.

3. Results and Discussion

3.1. Feedstock Characterization

The characteristics of PKS for various sizes are presented in Table 1. The moisture content was 6.1-8.1 wt.%. It shows that PKS is a suitable feedstock option for thermal conversion as for efficient performance, feedstocks for gasification or pyrolysis must not exceed 10-14% of moisture content [31]. This is to avoid utilisation of more energy consumption during drying operation to reduce moisture content, and it also represents low energy density feedstocks. However, the estimated moisture content is also influenced by location and climate differences.

The volatile matter (VM) of PKS was around 63.1-81.5 wt.%. This parameter is important as it signifies pyrolysis oil yield which is condensed from the volatiles. PKS's VM is lower compared to coconut copra (75.7 wt.%) but higher than rice husk (55.9 wt.%) [32]. The ash content for every particle size (dp) were 2.8 wt.% (dpA), 2.3 wt% (dpB), 1.2 wt.% (dpC) and 0.9 wt.% (dpD). The values obtained are within the range of PKS originated from Malaysia as reported by several researchers [29], [33]–[35]. For the past eight years, ash content reported by [36] and [37] had high ash (11.75% and 16.3 wt%) while most of the rest are within a lower ash content range of 1.6-2.6%.

It was observed that the ash content in Table 1 reduced as the particle size increased. The AAEM content in Fig. 2(a) – (d) also showed a similar trend. A plausible reason for this is because of soil contamination which is known to be a significant contributor of the total ash content during storage and harvest. Some of this contamination can be concentrated in the finest size fractions of the biomass [27]. This explains on the high ash content in the smallest particle size (dpA) which was about four times higher than the largest range (dpD) in this study. This data is supported by the previous finding where flax ash content of finer particle (<0.18mm) was higher by ten times than in the larger particle size (>0.84mm) [38]. The deviations could be due to soil contamination which some of the elements can contribute to the increase in ash content such as silica and calcium [6]. High ash content also could be due to physiological ash as high silica (SiO_2) was found soil elements [39].

The biggest jump of ash concentration was between dpC to dpB size where the ash concentration was doubled. This could be contributed from potassium element which was the highest concentration among other alkali and alkaline earth metals. Potassium was reported to be highly concentrated in lighter fractions thus contributes to large proportions of ash-forming elements [39]. This finding is supported by a recent research in biomass combus-

tion ash which reported that the potassium content in the ash is higher as the mass median diameter of biomass decreases [10]. Referring to [40], among the ash content of 13 types of biomass, only one (corn stalks) has higher sodium compared to potassium. The majority of trend shows potassium exist in a higher composition compared to sodium.

Table 1: Physicochemical properties of PKS

Analysis	dpA	dpB	dpC	dpD
Proximate analysis (d.b. wt. %)				
Moisture content	6.1	7.9	8.1	7.7
Ash content	2.8	2.3	1.2	0.9
Volatile matter	81.5	65.1	63.1	64.1
Fixed carbon[a]	12.4	27.0	28.8	28.2
Ultimate analysis (d.b. wt. %)				
Carbon	48.85	48.23	48.60	50.25
Hydrogen	6.32	6.28	6.24	6.40
Nitrogen	0.49	0.34	0.29	0.29
Sulfur	0.16	0.06	0.05	0.02
Oxygen[a]	44.17	45.10	44.82	43.04
High heating value (HHV) (MJ/kg)	14.04	14.72	17.15	18.73
Chemical composition (d.b. wt. %)				
Hemicellulose[b]	21.6-22.7			
Cellulose[b]	20.8-27.7			
Lignin[b]	44.0-50.7			

d.b wt. %: dry basis by weight per cent

[a] Calculated by difference

[b] Obtained from literature [41]

Fixed carbon is the final component of a proximate analysis which estimate the non-volatile carbon. It is expected that higher fixed-carbon content in biomass shows higher char yield upon pyrolysis or gasification. Volatile matter and fixed-carbon are also related to the yields of pyrolysis oil and gaseous products upon thermal degradation process. The ultimate analysis gives the chemical composition (carbon, hydrogen, oxygen, nitrogen and sulphur) of the biomass where the oxygen can be obtained by calculation. Typically, biomasses have deficient nitrogen and sulfur contents relative to fossil fuels [28]. A higher index of aromaticity and carbonation generally can be obtained from biomass having high carbon and hydrogen compared to oxygen. Higher energy density and HHV also signified from biomass having low O/C ratio due to more chemical energy in C-C bonds than in C-O bonds [42]. In this study, PKS has 48.9 wt.% carbon content, 6.3 wt.% hydrogen content but also quite high oxygen content (44.4 wt.%). With that, the HHV of PKS (18.01 wt.%) is lower than biomass having low oxygen content such as coconut copra which HHV is higher, 30.2 MJkg [32]. In other studies, elemental ratios also provide an indicator of biochar stability [43].

