Co-pyrolysis of Palm Empty Fruit Bunch and Palm Kernel Shell with Palm Oil Mill Effluent (POME) Sludge

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Abstract

In Malaysia, the largest contributor to biomass is from the palm oil sector. Therefore, palm-based biomass has been extensively studied for bioenergy applications. Fast pyrolysis of biomass provides a liquid fuel called bio-oil, which has many potential uses. However, a low pH of bio-oil made a challenge to utilize as it is. Therefore, in this study, empty fruit bunch (EFB) and palm kernel shell (PKS) were subjected to co-pyrolysis with POME sludge individually. The reason behind this was that the bio-oil derived from EFB and PKS are acidic, whereas bio-oil from POME sludge is basic. Hence, it was hypothesised that through the co-pyrolysis, bio-oil with lower acidity might be obtained. Chemical characterization revealed that POME sludge contains alkali and alkaline earth metals (AAEMs), which may play a significant role in influencing the weight loss of EFB and PKS, also the bio-oil yield. The co-pyrolysis of EFB and PKS with POME sludge at different ratios were initially carried out via thermogravimetric analysis (TGA). Results showed that for the co-pyrolysis of PKS, a positive synergistic effect was observed when 50 wt.% of POME sludge was employed. Then, pyrolysis and co-pyrolysis experiments were carried out in a fixed bed reactor at 600°C. The bio-oil yield obtained from PKS was 44.5 ± 0.7 wt.%. In contradiction to TGA studies, the bio-oil yield for co-pyrolysis of PKS and POME sludge showed a negative synergistic effect.

Introduction

Since the advancement of technology, human lifestyle has improved drastically through rapid transportation and rapid communication. In 2015, the total energy consumption throughout the world was approximately 13,000 Mtoe and predicted to increase by 48% by the year 2040 [1]. Renewable energy exists in many forms, such as solar energy, wind energy, bioenergy, geothermal energy, and ocean energy. Among these energy forms, biomass is the only sustainable, abundant, and renewable energy source that can provide carbon-based liquid fuel. Lignocellulosic biomass is a composition of mainly three components, namely, hemicellulose, cellulose, and lignin. As lignocellulosic biomass contains an insignificant amount of ash, sulphur, and nitrogen, it considered as clean energy [2]. Fast pyrolysis is one of the thermochemical conversion methods to produce liquid fuel from biomass. In fast pyrolysis, biomass is heated at a controlled temperature of approximately 500°C with high heating rates and resulting vapours are rapidly quenched, whereby mainly liquid product was produced, namely bio-oil.

Malaysia is known for its abundance in oil palm plantation. It is one of the world's largest palm oil-producing nations, wherein the year 2019, Malaysia accounts for approximately 27% of world palm oil production and 34% of world exports [3]. The palm oil sector is the largest contributor to biomass in Malaysia, which includes empty fruit bunches (EFB), palm kernel shell (PKS), fibres, and palm oil mill effluent (POME). With 421 mills available in the country, the highest amount of waste produced from the palm oil sector was POME, followed by EFB.

Many studies utilized lignocellulosic biomass for fast pyrolysis, for example, wood, wheat straw, rice straw, EFB, and many others [2]. Nevertheless, as compared to crude oil, the quality of bio-oil is still not suitable to be used for final applications. This quality is due to high water content (15-35wt.%) in bio-oil, which reduces the higher heating value (HHV) of bio-oil. With water content between (30- 45wt.%) *n*, phase separation of bio-oil may occur [4]. Besides that, a large number of oxygenated compounds that are present in the bio-oil results in the immiscibility of bio-oil in hydrocarbon mixtures. Other than that, the instability of bio-oil during storage is a major problem. Such instability causes an increase in the formation of carbon dioxide as well as increases the viscosity and water content of bio-oil [4]. This instability is suspected to be caused by the presence of highly reactive olefins, which induces repolymerization when air is present [5]. Therefore, the upgrading of bio-oil is required, to ensure the stability and suitability of bio-oil for transportation fuel. Furthermore, bio-oil produced from lignocellulosic biomass is highly acidic pH (2-4) due to the presence of organic acids [5].

Apart from lignocellulosic biomass, substances with high ash content such as sludge, waste tyre, poultry litter and many others were also used as feed for pyrolysis [6]-[8]. The bio-oil yield from high ash content materials ranges between 20-30wt% and is alkaline in nature. The pH of bio-oils that were derived from POME sludge and poultry litter were 9.4 and 9.0, respectively [9]-[10].

