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Influence of Washing Medium Pre-treatment on Pyrolysis Yields and Product Characteristics of Palm Kernel Shell

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Abstract: *As a renewable alternative energy source, biomass is currently receiving serious attention as a means to meet energy demands. Palm kernel shell (PKS) has been selected from among other oil palm wastes for thermochemical conversion studies for the purpose of solid/liquid fuel production. In this study, the influence of the washing pre-treatment process was observed by treating PKS feedstock with various types of washing medium to observe the impact of treated and untreated feedstock on pyrolysis yield and product characteristics. The washing mediums tested were reverse osmosis (RO), tap water and distilled water. Meanwhile, 5% dilute acetic acid and sodium hydroxide (NaOH) were prepared as mildly acidic and alkaline washing media, respectively. The highest percentage of ash reduction was clearly found in the treated PKS soaked in distilled water, reaching 43.05%. Untreated PKS was pyrolysed between 300°C to 500°C to observe the yield distribution of pyrolysis products, while treated PKS was pyrolysed at 400°C to investigate the influence of ash content on pyrolysis yields and product characteristics. Under the temperature profile, the highest yield of char was obtained at 300°C, amounting to approximately 54.40 wt%; meanwhile, the pyrolysis liquid yield reached its maximum at a temperature of 400°C but then decreased with further increases in temperature. For the treated PKS series, the highest char yield was produced from PKS treated with diluted alkaline, at 46.96 wt%, while the maximum yield of pyrolysis liquid was 46.01 wt% from PKS treated with diluted acid. The energy content in char was seen to increase as the ash content became lower. The presence of ash, which acts as a catalyst, promotes secondary reactions during pyrolysis and is thus considered a significant contributor to high water fractions in the organic liquid yield. Suggestions for improving the quality of pyrolysis products are also discussed in relation to this study.*

Keywords: Palm kernel shell, washing pre-treatment, pyrolysis, bio-char, pyrolysis liquid

1. INTRODUCTION

Energy use is currently rising faster than the world population, and the supply of energy sources is expected to become unbalanced with consumption. Major world nations have recently increased their demand for conventional energy sources such as coal, oil and natural gas to meet their energy needs. Thus, alternative new and/or renewable energy sources such as solar, wind, thermal, hydroelectric and biomass have been receiving serious attention. Biomass, as a renewable energy source, is now considered the most attractive source to meet demands in several areas where energy is much needed currently, such as in generating electricity, fuelling vehicles and heating substances for industrial use.[1] Various forms of biomass are used as major renewable energy sources to supplement limited fossil fuel resources. Because biomass can provide clean raw feedstock for energy generation, it is safe and economical to turn it into highly sustained value-added bio-products. Furthermore, the European Union (EU) energy policy emphasises the use of renewable sources for all energy production in relation to reducing hazards and particulate matter emissions.[2]

The palm oil industry contributes up to 94% of biomass feedstock in Malaysia, while other sectors including agricultural and forestry-related industries such as rice and sugar-cane generate the remaining 6%. Oil palm biomass such as palm kernel shell (PKS) is an appropriate renewable source for the production of energy in Malaysia. Approximately 4.21 million tonnes of PKS can be sourced from 4.69 million hectares of total potential oil palm biomass in Malaysia.[3] By using this biomass in a variety of valuable products, some environmental problems could be solved, such as indiscriminate waste disposal and the direct burning that results in pollution. The waste is currently used mostly for fertiliser, palm-based briquettes and solid/liquid fuel products by means of thermochemical processes. The thermochemical conversion processes include combustion, gasification and pyrolysis.

Pyrolysis is considered the highest-potential and most important process for biomass conversion energy technologies.[4–6] This technology could turn biomass into the quality hydrocarbon products of bio-char and pyrolytic oil for solid or liquid fuel applications. For example, pyrolysis work by Uemura et al.[7] at a temperature of 300°C has produced high-quality PKS char with a good higher heating value (HHV) amounting to approximately 21.68 MJ kg^{-1}, which is 8.76% greater than that of raw PKS. This research also found that the carbon content of the char increased from 46.68 wt% to 54.21 wt%. Meanwhile, the amount of bonded nitrogen and sulphur content was less than 0.5 wt%. Due to the good thermo-chemical properties, the produced bio-char offers great potential benefits as a precursor to new solid bio-product applications, such as briquettes and activated carbon.[8–11]

High-quality pyrolytic oil is recommended for use directly as liquid fuel, which is viable as an addition to petroleum refinery feedstock or can be catalytically enhanced to transport high-grade fuels.[12,13] However, a critical upgrade is definitely needed for any production of low-grade liquid oil to make the fuel usable for power generation. In one such example, Abnisa et al.[14] recommended an enhancement to their collected bio-oil due to the low HHV value, which is mainly due to the high oxygen content. The oxygenated contents in the bio-oil were measured at approximately 71.40 wt%. Unfortunately, the values of HHV and the lower heating value (LHV) of the bio-oil were found to be approximately 11.94 and 10 MJ kg^{-1}, respectively, which are considered low compared to the HHV and LHV of heavy fuel oil, which can reach 40 and 37.60 MJ kg^{-1}, respectively.[15] Therefore, physical or chemical treatments should be applied to the liquid fuel to reduce the undesirable oxygenated content and gain more hydrocarbon sources through the production of better-quality bio-oil.

Washing pre-treatment of biomass has been reported as a practical technique to improve the quality of biomass feedstock and pyrolysis products. Ash culprits such as dirt, sand and other alkaline earth matter are washed out from the biomass, remarkably reducing ash-related consequences such as slagging and fouling, which occur mainly during the thermal conversion process. The water washing was first applied by researchers to investigate the impact of washing medium on feedstock during the leaching process. For example, Jenkins et al.[16] applied tap and distilled water pre-treatments using various methods. Spraying, flushing and soaking methods have been tested for the reduction of ash concentrations in rice straw. The highest percentage of ash reduction was observed to reach 10.2%, which was only measured after soaking rice straw in 7 l distilled water for 24 h. Flushing methods using either distilled or tap water, showed no clear contribution, as the resulting ash content was approximately 18.2 wt% and 18.3 wt%, respectively. However, this method could be considered to be more effective than the spraying method, for which the reduced ash content was only approximately 19.1 wt%.