3.2. Thermogravimetric Analysis of PKS

The influence of particle size on thermal decomposition of PKS can be observed from the mass loss curve of thermogravimetric (TG) and derivative thermogravimetric (DTG) as plotted in Fig.3-4 respectively. Both TG and DTG curves can be divided into three phases. Based on Fig. 3, Phase I represents the free water and light components evaporation which occurred at temperature below 210°C. Free water referred to water or moisture that is available on the surface of the samples. Phase II exhibits the devolatilization of mostly hemicellulose and cellulose at a temperature range of 210-400°C. It was followed by Phase III which signifies lignin decomposition primarily occurred at a higher temperature range, 400-750°C.

Based on the pattern of the mass loss curve in Fig. 3, dpA decomposed at the most rapid pyrolysis rate at a low and narrow range of temperature. The similar curve from the smallest particle size biomass pyrolysis was also reported previously [44]. Particle size dpB, dpC and dpD curves had consistent and similar curve trend with the dpB degradations started first, followed by dpC and dpD. The first mass loss cycle completed at around 160°C for dpA, 185°C for dpB, 200°C for dpC and 210°C for dpD. he hemicellulose and cellulose pyrolysis reaction in Phase II finished almost
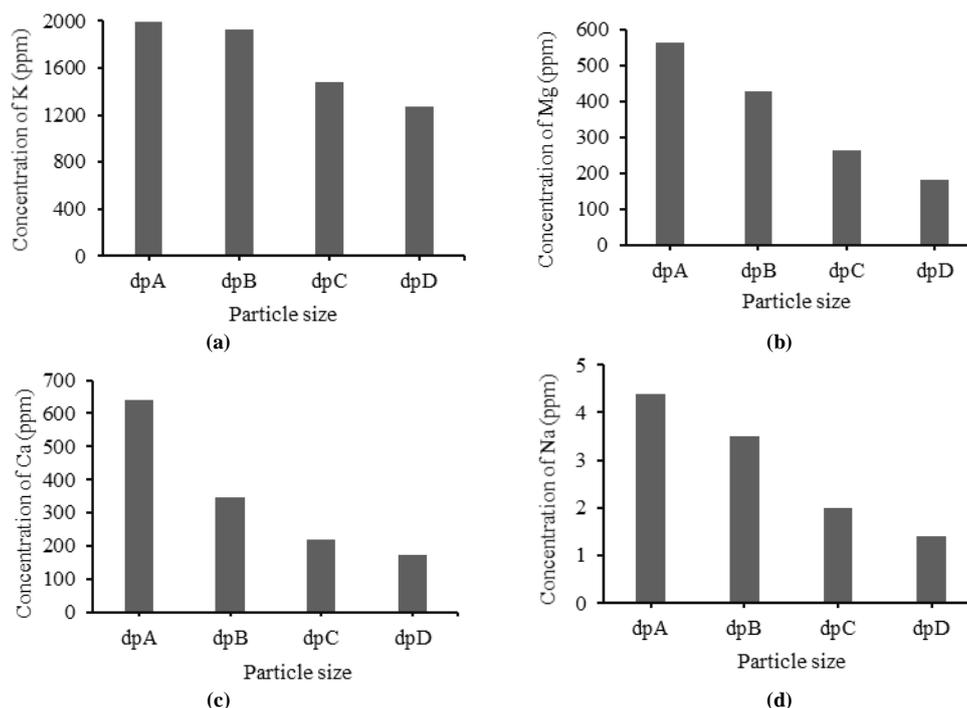
(a)

(b)

(c)

(d)

Fig 2: Graph of concentration (a) potassium (b) magnesium (c) calcium (d) sodium in ppm vs particle size.

entirely between 210-400°C with pyrolysis reaction favour at a lower temperature for smaller particle size. With no aromatic compounds, the celluloses are readily volatilized compared to lignins. The almost similar mass loss percent in Phase II between all curves also showed similar cellulose, hemicellulose and lignin composition (%) in each biomass samples. However, at a temperature higher than 400°C, curve deviation started to occur. In this phase III, the curve for all samples began to degrade at a much lower rate.