Two of the methods to upgrade bio-oil include fast catalytic pyrolysis (CFP) and hydrodeoxygenation (HDO). One of the most common catalysts used for CFP is zeolite HZSM-5 [11]-[12]. However, the downside of this method is that the catalyst rapidly

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loses its activity due to the formation of coke on the catalyst. It causes a reduction in bio-oil yield. For HDO, hydrogen is used to eliminate oxygen from bio-oil in the form of water under high pressure. The catalysts used for HDO includes Co–MoS_2/Al_2O_3, or metal catalysts, Pd/C, Ru/C [5],[13]. Although HDO has the potential to upgrade bio-oil quality, HDO incurs a high cost as a high amount of hydrogen is required [13]. Currently, both methods (CFP and HDO) stated above are not economically sustainable.

On the other hand, the co-pyrolysis of different types of feedstocks is an inexpensive method to improve the bio-oil quality. Studies on co-pyrolysis were carried out, such as co-pyrolysis of biomass with coal and plastic, co-pyrolysis of sewage sludge and pinewood sawdust, co-pyrolysis of waste-tyre and wood-based biomass, co-pyrolysis of poultry litter and woody biomass [6]-[8].

As discussed above, one of the major issues for pyrolysis of lignocellulosic biomass is the production of highly acidic bio-oil. In contrast, the pyrolysis of biomass with high ash substance produces highly alkaline bio-oil. Hence, it may be hypothesised that the co-pyrolysis of both these feedstocks would produce bio-oil with a better pH value (less acidic or neutral). In this study, EFB and PKS were taken as lignocellulosic biomass and POME sludge as waste high ash content feedstock due to the acidic compound in EFB degradation and alkaline compound in sludge degradation would react with each other during pyrolysis to produce bio-oil with pH near to neutral value. Besides that, the alkaline earth metals present in the sludge can act as relinquishing catalyst during pyrolysis. An added advantage for considering POME is to reduce its disposal as a soil amendment as it may cause health issues. This is because the contaminants may release methane gas to the atmosphere and will leach into the underground water is used as fertilisers, thereby affecting human health when ingested [14].

The main objectives of this study were to investigate the effects of POME sludge in the devolatilization of EFB and PKS, and on the bio-oil yield. Initially, co-pyrolysis of EFB-POME sludge and PKS-POME sludge were carried out via thermogravimetric analysis (TGA) to study the change in pyrolytic behaviour of biomasses at various blends. Then, bio-oil from varying EFB and PKS blends with POME sludge was produced in a fixed bed reactor.

Materials and Method

Empty fruit bunch (EFB), palm kernel shell (PKS), and sun-dried palm oil mill effluent (POME) sludge that was used in the current study were obtained from Seri Ulu Langat Palm Oil Mill Sdn. Bhd. Dengkil, Selangor, Malaysia. The EFB, PKS, and sludge collected were dried, ground and sieved to obtain biomasses with the particle size of < 2.0 mm. For effective pyrolysis, the moisture content of both feedstocks should be less than 10wt.%. If the high moisture content is present, it will slow down the heating rate of pyrolysis. Besides, the quality of bio-oil produced would be affected negatively [15]. Hence, the biomasses were dried as such. Moisture content of EFB, PKS and sludge were 5.8±0.03, 3.3±0.1 and 5.8±0.1wt% respectively. Ash content of sludge was 24.9±0.1wt% whereas EFB and PKS had less than 3wt.% ash content. Elemental contents of dried sludge were examined using a Field Emission Scanning Electron Microscope (FESEM, FEI Quanta 400F) equipped with energy dispersive X-ray (EDX) and X-Max detector (Oxford Instruments INCA 400).

For TGA, a thermogravimetric analyser (Mettler Toledo TGA DSC-1) was used to study the thermal behaviour of EFB, PKS, and POME sludge when heated in inert conditions. TGA was also used to study the proximate analysis (volatile matter) of the feedstocks. In this analysis, a known weight of each sample (approximately 10 mg) was heated in a nitrogen environment whereby the flow of nitrogen gas used was 20 mL/min. The samples were heated from ambient temperature until 900°C at a heating rate of 20°C/min, and the temperature was kept constant for 10 min.