An acid washing pre-treatment has also been reported to have significant influence on biomass feedstock and pyrolysis products. As reported by Tan and Wang,[17] Das et al.[18] and Davidsson et al.,[19] the acidic solution effectively removed most of the ash culprits in the biomass. The rate of inorganic and metal ions removal under acid pre-treatment was high compared with other washing mediums. However, acid washing also appeared to have negative impacts such as causing the breakage of hydrocarbon bonding and erosion of the fibre structure in biomass organic constituents. The overall effect would depend on the type and molarity of the acidic medium applied and also on the behaviour of the whole biomass structure used. Furthermore, acid treatment should be employed in a controlled and sustained manner to counter the disposal problems and harmful effects towards the environment and ecosystems.

Alkaline pre-treatment has been employed for various types of applications such as the production of fungal chitosan, improvement of sugar yield, solubilisation of biomass, and the production of bioethanol and feedstock preparation for thermal application.[20–25] With this type of pre-treatment, the absorption of ionic salts from the alkaline washing medium is favoured over leaching mechanisms from the biomass structure. A major factor influencing this phenomenon was the difference in the concentrations of ions measured between the feedstock and washing medium. Any other significant effects of alkaline pre-treatment could also be clarified by comparing other biomass behaviours such as physical and thermochemical properties with other types of treated feedstock. In addition to the thermochemical properties, thermal application to the treated feedstock would also describe their reactivity and combustible behaviour. Ash-related consequences would play a dominant role due to the high concentration of the ash content during the combustion process. Therefore, the devolatilisation rates in combination with the alterations to the organic phase are major factors influencing the final fractions of the total solid and liquid yield produced.

Variations in the ash concentrations in biomass due to the washing pre-treatment would influence the overall production and quality of pyrolysis products. For example, Abdullah et al.[26] has investigated the effect of ash content on empty fruit bunches (EFB) pyrolysis yields. Water washing pre-treatment was employed by soaking EFB in distilled water for different times (1 min, 10 min, 20 min and 24 h). The bound ash content varied in the range of 1.03 to 5.43 mf wt%. Consequently, the organic liquid yield increased drastically as the ash content decreased. Meanwhile, the char and gas yields behaved in the opposite manner. The highest organic yields reached 60 mf wt% at the lowest ash content. The trend of the results could correspond to reduced reactions occurring in the water, gas and char during pyrolysis, thus preventing secondary reactions. Furthermore, the organic liquid yield was a homogenate of tarry organic compounds and an aqueous phase due to decreased ash content.

In this paper, washing pre-treatments were employed to investigate the influence of different washing mediums on the properties of PKS feedstock and pyrolysis products. The first part of the research examined the application of various washing pre-treatment methods to PKS biomass to produce better feedstock conditions. The effectiveness of the washing pre-treatments was mainly verified by thoroughly analysing the resulting physical and thermochemical characteristics of the treated feedstock. Pyrolysis studies were performed to investigate the influence of heat in terms of temperature on the PKS feedstock. The yields and characteristics of the pyrolysis products were analysed to observe any significant trends under the application of selected pyrolysis temperature profiles. Furthermore, the effects of the ash content obtained through washing pre-treatment on thermal application were also investigated. Initially, the use of different washing mediums in this well-controlled manner caused the presence of varying amounts of ash content measured in the treated feedstock. Thus, the ash-related consequences, especially on the yields and characteristics of pyrolysis products, were also analysed throughout this work.

2. EXPERIMENTAL

2.1 Materials

PKS was selected and prepared for washing pre-treatment and pyrolysis studies. The biomass was collected in wet conditions from a palm oil factory in Nibong Tebal, Penang, with measured moisture content of approximately 24.4 wt%. Therefore, the biomass was oven-dried before packing and storing until the moisture content was below approximately 10 mf wt%, to prevent the growth of microorganisms and fungus on the biomass.[27] The PKS constituent components of lignocellulosic materials consist of 27.9 wt% cellulose, 45.7 wt% hemicellulose and 54.3 wt% lignin. PKS came in various sizes and is shown in broken form in Figure 1 with a bulk density of approximately 410 kg m^{-3}. The feedstock possessed superior hardness and a highly complex porous structure. These properties make the biomass material viable for various applications of solid bio-products, such as activated carbon and densified palm-based fuel briquettes. Furthermore, other thermo-chemical properties were determined by proximate, ultimate and heating value analysis.

Figure 1: Form and structural view of raw PKS.

2.2 Application of Washing Pre-treatment

Washing pre-treatment is an effective method for removing sand, dirt and large amounts of alkaline metals such as potassium and chlorine.[28,29] These culprits are generally considered to be the main proxy of ash in the biomass. Figure 2 shows the overall process of washing pre-treatment performed on the PKS material in this work. Washing pre-treatments were performed on the PKS using different types of washing medium. The wastes were soaked in neutral, diluted acid and diluted alkaline washing mediums. Three neutral washing media were used: reverse osmosis (RO), tap and distilled water. Meanwhile, 5% diluted acetic acid and sodium hydroxide (NaOH), previously diluted with distilled water were prepared as acidic and alkaline washing mediums, respectively. A volume of washing medium as low as 0.5 l was used to fully submerge over 100 g of PKS for approximately 20 min at room temperature (~30°C). After each washing process, treated PKS was drained and weighed, then oven dried before being stored for further analysis. The leachates were also collected to determine the effectiveness of the washing pre-treatment.