The lower rate was due to the presence of thermally stable composition of lignin. The mass loss curve of dpA in this phase degraded at a much higher mass loss rate compared to the other three particle sizes. At a temperature higher than 626.85°C (900K), secondary decomposition of tars (pyrolysis oil) also affected the pyrolysis reactions in Phase III [45]. At this phase also, char and inorganic compounds can be estimated from the curve. Previous studies reported the increase in char as the particle size increased during pyrolysis at higher temperature was once again proven in this study. As particle size increased, it favoured the exothermic reaction after the endothermic reaction resulting in the formation of char. It also exhibited significant temperature gradient from faster external heat transfer compared to slower internal heat transfer which does not occur in smaller particle size. While dpA having the highest ash content, the curve showed the effects of AAEM is not as significant as the effect of char formation in contributing to the total fixed carbon of PKS upon pyrolysis. However, AAEM seemed to contribute to the catalytic reaction of converting more volatiles at a higher temperature based on the high mass loss (%)
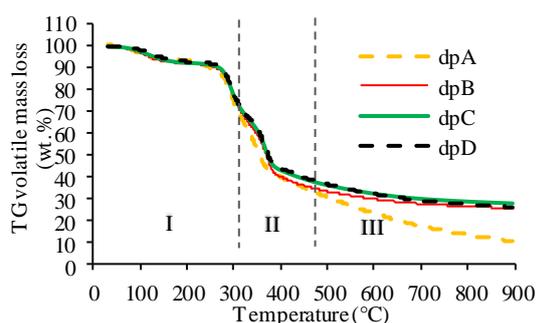
occurred at a higher temperature as shown in curve dpA in Fig. 3. Based on the DTG curve in Fig. 4, the first peak appeared at a temperature range below 200°C. The curve for smaller particle size slightly shifted to the left compared to larger particle size. It showed smaller particle size promotes thermal degradation towards lower temperature. At this phase, the maximum degradation rate followed the sequence of dpA > dpB > dpC > dpD. In phase II, two prominent peaks can be observed from every sample size. The first peak occurred at 210-320°C while the second peak occurred at a temperature of 320-400°C. Similar maximum degradation temperature from all four samples showed similar cellulose crystallinity index which is expected from the same type of biomass [46]. Particle size dpB, dpC and dpD showed the first peak is lower than the second peak while dpA showed the opposite. The maximum degradation rate for hemicellulose peak was from the dpD (12 wt.%/min) while cellulose peak showed the maximum degradation rate from dpB (12.8 wt.%).

DTG curve at temperature above 500°C denotes lignin decomposition occurred over a broad range of temperature. Lignin degradation was reported to occur as low as 160°C up to 800-900°C in a slow process [47]. A higher mass loss was depicted from dpA in compared to the other three larger particle sizes while dpB-dpD curves had levelled off from 650-800°C. Both lower temperature shift and higher degradation rate at higher temperature can be associated with the presence of alkali metals which act as a catalyst in the thermal degradation process.
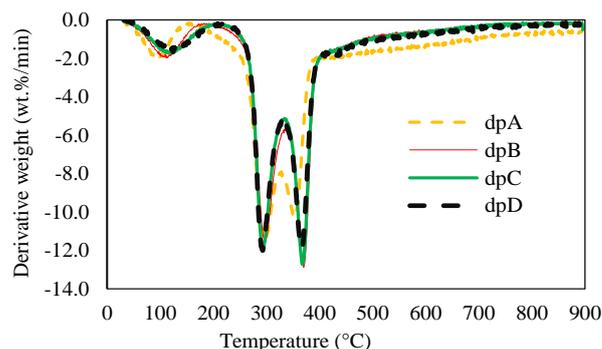

Fig 3: TG curves of PKS samples at a different particle size

Fig 4: DTG curves of PKS samples at a different particle size

3.3. Pyrolysis Experiment

3.3.1 Effect of Particle Size on Pyrolysis Product Yield

Fast pyrolysis of PKS was conducted on four different particle sizes to analyse the product yield distribution. Fig. 5-8 shows the effect of particle size on pyrolysis product yield (pyrolysis oil, char and gas) at a temperature range of 450-600°C. Pyrolysis temperature range for particle size dpA and dpB was extended to a broader temperature to determine the optimum degradation temperature for maximum pyrolysis oil yield. The results showed in Fig. 5 denotes a similar trend for all particle size where the oil yield increased until a certain temperature, followed by a decrease as the pyrolysis temperature increased. The pyrolysis oil yield increased due to the increase of supplied heat which enhance the primary decompositions of lignocellulosic materials [48]. Thermal reactions involved in this phase were fragmentation, cracking or recombination of volatiles which resulted in the formation of low and higher molecular weight compounds [49]. After the optimum temperature is reached, the pyrolysis oil yield decreased due to secondary cracking reactions [50].