Pyrolysis and Co-pyrolysis

The pyrolysis experiment setup was presented in the previous work [16]. The pyrolysis experiments were performed in a fixed bed reactor (L:600mm; ID 28.4 mm), which was heated using a split-able mini tube furnace (BSO-1200X, Malaysia) as simplified in Figure 1. Glass wool was fitted at the exit end of the reactor to prevent solid particles from exiting the reactor. Approximately 15.0 g of samples were filled into the reactor, and nitrogen gas purged through the reactor after that. A low flow of nitrogen of 20-40 cm^3/min was maintained throughout the experiment. The furnace was preheated until 600°C (for sufficient heat transfer) with a heating rate of 10°C/min and maintained throughout the experiment. Once the furnace achieved a steady temperature at 600°C, the reactor was placed into the furnace, and the temperature inside the reactor was measured using a K-type thermocouple. The temperature was recorded every 3 min until they reach a constant temperature of 500°C. It was observed that the average heating rate of the reactor was 23.8 ± 1.87°C/min, indicating a fast/intermediate pyrolysis for bio-oil production. As seen in Figure 1, two condensers in series were used to condense the vapour produced by placing them in an ice bath with a temperature of 0-1.0°C. The non-condensable gas produced was then vented out. The average time taken for fumes to appear in the condensers was noted (5.8 ± 1.9 min).

After the experiment, bio-oil and bio-char weight were measured and calculated to obtain the product yields. Gas yield also calculated simply by subtracting the bio-oil and biochar wt% yield from the total (100 %). This method was repeated for co-pyrolysis of EFB with POME sludge and PKS with POME sludge at varying ratios (POME sludge wt.% of 10, 20, 35, and 50). All the experiments were triplicated for consistency of results.

ANOVA analysis was performed using MATLAB R2013a to determine whether there was any statistically significant relationship between the change in composition and the yield of bio-oil. In general, the null hypothesis of ANOVA states that there is no interaction between the parameters studied. If a *p*-value of < 0.05 was obtained, the null hypothesis would be rejected.

In addition, the theoretical yield of each product was also calculated using Equation 1 and compared with the experimental yield. Then, the percentage of the synergistic effect was calculated using Equation 2.

$$Y_{calculated} = x \text{ x } Y_{Experimentalo,EFB/PKS} + (1-x) \text{ x } Y_{Experimental,Sludge} \quad (1)$$

where, is the calculated or theoretical yield; is the percentage of EFB/PKS added (wt%), is the experimental yield obtained from pure EFB/PKS pyrolysis and is the experimental yield obtained from pure sludge pyrolysis.

$$\%\ Synergistic\ Effect = \frac{(Experimental\ Yield - Calculated\ yield)}{Calculated\ yield} \quad (2)$$

Table 1 Elemental analysis results of sludge, and its ash

Elements	Standard	Sludge	Sludge ash
C	$CaCO_3$	46.4 ± 1.8	19.8 ± 0.0
N	--	5.3 ± 1.1	-
O	SiO_2	34.4 ± 1.8	48.3 ± 0.0
Mg	MgO	1.1 ± 0.4	0.7 ± 0.0
Al	Al_2O_3	0.9 ± 0.3	1.0 ± 0.0
Si	SiO_2	2.1 ± 0.3	24.7 ± 0.0
P	GaP	1.6 ± 0.2	0.4 ± 0.0
S	FeS_2	2.1 ± 0.6	0.1 ± 0.0
Cl	-	0.6 ± 0.1	-
K	MAD-10 Feldspar	2.2 ± 0.6	2.0 ± 0.0
Ca	Wollastonite	1.7 ± 0.5	0.7 ± 0.0
Mn	Mn	0.1	-
Fe	Fe	1.4 ± 0.4	2.3 ± 0.0