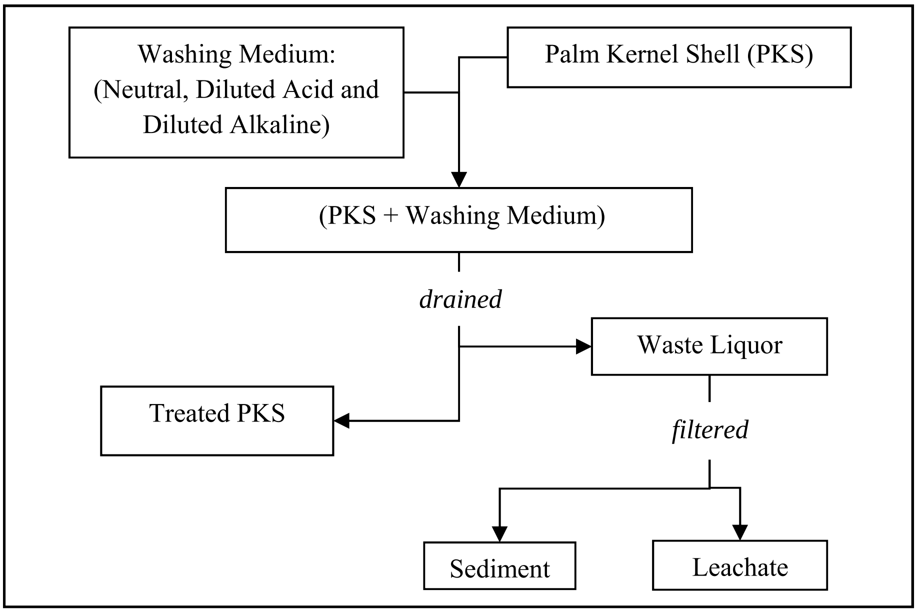

Figure 2: Water washing pre-treatment process of PKS.

2.3 Effectiveness of Washing Pre-treatment

Several analyses were performed on treated PKS to study the effectiveness of the washing pre-treatments applied in this work. The ash content of treated PKS was mainly measured as the precursor to determine the amount of ash reduction, which was influenced by the different types of washing medium. The HHVs of treated feedstock were then measured to investigate the significant consequences of ash content on the properties. Furthermore, the weight of PKS before and after the treatment process was analysed for biomass weight loss determination. Soaking PKS in different washing mediums caused varying degrees of mass reduction. The mass reduction of the treated PKS was presented in terms of percentage.

The effectiveness of pre-treatment was also determined via electrical conductivity (EC) measurement. The values of EC were measured by a HANNA HI 8733 conductivity metre. Via the conductivity metre, the recent value of EC could be measured for each type of washing medium or collective leachate. The EC values of the washing mediums are as follows: RO water: 53.59 µS cm^{-1}, tap water: 55.99 µS cm^{-1}, distilled water: 1.34 µS cm^{-1}, diluted acidic: 1105.25 µS cm^{-1} and diluted alkaline: 1997.77 µS cm^{-1}. The leaching process mainly caused alkaline metals and other leachable matter to diffuse into the washing medium. Therefore, the EC increments were compared by taking the differences between the initial EC values of the washing medium and the EC values of the collected leachate. Different amounts of measured EC values could indicate good diffusion and the removal of ash and its components from the biomass. Various deflection changes of EC readings were observed under the application of different washing mediums. As in the previous reports cited, feedstock with less ash and its components are more favourable for pyrolysis applications due not only to producing better yields of char and pyrolysis liquid but also to enhancing their physical, thermochemical and combustion behaviours.

2.4 Pyrolysis Experiments

The thermal characteristics of PKS were first analysed to distinguish its thermal degradation behaviour. The analysis was performed using a thermogravimetric analyser (Perkin Elmer/TGA7, Norwalk, CT). The changes in PKS weight were mainly measured as a function of temperature and time. The decomposition of PKS constituents was identified by burning throughout the temperature range from ambient temperature to 900°C. The second part of the investigation was attempted by allowing the PKS feedstock to pyrolyse over the range of temperatures from 300°C to 500°C. The PKS was fully packed inside a cylindrical stainless steel pyrolyser and then burned in an electrical muffle furnace (Type F62700-33-80, Barnstead International, Dubuque, IA 52004, USA). The furnace was manually programmed with a heating rate of 10°C min^{-1} for at least 2 h. The vapour released during pyrolysis was then condensed thoroughly using a liquid collecting system, which was equipped with a condenser, electrostatic precipitator and cotton wool filter. The char and pyrolysis liquid yields were calculated by referring to Equation 1 as suggested by Khor et al.[30]:

$$Yield\ (wt\%) = \frac{Weight\ of\ desired\ product\ \ (g)}{Weight\ of\ dry\ raw\ feed\ (g)} \times 100\% \qquad (1)$$

This research work investigated the influence of ash content in treated feedstock on the pyrolysis yields and their product characteristics. The investigation was performed on treated PKS by employing the pyrolysis process only at a single pyrolysis temperature, approximately 400°C, at a heating rate of 10°C min^{-1} for

2 h. The employment of a single heat point provided a clear trend and description regarding the effect of ash culprits in the treated feedstock on pyrolysis product yields and properties. Furthermore, ash-related consequences for the production and characterisation of pyrolysis products were decisively examined by comparing the phenomena that occurred in the obtained treated feedstock under the selected thermal conditions applied.

2.5 Bio-char and Pyrolysis Liquid Experimental Test

Bio-chars of treated and untreated PKS were characterised by proximate and heating value analysis. Proximate analysis of PKS was measured with reference to the standard test method by determining the weight percentage of the moisture content (ASTM E871-82), ash content (ASTM E872-82), volatile matter (ASTM E830-87) and fixed carbon (by differences). The moisture content was measured by drying 1 g ground PKS for 24 h at 105°C in an electric oven, and the differences were weighed and calculated. Dry PKS was then used for ash content determination by burning in a muffle furnace for 6 h at 575°C. Meanwhile, for volatile matter, it was burned at 970°C for 7 min. The HHVs of bio-char and pyrolysis liquid were measured experimentally using an adiabatic oxygen bomb calorimeter, Nenken 1013-B. The standard test method was employed according to ASTM E711-87. The ash content of pyrolysis liquid was also analysed by a standard test method, ASTM D482-07. A Metrohm KF Titrino and a standardised Karl-Fisher reagent were used to measure the water content in the liquid phase. Finally, the pH value of pyrolysis liquid was measured in the laboratory using a digital pH metre, an Accumet AB 15/15+ bench-top metre, with the expectation that the pH of the produced pyrolysis liquids would be between 3.0 and 6.0.