The temperature at which the maximum pyrolysis oil yield occurred also increased as the particle size increased. The temperature for maximum oil yield for dpA and dpB occurred at 400°C, followed by dpC at 500°C and dpD at 550°C. Small particle size tends to shift the pyrolysis process to lower temperature which is also justified from the thermogravimetric analysis results, where the cracking or secondary reactions occurred at a much lower temperature for dpD compared to dpA which causes loss of pyrolysis oil yields to gases.

Fig. 6 shows the curve trend at different pyrolysis temperature. The results show various trends of pyrolysis oil yield which change as the temperature changes. At 450°C, the curve shows decreasing oil yield as the particle size increased. At 500°C, the curve decreased, increased and decreased again. At 550°C and 600°C, the yield decreased and increased afterwards as the particle size increased. A similar curve trend to 450°C pyrolysis curve was reported previously [51]. The reason behind the decreasing yield as the particle size increase was due to lower reaction rate when the diameter of biomass particle increases. It is caused by the heating rate and mass transfer limitation where larger particles will heat up more slowly than small ones which resulted in the decrease in the formation of volatile yields. This can also be due to the difference in the types of biomass where bulk density and oxygen content could have contributed to the relationship with the heat transfer mechanism and the rate of pyrolysis reaction [52].
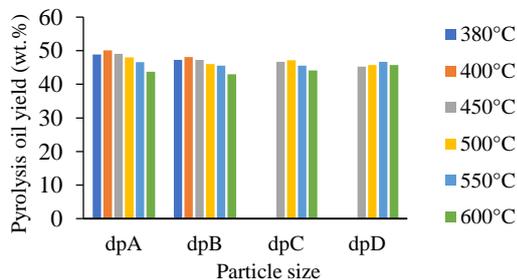

Fig 5: Pyrolysis temperature for maximum oil yield

Fig. 6 also shows a significant difference of pyrolysis oil yield when pyrolyzed at different temperature between the smallest (dpA) and the largest (dpD) particle size. The smallest particle size, dpA, produced a broader difference in yield difference (5.59 wt%) compared to dpD (0.4 wt%) when pyrolyzed at different pyrolysis temperature between 450-600°C. A plausible reason could be due to the high alkali and alkaline metals, particularly potassium in dpA which presence could cause a catalytic reaction in hot reacting particle surface (>530°C) [53].

Fig. 7 shows the char yield as a function of particle size and reactor temperature. Results showed that the char yield increased as the particle size increased. For instance, pyrolysis at 450°C generated 29.3 wt.% from dpA (<0.355mm) and 33.7 wt.% char from dpD (1-2mm). Larger particle size employs a higher retention time of volatiles in the particles [54]. This leads to lower gas flow rates and leads to more charring in larger particle size. Through modelling study, [55] also has justified the statement where the conversion rate increases as the particle size decreases. Therefore, smaller particle size converts to volatiles and solid products at a faster rate during pyrolysis in any reactor.
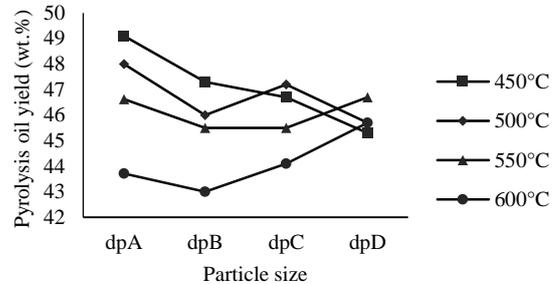

Fig 6: Pyrolysis oil yield curve trends at different particle size and temperature

For every particle size, pyrolysis at different temperature shows a similar trend where the char yield decreases as the temperature increases from 450-600°C. Char yield was higher at low temperature region because the internal particle temperature of biomass takes a longer time to reach the pyrolysis temperature. The situation increased char yield due to the dehydration and charring reaction of cellulose and lignin [56]. Hemicellulose was also reported to contribute to char yield due to its higher mineral content compared to cellulose. The reaction involved was amorphous phase rearrangement reaction which promotes char yield compared to crystalline phase [49].

It was reported that the inorganic material in the biomass ash also contributes to the char yield during pyrolysis. Presence of inorganics also leads to more charring. However, in this study, the decrease of ash content from dpA (2.8 wt. %) to dpD (0.9 wt.%) was not significant enough to affect the increase in char yield. This could be due to the insufficient concentration of AAEM or the effect of higher pyrolysis rate in dpA due to smaller particle size is more pronounced compared to the concentration of AAEM.