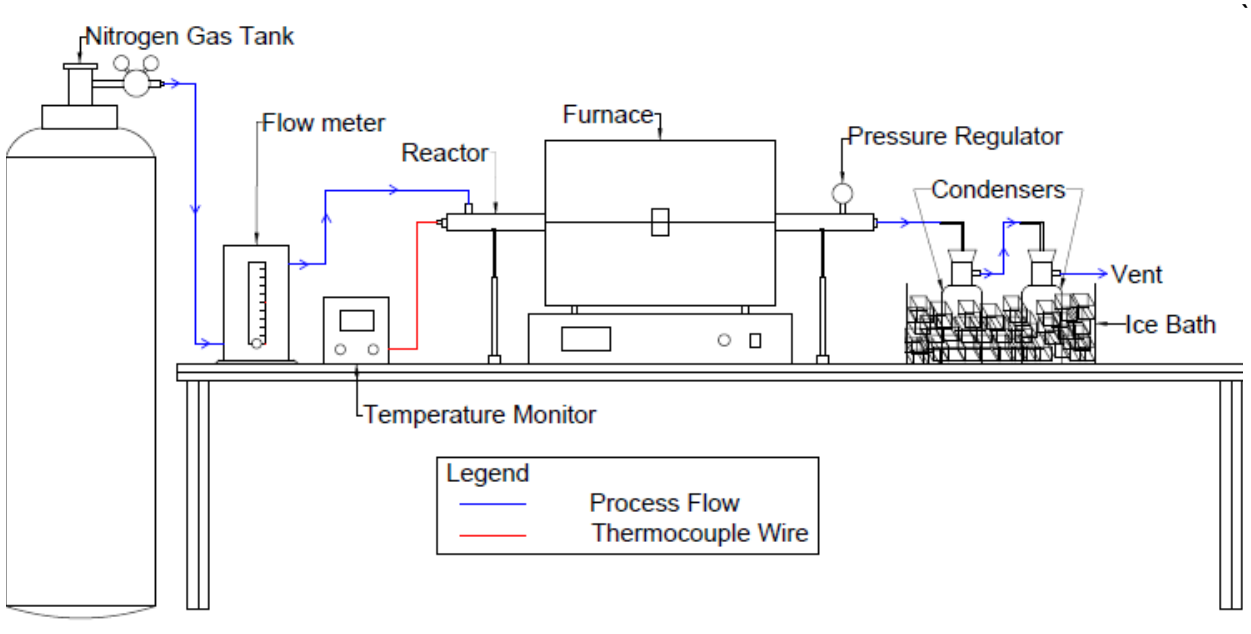


Figure 1 Pyrolysis setup

Results and Discussion

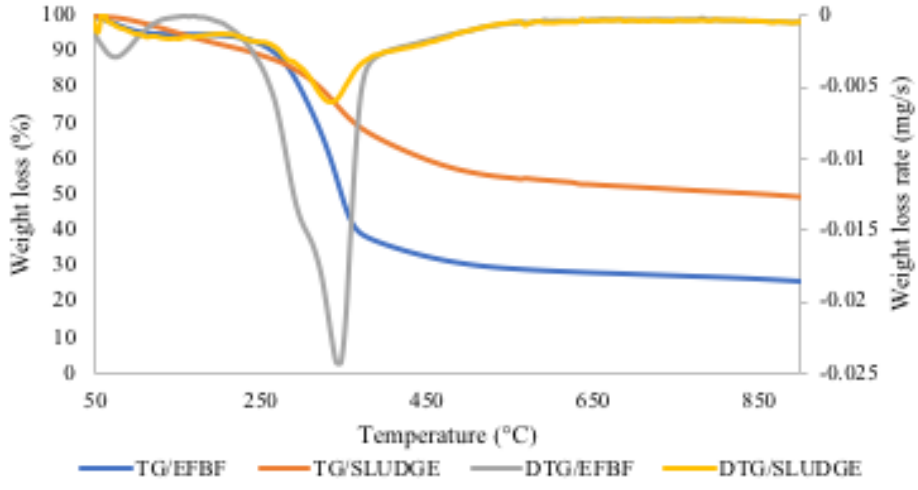
Feedstock Characterization

The elemental analysis of the sludge and its ash is presented in Table 1. The higher ash content in POME sludge may be attributed to the presence of alkali and alkaline earth metals (AAEMs), as shown in Table 1. These inorganic metals can behave as a catalyst to increase the rate of specific pyrolytic reactions and eventually cut down the cost for a catalyst.

Thermogravimetric Analysis (TGA)

Figure 2 depicts the weight loss (TG) and derivative weight loss (DTG) curves upon the degradation of EFB, PKS, and sludge under an inert atmosphere. As observed, the weight losses of EFB and PKS were higher than those of POME sludge. This is because POME sludge has a comparatively high ash content, resulting in the lesser volatile matter. As reflected from the higher maximum thermal degradation rate (DTG curve peak), it may be deduced that EFB and PKS are more reactive than POME sludge [17].