Table 1: Characteristics of raw PKS and other oil palm wastes.

Characteristics	PKS (this work)	PKS[31]	OPT[30]	OPF[32]
Proximate Analysis (mf wt%, dry basis)				
Ash	5.97	3.04	4.79	3.92
Volatile matter	76.48	76.35	75.20	73.92
Fixed carbon (by difference)	17.55	21.75	10.04	17.09
Ultimate Analysis (mf wt%, dry basis)				
Nitrogen	0.37	0.42	3.76	0.03
Sulphur	0.09	0.04	0.35	0.49
Hydrogen	4.09	6.21	5.98	4.56
Carbon	50.39	49.97	41.88	41.13
Oxygen (by difference)	45.06	42.62	43.24	49.87
Heating Value (MJ kg^{-1})				
Higher Heating Value (HHV)	18.08	22.07	17.52	15.66

3. RESULTS AND DISCUSSION

3.1 Properties of Raw PKS

Table 1 shows the thermo-chemical characteristics of PKS and other oil palm wastes. The natural behaviours of typical wastes were the major influences on their characteristics, which were mainly based on the procedures of production, collection and disposal. In this study, the collected PKS has quite high ash content, amounting to approximately 5.97 mf wt%. The ash content of the measured PKS in this work is high compared with the reported value. Compared to the other feedstock properties, the two feedstocks have similar characteristics and behaviours, differing only in the weight percentage of ash and their energy value. Slightly higher amounts of ash concentration in the measured PKS are confidently attributed to the improper disposal procedure of the waste at the selected processing factory during the collection activity. The waste was clearly disposed on the ground and thoroughly exposed to dirt, sand and fly ash from the waste burning activity from the surroundings, which mainly consisted of various types of alkaline metals and other inorganic components. The presence of high ash concentrations would have bad consequences, such as the formation of agglomeration and slag during the combustion process. These problems have attracted attention from researchers such as Bakker and Jenkins[33] and Thy et al.[34]

in efforts to avoid critical issues in maintenance and operating cost problems. Furthermore, the volatile matter and fixed carbon of PKS were measured at approximately 76.48 and 17.55 mf wt%, respectively. Because PKS includes highly volatile matter, this biomass is expected to release great volumes of vapour during the pyrolysis process. Based on its elemental composition, PKS contained 50.39 mf wt% carbon, 4.09 mf wt% hydrogen, 45.06 mf wt% oxygen, 0.37 mf wt% nitrogen and 0.09 mf wt% sulphur. PKS could be considered a sustainable feedstock for the environment, because the waste has low nitrogen and sulphur content.

3.2 Characterisation of Pre-treatment Effectiveness and Treated PKS Behaviours

In this work, experiments using different washing mediums were employed to determine the optimum washing medium for the pre-treatment process. Figure 3 shows the ash contents and HHVs of feedstock treated with different types of washing medium. The highest ash reduction measured was 5.97 to 3.40 mf wt% after raw PKS was soaked in distilled water. For the other neutral washing mediums, the ash content was measured to be approximately 5.26 and 5.43 mf wt% in RO and tap water-treated feedstock, respectively. RO and tap water washing pre-treatments caused a smaller ash reduction than distilled water, but both mediums are still viable and practical for use in other specific washing pre-treatments and applications. Meanwhile, the ash content of treated PKS washed with diluted acid and alkaline media were approximately 4.26 and 12.56 mf wt%, respectively. It was expected that the ash content after soaking in diluted acid would be reduced more than in other washing mediums. However, the use of 5% acetic acid reduced ash weight by only a few percentage points through this work, which was attributed to the weakness of the acidic washing solution being insufficient to remove the other large parts of the ash components. Based on this work, pre-treatment using a diluted alkaline solution was not recommended for the leaching process because the treatment only increased the ash concentration. It was theorised that sodium ions, which are abundant in the washing medium, were absorbed by the solid biomass structure. The absorption of the sodium ions would occur due to the low concentration gradient of sodium matter in the feedstock compared to the washing medium. Therefore, sodium ions might diffuse through the porous structure of the biomass solid particles due to the concentration gradient. Deng et al.[35] reported that alkaline matter would enter or withdraw from the biomass depending on the concentration of the washing medium. Because low alkaline matter is present in a neutral washing medium, the amount of ash components and organic matter in biomass would leach more easily into a washing medium, but the reverse is true for washing with a diluted alkaline pre-treatment. Due to the high concentration of sodium ions in the washing medium, the leaching mechanism seemingly prevented the other inorganic species in the biomass from passing readily through the cell walls of the PKS. Therefore, abundant sodium ions and unleached ash culprits might have thoroughly bound and interacted with biomass hydrocarbon matrix components. However, it was undeniable that certain other types of alkaline earth matter might also leach at low rates and amounts through the pre-treatment based on their reactivity and diffusivity towards washing mediums.

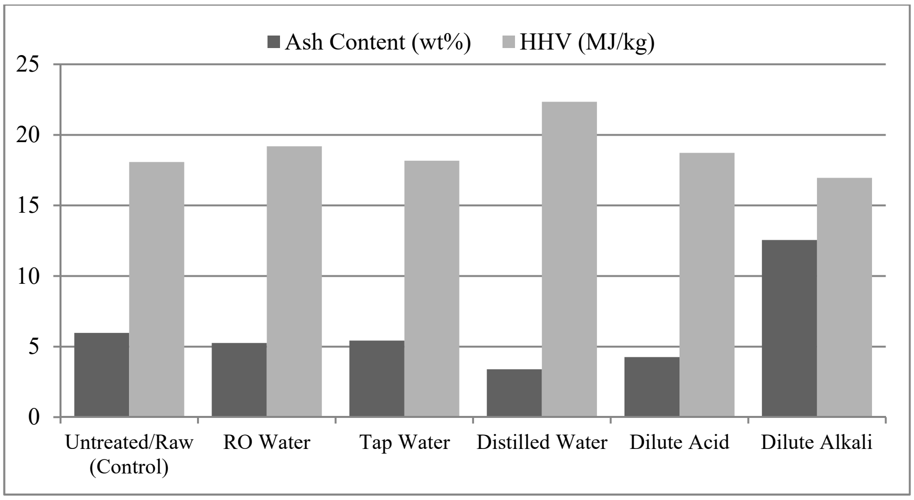

Figure 3: Ash content and high heating value (HHV) of treated raw PKS.