In this study, pyrolysis from 450°C to 600°C showed a higher char yield reduction from larger particle size (dpD) of around 4.3 wt.% compared to 3.37 wt.% from smaller particle size (dpA). While on the effect of temperature, lower temperature (450°C) produced a higher increase in char yield (4.4 wt.%) compared to a higher temperature (3.47 wt.%). Therefore, both large particle size and low temperature enhance the yield of char from pyrolysis of palm kernel shell. This is supported by [57] where larger feedstock particle size affect the biochar yield produced. While the almost similar yield difference of 4.3 wt.% and 4.4 wt.% showed upon changing particle size and temperature showed both parameters affect the pyrolysis process to the same extent given the conditions are similar to the above statement.
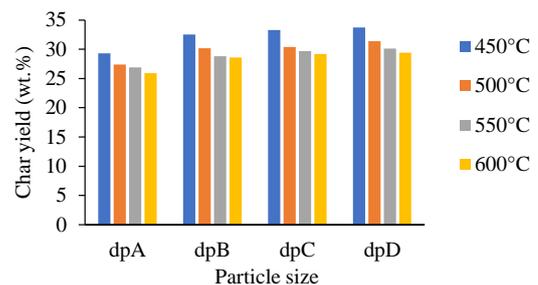

Fig 7: Char yield as a function of particle size and temperature

Fig. 8 shows the graph of gas yield as a function of particle size and reactor temperature. The graph shows gas yield increased as the temperature increased. As the pyrolysis temperature increased, the volatilisation rate of organic compounds such as extractives and proteins will also increase. Therefore, primary decomposition reaction affects the char and at the same time, contributes to higher yields of liquids and gas. Another plausible reason was due to faster heating rate which occurs across the particle, which favours fragmentation of biomass into smaller volatiles [58]. Based on the difference of particle size, more gaseous yield was produced as the particle size is reduced. This is due to the increased in biomass conversion rate for smaller particle size which leads to decomposition of more char and tar (pyrolysis oil) into gaseous components.
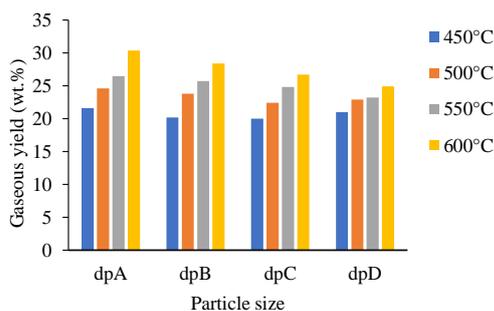

Fig 8: Gas yield as a function of particle size and temperature

4. Conclusion

Pyrolysis of palm kernel shell was studied to determine the thermal and the effect of particle size on pyrolysis product yield. In this work, it has been demonstrated that the smallest particle size has the highest ash (2.8%) and AAEM content. The thermogravimetric analysis showed smallest particle size curve shifted to lower temperature and has narrow temperature range upon analysis. The highest pyrolysis oil yield was 50.1 wt.%, occurred at 400°C from the smallest particle size dpA (<0.355mm). The highest char yield was 33.70 wt.% obtained at temperature 450°C from the largest particle size, dpD (1-2mm). The highest gaseous yield was 30.36 wt.% occurred at temperature 600°C from the smallest particle size in this experiment, dpA (<0.355mm).

The curve trend for pyrolysis oil must be determined by experimental as the curve depends on biomass density, composition and type of reactor as they affect the heat transfer rate of the process. Char yield increased as the particle size increased. The char yield difference at a different pyrolysis temperature (450-600°C) was more pronounced at a lower temperature and large particle size diameter. While for gaseous yield, high temperature and small particle size diameter favoured the production of gas. For pyrolysis oil yield based on the effects of particle size, results showed different curve trends at different pyrolysis temperature. There were no exact curve trends for pyrolysis oil yield as it corresponds to the residence time which influence the heat-transfer during the pyrolysis process.

Acknowledgement

References

[1] National Biomass Strategy, "National Biomass Strategy 2020: New wealth creation for Malaysia's palm oil industry," 2013.

[2] S. V. Pisupati and A. H. Tchapda, "Thermochemical processing of biomass," in *Advances in Bioprocess Technology*, 2015, pp. 277–314.

[3] A. Magdziarz, A. K. Dalai, and J. A. Koziński, "Chemical composition, character and reactivity of renewable fuel ashes," *Fuel*, vol. 176, pp. 135–145, 2016.

[4] I. Y. Eom *et al.*, "Effect of essential inorganic metals on primary thermal degradation of lignocellulosic biomass," *Bioresour. Technol.*, vol. 104, pp. 687–694, 2012.