(a)



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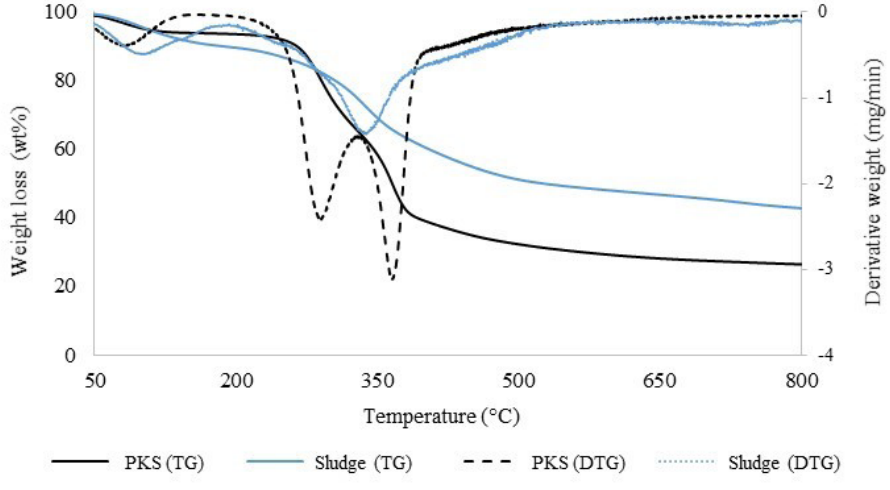


Figure 2 TG and DTG curves of (a) EFB and POME sludge; (b) PKS and POME sludge

A similar trend was seen from the co-pyrolysis of sewage sludge and pinewood sawdust as well as for oily sludge and agricultural biomass [8],[18].

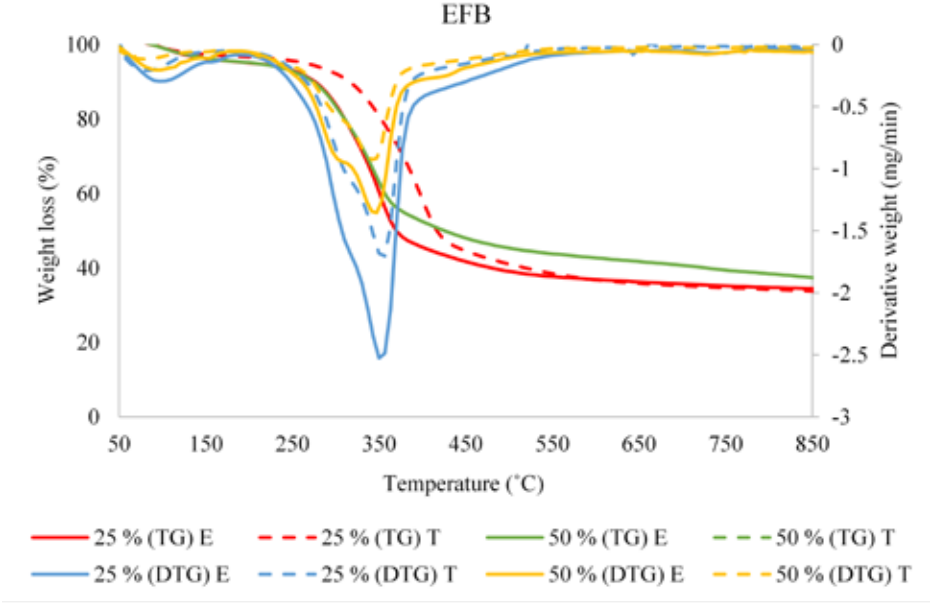
EFB and POME sludge exhibit similar thermal degradation trends, where they can be split into three sections. The first section (50-200°C) indicated the removal of moisture present in biomass as well as some highly volatile compounds. The second section at a temperature range of 200-500°C showed the most significant change in weight for both the biomasses. This was due to the degradation of hemicellulose followed by cellulose compound for EFB whereas, for sludge, it could be associated with the degradation of volatile compounds. Hemicellulose was degraded first due to it having an amorphous structure as well as it is highly branched, whereas cellulose is a long polymer of glucose with low branching structure [19]. The third section (500-900°C) showed a slow degradation in weight loss for both the biomasses. For EFB, this could be depicted as lignin degradation. Lignin was the hardest to decompose as it is an aromatic polymer which is linked by carbon-carbon linkage or ether bonds [20]. On the other hand, for POME sludge, this stage could be accredited to the degradation of carbonaceous material and inorganic compounds. The degradation of PKS is similar to that of EFB and POME sludge but with an extra weight-loss stage, where the dewatering of the biomass contributed to the first weight loss section (50-200°C). The subsequent weight loss stages can be divided according to the following range of temperatures: 150-330°C, 330-400°C, and 400-850°C. The second and third stages were classified as fast devolatilization stages. The former peak denoted the decomposition of hemicellulose, whereas the latter corresponded to cellulose degradation. The presence of the two noticeable weight loss peaks in these stages was mainly due to the high content of lignin in PKS. Lastly, the final stage contributed by lignin degradation.