The heating value essentially indicates the energy contained by the biomass that can be totally consumed during power and heat generation. The presence of a high concentration of ash content remarkably lowers the energy value. The correlation of the energy value was seemingly contradictory to the ash content measured. This correlation could be verified by referring to the series of results obtained for washing pre-treatment in this work. For example, the decrease in HHV value measured for alkaline-treated feedstock was up to 6.52% compared to the initial energy value of raw PKS. The reduction was confirmed by the drastic increase in ash concentration from 5.97 to 12.56 mf wt%. Meanwhile, the HHVs of treated PKS washed with neutral and acidic washing mediums increased in a range from 0.5 to 19.1%. The highest HHV increase was observed for the distilled water-treated feedstock, reaching 22.35 MJ kg^{-1}, with an ash reduction of approximately 43% from its initial raw biomass value. The trend was then followed by treated feedstock washed with RO water, dilute acid and tap water, resulting in approximately 19.19, 18.73 and 18.17 MJ kg^{-1}, respectively. Through the pre-treatment process, the use of distilled water on the feedstock appeared sufficient to produce and sustain fuel for heat and thermal applications. The feedstock contained the lowest amount of ash and presented the highest energy value. Fuel with less ash and a higher energy value would provide enhanced efficiency in the thermal conversion process. Furthermore, both properties can prevent serious problems such as slagging, agglomeration and corrosion during the thermal process.[36] Aside from the ash content, the energy values of the biomass would also be influenced by other properties such as the volatile matter and hydrocarbon elemental composition.

The effectiveness of washing pre-treatment could also be identified based on the mass reduction of the feedstock during the leaching process. Conceptually, the phenomenon was affected, considering that pre-treatment removed most of dirt and dust from the outer surface of the PKS during the leaching process and more or less diffused leachable components from the interior plant cell wall of the biomass. The removal and diffusion of the ash culprits are the main indicators of the effectiveness of the washing mediums. As shown in Figure 4, the pre-treatment using 5% diluted acetic acid gave the highest percentage of weight loss, at approximately 11.87%, while the lowest weight loss percentage of approximately 5.75% was achieved by using distilled water. The large weight loss likely occurred due to the extent of the reduction in the biomass chemical composition (i.e., cellulose, hemicellulose). This possibility was supported by researchers such as Tan and Wang[17] and Das et al.[18] Although the medium removed the dirt, dust and ash components drastically, washing with an acidic solution could influence the degradation rate and the remaining percentage of overall cellulose, extractives and hemicellulose composition in biomass. For the diluted alkaline washing pre-treatment, an increase in weight of approximately 3.38% was measured after the leaching process. This phenomenon was expected due to the absorption of sodium ions through the inner and outer surfaces of the biomass porous structure. Clear white spots were observed on the surface, which likely confirmed the sodium matter deposition.

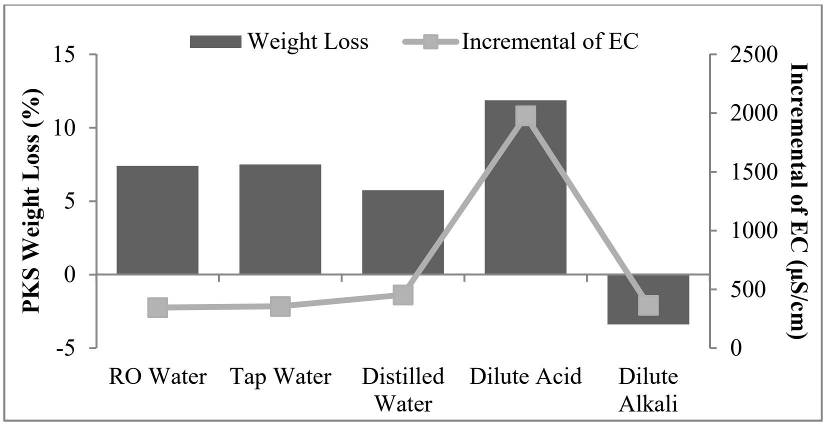

Figure 4: Percentage of treated raw PKS weight loss and the EC value increases of leachates.

The increased EC values of leachate after washing pre-treatments are presented in Figure 4. The highest increase in EC value was observed from the leachate treated with diluted acid, at 1078 μS cm^{-1}. For the case of the neutral washing medium, the EC of leachate was only measured within 345 to 453 μS cm^{-1}, and treatment with distilled water was considered the most effective washing pre-treatment. The removal of unwanted and leachable elements such as dirt and alkaline metal are the major possible cause of the increased leachate EC values. The alkaline metals present in the leachate were almost entirely transformed into free anions or cations[37] and thus were easily extracted by any washing medium. Alternatively, the increased EC values in the diluted acid and alkaline leachates may be due to the extensive degradation of the biomass chemical composition. As mentioned by Cuvilas and Yang,[25] treatment with diluted acid removed and recovered hemicellulose components as dissolved sugar, while solubilised lignin was precipitated onto biomass. Meanwhile, a saponification mechanism of intermolecular ester bond cross-linking between hemicelluloses and lignin occurred during alkaline pre-treatment. Thus, it was confirmed that the formation of other soluble compounds from lignocellulosic components after treatment with different washing mediums could drastically increase the EC values of the leachate instead of the removal and diffusion phenomena of the alkaline metals.