[5] R. Mahadevan *et al.*, "Effect of Alkali and Alkaline Earth Metals on in-Situ Catalytic Fast Pyrolysis of Lignocellulosic Biomass: A Microreactor Study," *Energy and Fuels*, vol. 30, no. 4, pp. 3045–3056, 2016.

[6] J. A. Lacey, R. M. Emerson, D. N. Thompson, and T. L. Westover, "Ash reduction strategies in corn stover facilitated by anatomical and size fractionation," *Biomass and Bioenergy*, vol. 90, pp. 173–180, 2016.

[7] S. Wang, G. Dai, H. Yang, and Z. Luo, "Lignocellulosic biomass pyrolysis mechanism: A state-of-the-art review," *Prog. Energy Combust. Sci.*, vol. 62, pp. 33–86, 2017.

[8] B. M. Jenkins, R. R. Bakker, and J. B. Wei, "On the properties of washed straw," *Biomass and Bioenergy*, vol. 10, no. 4, pp. 177–200, 1996.

[9] P. Bartocci *et al.*, "Thermal degradation of driftwood: Determination of the concentration of sodium, calcium, magnesium, chlorine and sulfur containing compounds," *Waste Manag.*, vol. 60, pp. 151–157, 2016.

[10] N. Maeda, T. Katakura, T. Fukasawa, A. N. Huang, T. Kawano, and K. Fukui, "Morphology of woody biomass combustion ash and enrichment of potassium components by particle size classification," *Fuel Process. Technol.*, vol. 156, pp. 1–8, 2017.

[11] G. T. Nakashima, M. P. Martins, A. L. S. Hansted, H. Yamamoto, and F. M. Yamaji, "Sugarcane trash for energy purposes: Storage time and particle size can improve the quality of biomass for fuel?," *Ind. Crops Prod.*, vol. 108, no. July, pp. 641–648, 2017.

[12] C. Thiel, M. Pohl, S. Grahl, and M. Beckmann, "Characterization of mineral matter particles in gasification and combustion processes," *Fuel*, vol. 152, pp. 88–95, 2015.

[13] P. Ninduangdee and V. I. Kuprianov, "Combustion of palm kernel shell in a fluidized bed: Optimization of biomass particle size and operating conditions," *Energy Convers. Manag.*, vol. 85, pp. 800–808, 2014.

[14] S. Hu *et al.*, "Effects of inherent alkali and alkaline earth metallic species on biomass pyrolysis at different temperatures," *Bioresour. Technol.*, vol. 192, pp. 23–30, 2015.

[15] L. Jiang *et al.*, "Catalytic effects of inherent alkali and alkaline earth metallic species on steam gasification of biomass," *Int. J. Hydrogen Energy*, vol. 40, no. 45, pp. 15460–15469, 2015.

[16] A. Biswas, "Effect of Chemical and Physical Properties on Combustion of Biomass Particle," 2015.

[17] J. Li, M. C. Paul, and K. M. Czajka, "Studies of Ignition Behavior of Biomass Particles in a Down-Fire Reactor for Improving Co-firing Performance," *Energy and Fuels*, vol. 30, no. 7, pp. 5870–5877, 2016.

[18] R. Mehrabian, R. Scharler, and I. Obernberger, "Effects of pyrolysis conditions on the heating rate in biomass particles and applicability of TGA kinetic parameters in particle thermal conversion modelling," *Fuel*, vol. 93, pp. 567–575, 2012.

[19] Y. Huang, W. Kuan, and C. Chang, "Effects of particle size, pretreatment, and catalysis on microwave pyrolysis of corn stover," *Energy*, vol. 143, pp. 696–703, 2018.

[20] Y. L. Tan, A. Z. Abdullah, and B. H. Hameed, "Fast pyrolysis of durian (Durio zibethinus L) shell in a drop-type fixed bed reactor: Pyrolysis behavior and product analyses," *Bioresour. Technol.*, vol. 243, pp. 85–92, 2017.

[21] S. H. Beis, Ö. Onay, and Ö. M. Koçkar, "Fixed-bed pyrolysis of safflower seed: Influence of pyrolysis parameters on product yields and compositions," *Renew. Energy*, vol. 26, no. 1, pp. 21–32, 2002.

[22] M. N. Islam, M. N. Islam, M. R. A. Beg, and M. R. Islam, "Pyrolytic oil from fixed bed pyrolysis of municipal solid waste and its characterization," *Renew. Energy*, vol. 30, no. 3, pp. 413–420, 2005.

[23] İ. Demiral and S. Şensöz, "Fixed-Bed Pyrolysis of Hazelnut (Corylus Avellana L.) Bagasse: Influence of Pyrolysis Parameters on Product Yields," *Energy Sources*, vol. 28, no. 12, pp. 1149–1158, 2006.