Figure 3 presents the TG and DTG curves of EFB and PKS with POME sludge blends at a heating rate of 20°C/min in a nitrogen atmosphere. Synergistic effect analyses the interaction between two or more compounds, be it positive or negative and may

be determined from the difference between experimental and theoretical values [21]. Synergistic effect between biomasses upon co-pyrolysis depends on many factors such as pyrolysis duration, heating rate, temperature, the addition of catalysts, an equilibrium of volatiles, as well as type and contact of components [22]. Despite all that, the type of feedstock utilized at different blending ratios was the major factor that affects the synergy.

The synergistic effects between EFB and POME sludge, kinetics, and mechanisms involved in the co-pyrolysis of EFB and POME have been studied in the previous work [23]. As may be observed from Figure 3(a), the experimental values showed higher weight loss than theoretical values when 25wt.% and 50wt.% of POME sludge were employed, indicating a positive synergistic effect. On the other hand, for PKS and POME sludge, the difference

(a)



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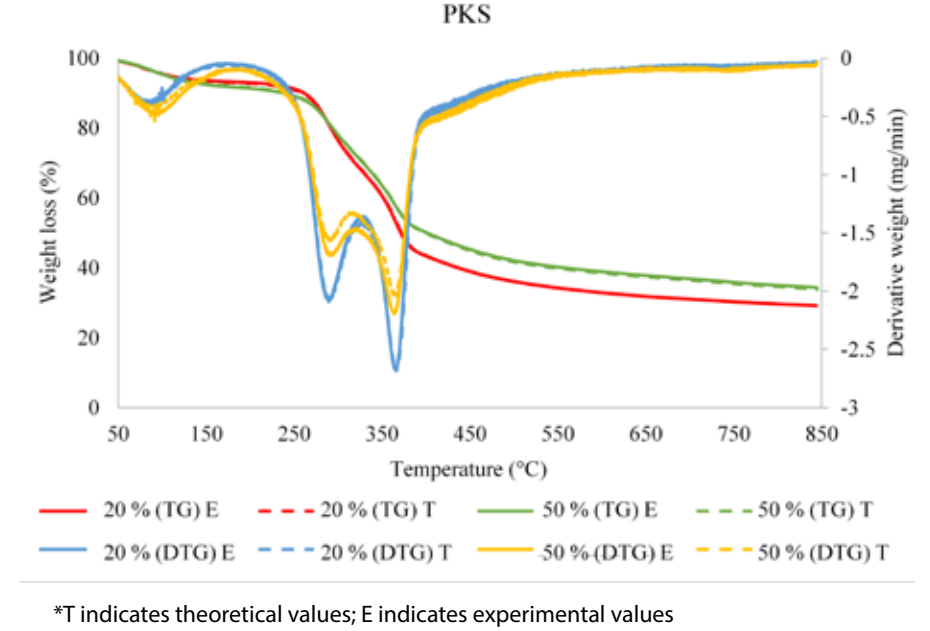

*T indicates theoretical values; E indicates experimental values

Figure 3 TG and DTG curves of (a) EFB with POME sludge at blends of 25 wt.% and 50 wt.% sludge (Chong *et al.*, 2017) and (b) PKS with POME sludge at blends of 20 wt.% and 50 wt.% sludge

between experimental and theoretical values was insignificant when only 20wt.% POME sludge was used, indicating that the was no synergistic effect between PKS and POME sludge. This could be possibly caused by the small mass proportion of POME sludge used. However, the theoretical and experimental DTG curves for the 50wt.% PKS blends displayed an apparent positive synergistic effect. The reason for positive synergistic effects was due to relatively high ash content in the mixture. The ash in the POME sludge contained AAEM species that might have acted as a catalyst to enhance the rate of degradation of hemicellulose, cellulose, lignin and carbonaceous materials in EFB and PKS. The AAEM species generally shortened the time required for the degradation process in co-pyrolysis of both the lignocellulosic biomasses. Zhang et al. [24] also reported that AAEMs found in sewage sludge and rice husk during co-pyrolysis was beneficial and aided to promote gasification process during co-pyrolysis reaction.