3.3 Thermogravimetric Analysis of PKS

Thermogravimetric analysis was performed on raw PKS to determine the thermal degradation behaviour of cellulose, hemicelluloses and lignin. These three major constituents could be identified by analysing TG and DTG curves, as shown in Figure 5. According to the DTG curve, two clear peaks were found at temperatures of approximately 277°C and 346°C, which might correspond to hemicelluloses and cellulose. These two temperatures were located in two main weight loss regimes, the lower temperature (LT) and the upper temperature (UT) regime, as reported by Khor et al.[30] The LT regime correlated with the decomposition of hemicelluloses and the initial stages of cellulose decomposition, while the UT regime correlated with the remaining decomposition of cellulose constituents. Meanwhile, a slight drop in weight loss can be observed in the early stage of PKS degradation from the TG curve. It occurred in the temperature range of 98°C–100°C, very possibly due to the removal of moisture from PKS. The devolatilisation of PKS was almost complete at the temperature of 600°C, and the remaining residue amounted to approximately 31wt%.

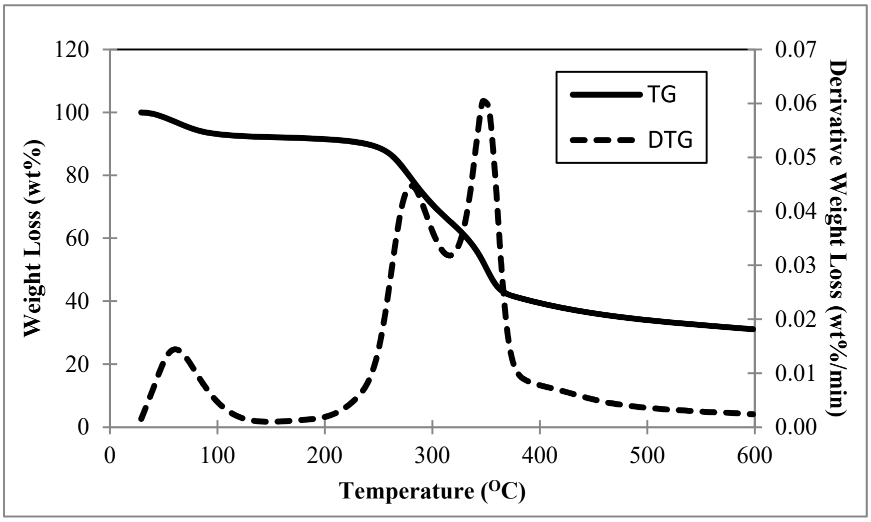

Figure 5: TG and DTG profiles from thermogravimetric analysis of raw PKS.

3.4 Analysis of Treated and Untreated PKS Pyrolysis Yields

Figure 6 shows the pyrolysis yields of PKS in a temperature range of 300°C to 500°C to evaluate the thermal decomposition profiles. The results indicated that the yields of bio-char decreased from 54.40 wt% to 31.38 wt% as the temperature increased. Meanwhile, the gaseous product yield increased slightly from 13.12 wt% to 22.83 wt%. The pyrolysis liquid yield reached its maximum value at a temperature of 400°C, which amounted to approximately 50.42 wt%. Carrier et al.[38] agreed with this trend of the temperature profile, reporting that the mass loss was low when biomass was pyrolysed at temperatures below 310°C, but prominent degradation increased over the temperature range from 300°C to 500°C. Therefore, the high yield of bio-char at an earlier stage of pyrolysis temperature corresponded to the partially pyrolysed PKS organic components. As the temperature increased, the bio-char yield began to decrease significantly due to the rapid release of volatiles. Excessive amounts of volatiles, as well as the loss of water content in biomass could also contribute to the large weight loss of the bio-char product at the end of the temperature profile. In the case of pyrolysis liquid yields, the trend obtained in this study appear similar to the change in liquid yield found by Cao et al.[39] in their research report. They concluded that the variations in liquid yields include two steps of decomposition reactions, namely the faster and slower changing steps. The faster changing step occurred when the temperature was approximately 350°C–400°C, which corresponded to the rapid release of most of the volatilisable components. Meanwhile, the slower changing step occurred when the temperature was above 400°C, when only certain parts of the components decomposed, thus resulting in the low weight percentage of the pyrolysis liquid yield.

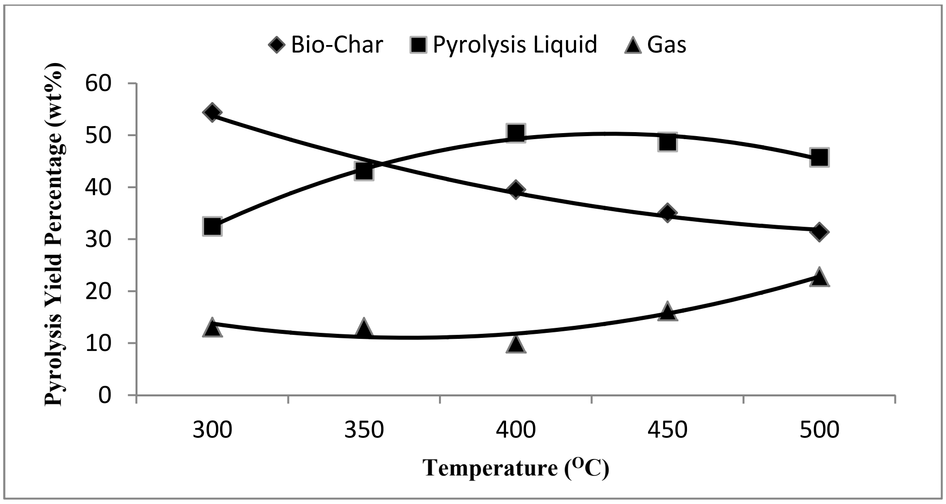

Figure 6: Pyrolysis yields of raw PKS for the temperature profile between 300°C and 500°C.