[24] O. Onay and O. M. Koçkar, "Fixed-bed pyrolysis of rapeseed (Brassica napus L.)," *Biomass and Bioenergy*, vol. 26, no. 3, pp. 289–299, 2004.

[25] G. Aguilar, P. D. Muley, C. Henkel, and D. Boldor, "Effects of

biomass particle size on yield and composition of pyrolysis bio-oil derived from Chinese tallow tree (*Triadica Sebifera L.*) and energy cane (*Saccharum complex*) in an inductively heated reactor," *AIMS Energy*, vol. 3, no. 4, pp. 838–850, 2015.

[26] A. Chouchene, M. Jeguirim, B. Khiari, F. Zagrouba, and G. Trouvé, "Thermal degradation of olive solid waste: Influence of particle size and oxygen concentration," *Resour. Conserv. Recycl.*, vol. 54, no. 5, pp. 271–277, 2010.

[27] T. G. Bridgeman, L. I. Darvell, J. M. Jones, P. T. Williams, and R. Fahmi, "Influence of particle size on the analytical and chemical properties of two energy crops," vol. 86, pp. 60–72, 2007.

[28] W. de Jong, "Biomass composition, properties and characterization," in *Biomass as a Sustainable Energy Source for the Future: Fundamentals of Conversion Processes*, W. de Jong and J. R. van Ommen, Eds. New Jersey: Wiley, 2015, pp. 52–61.

[29] S. J. Oh, G. G. Choi, and J. S. Kim, "Characteristics of bio-oil from the pyrolysis of palm kernel shell in a newly developed two-stage pyrolyzer," *Energy*, vol. 113, pp. 108–115, 2016.

[30] S. Gaur and T. Reed, *An atlas of thermal data of biomass and other fuels*, vol. 7, no. 1–6. Golden, Colorado, 1995.

[31] M. Danish, M. Naqvi, U. Farooq, and S. Naqvi, "Characterization of South Asian Agricultural Residues for Potential Utilization in Future 'energy mix,'" *Energy Procedia*, vol. 75, pp. 2974–2980, 2015.

[32] V. Balasundram *et al.*, "Thermogravimetric catalytic pyrolysis and kinetic studies of coconut copra and rice husk for possible maximum production of pyrolysis oil," *J. Clean. Prod.*, vol. 167, pp. 218–228, 2018.

[33] Z. Ma, D. Chen, J. Gu, B. Bao, and Q. Zhang, "Determination of pyrolysis characteristics and kinetics of palm kernel shell using TGA-FTIR and model-free integral methods," *Energy Convers. Manag.*, vol. 89, pp. 251–259, 2015.

[34] G. G. Choi, S. J. Oh, S. J. Lee, and J. S. Kim, "Production of bio-based phenolic resin and activated carbon from bio-oil and biochar derived from fast pyrolysis of palm kernel shells," *Bioresour. Technol.*, vol. 178, pp. 99–107, 2015.

[35] J. E. Omoriyekomwan, A. Tahmasebi, and J. Yu, "Production of phenol-rich bio-oil during catalytic fixed-bed and microwave pyrolysis of palm kernel shell," *Bioresour. Technol.*, vol. 207, pp. 188–196, 2016.

[36] R. Ahmad, N. Hamidin, U. F. M. Ali, and C. Z. A. Abidin, "Characterization of Bio-Oil From Palm Kernel Shell Pyrolysis," *J. Mech. Eng. Sci.*, vol. 7, no. December, pp. 2289–4659, 2014.

[37] M. Asadieraghi and W. M. A. W. Daud, "In-depth investigation on thermochemical characteristics of palm oil biomasses as potential biofuel sources," *J. Anal. Appl. Pyrolysis*, vol. 115, pp. 379–391, 2015.

[38] Y. Tamaki and G. Mazza, "Measurement of structural carbohydrates, lignins, and micro-components of straw and shives: Effects of extractives, particle size and crop species," *Ind. Crops Prod.*, vol. 31, no. 3, pp. 534–541, 2010.

[39] J. A. Lacey, J. E. Aston, T. L. Westover, R. S. Cherry, and D. N. Thompson, "Removal of introduced inorganic content from chipped forest residues via air classification," *Fuel*, vol. 160, pp. 265–273, 2015.

[40] K. Raveendran, A. Ganesh, and K. C. Khilar, "Influence of mineral matter on biomass pyrolysis characteristics," *Fuel*, vol. 74, no. 12, pp. 1812–1822, 1995.