Pyrolysis and Co-pyrolysis

As observed from Figure 4, the bio-oil yield from pure EFB and PKS was higher than the yield obtained from pure sludge due to more volatile matters in EFB and PKS, as discussed in earlier section. The higher volatile matter and lower ash content in EFB and PKS favoured the production of bio-oil. A few studies done on the pyrolysis of lignocellulosic and high ash content biomass presented similar results [7], [25].

Based on the results presented in Figure 4, the negative synergetic effect was observed for bio-oil yields of all EFB and PKS to POME sludge ratios. Similar results were obtained by Ding and Jiang [26] and Alvarez et al. [8]. The negative synergistic effects in bio-oil yield could be due to the catalytic activity of metals present in POME sludge (e.g. K, Mg, and Ca, Table 1). The AAEMs would have enhanced secondary reactions such as dehydration and cracking of organic matters in the lignocellulosic biomasses, leading to the reduction in bio-oil yield. Besides that, the AAEMs would enhance the thermal degradation of organic molecules promoting the formation of lighter compounds that could not be easily condensed into liquid bio-oil but instead escaped quickly as non-condensable gas through the vent [8],[26].

The negative synergistic effect of bio-oil yield contradicts the results obtained from those obtained from TGA, which showed that more volatile matters should have been degraded and hence, higher bio-oil yield. The reasons for the contradiction include the contact conditions between the biomasses (e.g., sample amount and height) and contact time between the biomasses and volatiles (e.g., the direction of gas flow) [27]. This ultimately affects the heat transfer characteristics and reactions between the biomass particles. AAEMs in POME sludge did affect the releasing of volatiles in the lignocellulosic biomasses (e.g., EFB and PKS) and the bio-oil yield. Nevertheless, the effects are dependent on the reaction conditions and scale of the experiment.

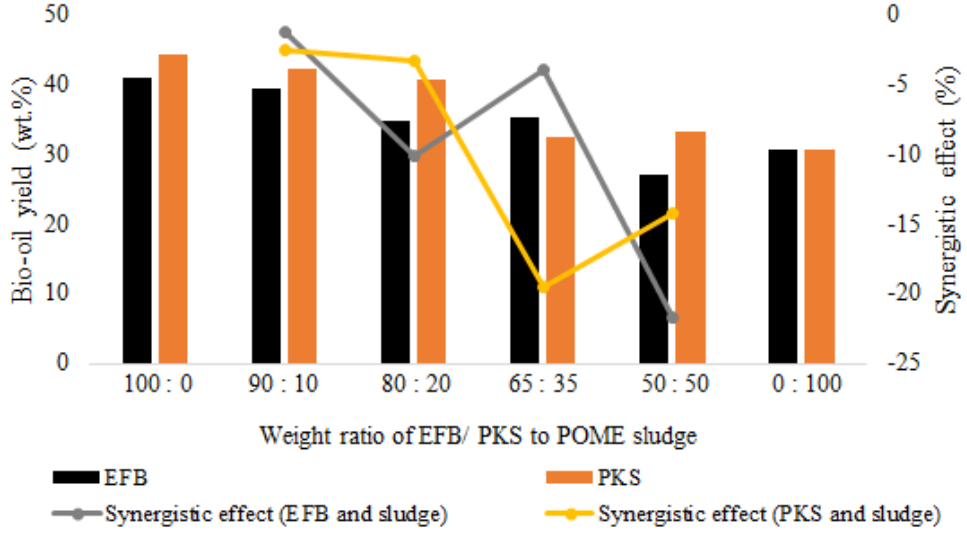

Figure 4 Bio-oil yield of EFB and PKS at various POME sludge weight ratios and their respective synergistic effects

Table 2 *p*-values of product yields for co-pyrolysis of EFB/ PKS with POME sludge

Biomass	*p*-values		
	Bio-oil yield (wt.%)	Biochar yield (wt.%)	Gas yield (wt.%)
EFB and POME sludge	4.786×10^{-5}	2.226×10^{-5}	0.0321
PKS and POME sludge	1.128×10^{-3}	1.060×10^{-11}	6.268×10^{-2}

Biochar yield from pyrolysis of POME sludge was higher than EFB and PKS because the former has a higher ash content than EFB. Hence, as the amount of POME sludge increased in co-pyrolysis experiments, so did the biochar yield. Based on the p-values in Table 2, the change can be considered as significant. A similar trend was observed from studies on co-pyrolysis of corn cob and cattle manure, woody biomass and poultry litter as well as studies on co-pyrolysis of high-density polyethylene and corn cob [7], [28]-[29].