The influence of various amounts of ash content on the pyrolysis products is presented in Figure 7. The amounts of different ash concentration were obtained through the application of different types of washing medium to the PKS feedstock. For the case of a neutral washing medium, the yields of bio-char, pyrolysis liquid and gas were found to range from 41.91 wt% to 42.04 wt%, 40.27 wt% to 42.11 wt% and 15.98 wt% to 17.69 wt%, respectively. The highest bio-char yield was measured in diluted alkaline-treated feedstock, at approximately 46.96 wt%. Meanwhile, the maximum yield of pyrolysis liquid reached 46.01 wt%, from the PKS treated with diluted acid. The distribution of pyrolysis products could relate well to the various amounts of ash content remaining in treated PKS. Abdullah et al.[26] and Deng et al.[35] also agreed that the ash and its components would primarily influence the degradation rate of biomass constituents under the wide range of heat applied. The presence of excluded sodium ions after the diluted alkaline washing pre-treatment led to the high production of bio-char and gas yield but decreased the yield distribution of pyrolysis liquid. The deposition of sodium matter on the entire surface of the biomass limited the heat and thermal transfer towards the inner porous structure of the biomass. Abundant concentrations of sodium and other alkaline minerals would also act as a catalyst, favouring secondary reactions either in char or in the pyrolysis liquid. This phenomenon could clearly decrease the fractions of solid char composition and undesirable compounds of pyrolytic liquids (acids, alcohols and carbonyls).[40] An increased devolatilisation rate has caused large fractions of pyrolysis liquid yield to occur in diluted acid-treated feedstock. The decomposition reactions of the biomass are affected by the reduction of hemicelluloses and extractive constituents rather than by ash components.[25] Treatment with diluted acidic solutions would lead to breakage of the hemicellulose structure, introducing large interspaces and allowing the cellulose constituent to be more vulnerable to the application of heat. Major pyrolysis liquid compounds, such as levoglucosan, hydroxyacetaldehyde, acetol and acetic acid, are directly derived from the cellulose constituents rather than hemicelluloses and lignin.[41] Cellulose is more exposed by the diluted acetic acid medium, favouring comprehensive degradation, and thus significantly contributes to the higher yield production of pyrolysis liquid.

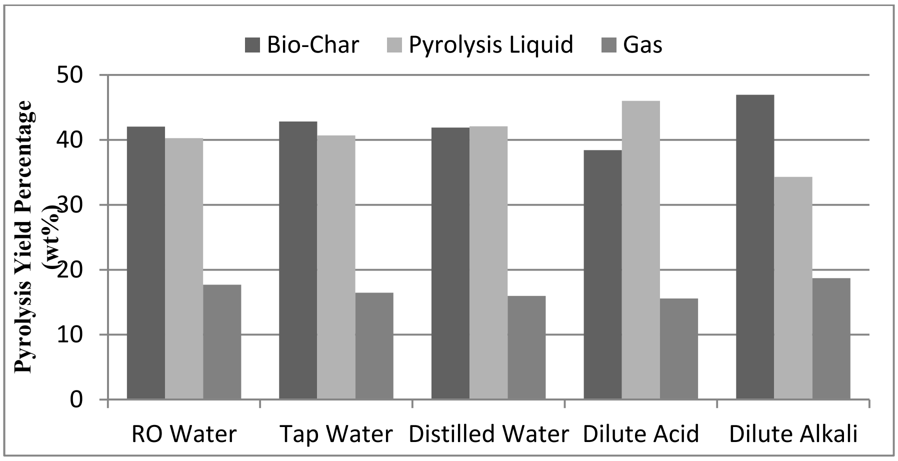

Figure 7: Pyrolysis yield distributions of the treated raw PKS.

3.5 Characterisation of Pyrolysis Products

The characteristics of treated and untreated PKS bio-char are presented in Table 2. Based on the temperature profile, the HHV values of untreated PKS bio-char clearly increased with the pyrolysis temperature. The values fluctuated in amounts ranging from 24.32 to 27.39 MJ kg^{-1}, approximately 25% to 34% higher than their raw biomass energy value. The results also showed a decrease in volatile matter in the untreated PKS bio-char, from 38.58 mf wt% to 25.28 mf wt%, as the pyrolysis temperatures increased. As the temperature increased, the biomass constituents underwent rapid thermal decomposition, especially at higher temperatures. The organic composition was drastically devolatilised and turned into more stable hydrocarbon molecules, such as char and pyrolytic oil. The devolatilisation of hydrocarbon constituents was a major phenomenon compared to the volatilisation of the ash components, resulting in abundant concentrations of ash remaining in the solid matrix form. The ash content of the bio-char was high, at approximately 19% to 37%, compared to their raw PKS value. However, a slight drop in ash content at 400°C was believed to be due to the minor loss of some alkaline mineral that could volatilise at the selected terminal temperature applied.[42]

In the case of treated PKS bio-char, a wider range of ash content was measured, fluctuating between approximately 5.46 mf wt% and 14.43 mf wt%. Diluted alkaline PKS bio-char contained the highest amount of ash after the pyrolysis process. Meanwhile, distilled water PKS bio-char contained the lowest concentration of ash. The results showed that a low amount of ash in raw treated feedstock contributed to the production of better bio-char properties. As in previous cited reports, HHV was a property commonly influenced by ash-related consequences. The HHV of treated PKS bio-chars showed wider variations in the range from 24.12 to 27.75 MJ kg^{-1}, due to the various amounts of ash content measured earlier. The highest HHV was exhibited by distilled water-bio-char, while diluted alkaline-bio-char produced the lowest value. The bio-chars differed in HHV value mainly due to the various ash concentrations previously present in the feedstock, which limited the generation of good thermal profiles for heat and power applications.

The properties of treated and untreated PKS pyrolysis liquid are presented in Table 3. Under the influenced of the temperature range, the obtained pyrolysis liquids were discovered to be present in two clearly separate phases: a tarry organic phase, which was black, smoky and viscous, and a watery aqueous phase, which was slightly opaque and yellow-brown in colour. These non-homogeneous mixtures were clearly observed in all untreated PKS pyrolysis liquid. This condition clarified that the temperature profiles are not the sole influence on the homogeneity of PKS pyrolysis liquids. The homogeneity could also be related to the water content of the pyrolysis liquid. Large amounts of water content (~57%) in pyrolysis liquids caused them to separate. The presence of such amounts of watery phase was believed to be due to the numerous reactions that occurred either in bio-char or in the pyrolysis liquid itself. Those reactions were likely influenced by the ash and its components during the pyrolysis process. In addition, the collected pyrolysis liquid of untreated PKS seemed favourable for industrial usage, with low acidic values in the range of 4.46 to 5.98 and a weight percentage of ash content amounting to less than 1 wt%.