[41] S. Nizamuddin, S. Shrestha, S. Athar, B. S. Ali, and M. A. Siddiqui, "A critical analysis on palm kernel shell from oil palm industry as a feedstock for solid char production," *Rev. Chem. Eng.*, vol. 32, no. 5, pp. 489–505, 2016.

[42] C. E. Braz and P. M. Crnkovic, "Physical – Chemical Characterization of Biomass Samples for Application in Pyrolysis Process," *Chem. Eng. Trans. VOL. 37*, vol. 37, pp. 523–528, 2014.

[43] K. Crombie, O. Mašek, S. P. Sohi, P. Brownsort, and A. Cross, "The effect of pyrolysis conditions on biochar stability as determined by three methods," *GCB Bioenergy*, vol. 5, no. 2, pp. 122–131, 2013.

[44] D. Lv, M. Xu, X. Liu, Z. Zhan, Z. Li, and H. Yao, "Effect of cellulose , lignin , alkali and alkaline earth metallic species on biomass pyrolysis and gasi fi cation," vol. 91, pp. 903–909, 2010.

[45] A. Janse, R. Westerhout, and W. Prins, "Modelling of flash pyrolysis of a single wood particle," *Chem. Eng. Process*, vol. 39, pp. 239–52, 2000.

[46] F. Nsaful, F. X. Collard, M. Carrier, J. F. Görgens, and J. H. Knoetze, "Lignocellulose pyrolysis with condensable volatiles quantification by thermogravimetric analysis - Thermal desorption/gas chromatography-mass spectrometry method," *J. Anal. Appl. Pyrolysis*, vol. 116, pp. 86–95, 2015.

[47] R. Venderbosch and W. Prins, "Fast pyrolysis technology development," *Biofuels, Bioprod. Biorefining*, vol. 4, pp. 178–208, 2010.

[48] B. Biswas, N. Pandey, Y. Bisht, R. Singh, J. Kumar, and T. Bhaskar, "Pyrolysis of agricultural biomass residues : Comparative study of corn cob , wheat straw , rice straw and rice husk," *Bioresour. Technol.*, vol. 237, pp. 57–63, 2017.

[49] F. X. Collard and J. Blin, "A review on pyrolysis of biomass constituents: Mechanisms and composition of the products obtained from the conversion of cellulose, hemicelluloses and lignin," *Renew. Sustain. Energy Rev.*, vol. 38, pp. 594–608, 2014.

[50] L. Fan *et al.*, "Bioresource Technology Fast microwave-assisted catalytic co-pyrolysis of lignin and low-density polyethylene with HZSM-5 and MgO for improved bio-oil yield and quality," vol. 225, pp. 199–205, 2017.

[51] T. Aysu, "Catalytic pyrolysis of Eremurus spectabilis for bio-oil production in a fixed-bed reactor: effects of pyrolysis parameters on product yields and character," *Fuel Process. Technol.*, vol. 129, pp. 24–38, 2015.

[52] J. Akhtar and N. Saidina Amin, "A review on operating parameters for optimum liquid oil yield in biomass pyrolysis," *Renew. Sustain. Energy Rev.*, vol. 16, no. 7, pp. 5101–5109, 2012.

[53] P. S. Marathe, S. R. G. Oudenhoven, P. W. Heerspink, S. R. A. Kersten, and R. J. M. Westerhof, "Fast pyrolysis of cellulose in vacuum: The effect of potassium salts on the primary reactions," *Chem. Eng. J.*, vol. 329, pp. 187–197, 2017.

[54] A. Anca-Couce, "Reaction mechanisms and multi-scale modelling of lignocellulosic biomass pyrolysis," *Prog. Energy Combust. Sci.*, vol. 53, pp. 41–79, 2016.

[55] A. Sharma, Y. Shinde, V. Pareek, and D. Zhang, "Process modelling of biomass conversion to biofuels with combined heat and power," *Bioresour. Technol.*, vol. 198, pp. 309–315, 2015.

[56] S. Wang and Z. Luo, *Pyrolysis of Biomass*. Walter de Gruyter GmbH & Co KG, 2017.

[57] X. Liu, Y. Zhang, Z. Li, R. Feng, and Y. Zhang, "Characterization of corncob-derived biochar and pyrolysis kinetics in comparison with corn stalk and sawdust," *Bioresour. Technol.*, vol. 170, pp. 76–82, 2014.

[58] S. Luo, B. Xiao, Z. Hu, S. Liu, Y. Guan, and L. Cai, "Influence of particle size on pyrolysis and gasification performance of municipal solid waste in a fixed bed reactor," *Bioresour. Technol.*, vol. 101, no. 16, pp. 6517–6520, 2010.