On the other hand, gas yields of EFB and PKS were found to be higher than POME sludge due to the higher amount of volatile matter in the lignocellulosic biomasses, which goes through secondary cracking to produce gaseous products [30]. Besides, the difference could also be due to the structure of biomass. Hemicellulose, cellulose and lignin in EFB and PKS decompose to produce carbon dioxide (CO_2), methane (CH_4), and other light hydrocarbons [31]. As observed in Figure 5, the gas yields with different EFB and PKS to POME sludge ratios did not show a typical trend but may be regarded as a significant change, as reflected from the p-value (Table 2). Since in this study, without compositional analysis on non-condensable gas, it was unable to determine the trend or changes of CH_4, light hydrocarbons, CO_2 and carbon monoxide (CO) according to different feed composition. According to Mante and Agblevor [32], the increase of lignocellulosic biomass ratio would increase the production of CO, whereas the production of CO_2 would be reduced. A very high positive synergistic effect was noticed when 50 wt% POME sludge was mixed with EFB and PKS, which showed that AAEM in sludge acted as a catalyst to crack bio-oil compounds to simpler non-condensable molecules.

Conclusion

The current study investigated the effects of palm oil mill effluent (POME) sludge upon co-pyrolysis with empty fruit bunch (EFB) and palm kernel shell (PKS), respectively in terms of devolatilization and bio-oil yield. Due to the lesser volatile matters, POME sludge was less reactive than EFB and PKS. The high ash content of POME sludge also contributed to the lower weight loss, as observed from thermogravimetric analysis (TGA). Besides, in the production of bio-oil in a fixed bed reactor, the bio-oil yield from POME sludge was also lower than that of EFB and PKS.

Nevertheless, the presence of alkali and alkaline earth metals (AAEMs) in POME sludge ash posed significant effects on the pyrolytic behaviour of EFB and PKS upon co-pyrolysis, as reflected from TGA and bio-oil yield. Upon TGA, where the weight of samples used was small, a positive synergistic effect was observed regarding the degradation of the biomasses. However, a negative synergistic effect was obtained with regards to the bio-oil yield from fixed bed reactor experiments.

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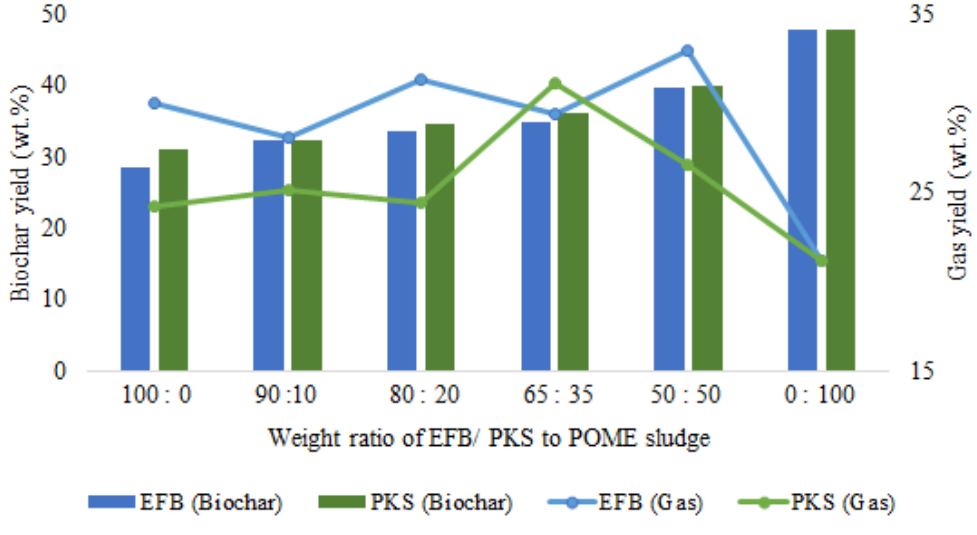

Figure 5 Biochar and gas yield of EFB and PKS at various POME sludge weight ratios

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