Table 2: The properties of untreated and treated PKS bio-char.

PKS	Bio-char				
	Moisture content (mf wt%)	Volatile matter (mf wt%)	Ash content (mf wt%)	Fixed carbon (mf wt%)	High heating value (HHV) (MJ kg^{-1})
Temperature profile					
300	0.52	38.58	9.41	51.99	24.32
350	2.63	30.80	8.01	61.18	26.37
400	0.34	27.01	7.43	65.55	27.33
450	4.92	26.69	8.49	64.82	27.01
500	0.09	25.28	8.20	66.51	27.39
Treated feedstock					
RO water	1.66	28.51	6.38	65.09	27.41
Tap water	0.13	23.43	9.86	66.70	27.16
Distilled water	1.81	28.46	5.46	66.07	27.75
Dilute acid	1.93	27.17	7.78	65.04	27.17
Dilute alkali	3.85	30.28	14.43	33.27	24.12

Similar results of acidity values and ash concentration were also observed through the pyrolysis liquid collection of treated PKS. The measured pH values of the pyrolysis liquid are approximately 4.09 to 5.96, with the ash concentration amounting to less than 1 wt%. However, treated PKS has produced various results regarding the effect of ash content on the other properties of collected pyrolysis liquid. The water content percentage occupied by pyrolysis liquids of treated PKS ranged between 24.14% to 28.91%. The range was approximately half the water content of the series of untreated PKS pyrolysis liquids. The high amounts of ash content measured in alkaline-treated PKS showed that the strong action of the catalyst appeared to be drastic compared to other treated feedstocks. The catalysts caused surprising production of watery aqueous fractions. The presence of catalytic material contributed remarkably to numerous reactions in solid char and pyrolytic oil, which significantly increased the water production and decreased the tarry organic yield.[34] The increased water content led to a remarkable reduction in the HHV values of the pyrolysis liquids. The average HHV of untreated PKS pyrolysis liquids only reached approximately 18.86 to 19.16 MJ kg^{-1}; meanwhile, a definite difference could be observed in treated pyrolysis liquids, with the highest HHV measured in diluted acid pyrolysis liquid, at approximately 21.69 MJ kg^{-1}, followed by the neutral washing pyrolysis liquids: distilled water: 20.58 MJ kg^{-1}, RO water: 19.90 MJ kg^{-1} and tap water: 19.82 MJ kg^{-1}.

Table 3: The properties of untreated and treated PKS pyrolysis liquid.

PKS	Pyrolysis liquid				
	pH	Homogeneity	Ash content (wt%)	Water content (wt%)	High heating value (HHV) (MJ kg^{-1})
Temperature profile					
300	5.58	Non-homogeneity	0.2033	57.38	18.86
350	5.98	Non- homogeneity	0.6825	56.60	18.89
400	4.99	Non- homogeneity	0.6271	56.23	19.10
450	4.46	Non- homogeneity	0.7225	57.22	19.16
500	4.82	Non- homogeneity	0.7434	56.96	19.07
Treated feedstock					
RO water	4.29	Homogeneity	0.4790	25.01	19.90
Tap water	5.87	Homogeneity	0.3852	24.91	19.82
Distilled water	4.09	Homogeneity	0.3525	24.14	20.58
Dilute acid	5.78	Homogeneity	0.8330	26.22	21.69
Dilute alkali	5.96	Non-homogeneity	0.5950	28.91	18.87

The dominance of oxygen molecules from aqueous phase products is confirmed to lower the energy value of the obtained pyrolysis liquid. Therefore, improving the pyrolysis liquid quality will require removing as much of the oxygen content as possible to achieve at least the energy value of petroleum fuels (40 MJ kg^{-1}).[38] For example, the fuel could be enhanced by incubating the pyrolysis liquid in a rotary evaporator for 30 min at 45°C, as suggested by Garcia-Perez et al.[43], so that the lightest pyrolytic compounds (i.e., water) could evaporate and be removed from the mixture completely. Moreover, the addition of polar solvents such as methanol or ethanol to the pyrolysis liquid was identified as a convenient and practical method. With the addition of a precise amount of the selected solvent, the organic tarry and aqueous watery phases are simply dissolved to obtain a homogeneous single fraction product in a sustained and controlled manner.[44] Moreover, the pyrolysis liquids are believed not only to be homogenised perfectly into single-phase liquid but also to exhibit reduced corrosivity, viscosity and instability.

4. CONCLUSION

The effect of washing pre-treatment on PKS was studied using neutral, diluted acidic and diluted alkaline washing mediums. Distilled water was determined in this study to be the optimum washing medium for PKS. The results showed that the distilled water-treated PKS exhibited a low amount of ash and a low percentage of weight loss, at only 3.39 mf wt% and 5.75%, respectively. Pyrolysis performed on PKS under the influence of a temperature profile showed that the yield of bio-char decreases with increasing temperature, and the highest yield of bio-char was obtained at a relatively low temperature range, at approximately 54.40 wt%. Meanwhile, the pyrolysis liquid shows a different trend, with the maximum yield at 400°C followed by a decrease as the temperature increased further. For the case of treated PKS, the highest bio-char yield is produced from PKS treated with diluted alkaline medium, amounting to approximately 46.96 wt%, while the maximum yield of pyrolysis liquid was 46.01 wt% from diluted acid-treated PKS. The presence of ash and its components seriously influenced the pyrolysis yield, acting as a catalyst to promote secondary reactions during the pyrolysis process. The HHV of treated PKS bio-char clearly increased as the ash content was reduced. Furthermore, the influence of ash also caused large amounts of water fractions to be present in the collected pyrolysis liquid. The liquid fraction of PKS separated into two phases, with the tarry organic/watery aqueous phases of treated and untreated PKS pyrolysis liquid showing ratios of approximately ~75/25% and ~44/56%, respectively. In conclusion, distilled water washing medium was identified as a potential and practical washing pre-treatment for obtaining optimum yields and qualities of pyrolysis products.

5. ACKNOWLEDGEMENT

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