

# King Saud University

# Arabian Journal of Chemistry

www.ksu.edu.sa



# **ORIGINAL ARTICLE**

# **Co-pyrolysis of oil palm empty fruit bunch and oil palm frond with low-density polyethylene and polypropylene for bio-oil production**



# Mohammed Abobakr Al-Maari<sup>a,c</sup>, Mohd Azmier Ahmad<sup>a,\*</sup>, Azam Taufik Mohd Din<sup>a</sup>, Hamizura Hassan<sup>b</sup>, Ahmed Mubarak Alsobaai<sup>c</sup>

<sup>a</sup> School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia <sup>b</sup> Faculty of Chemical Engineering, Universiti Teknologi MARA (UiTM) Cawangan Pulau Pinang, 13500 Permatang Pauh, Penang, Malaysia

 $^\circ$  Chemical Engineering Department, Faculty of Engineering and Petroleum, Hadhramout University, Mukalla, Yemen

Received 6 May 2021; accepted 15 June 2021 Available online 20 June 2021

# **KEYWORDS**

Co-pyrolysis; Bio-oil; Biomass-plastic blend; Empty fruit bunch; Palm frond; Low-density polyethylene; Polypropylene **Abstract** Co-pyrolysis of palm wastes of empty fruit bunch (EFB) and palm frond (PF) with lowdensity polyethylene (LDPE) and polypropylene (PP) were investigated to find the synergistic effect of biomass-plastic pair on the yield and composition of bio-oil produced. The pyrolysis process of individual materials and their corresponding blends were employed in a fixed bed reactor at heating rate of 20 °C/min with a nitrogen flow rate of 250 mL/min. The co-pyrolysis results showed that EFB:LDPE with weight ratio of 1:1 has the largest synergy on bio-oil yield, while a negative synergy was revealed for PF:PP co-pyrolysis. In regard of bio-oil chemical composition, the synergistic effect was positive for the formation of aliphatic hydrocarbons and all feedstock decreased the overall oxygenated compounds of fuel substitute. The hydrogen generated from plastic promoted the decarboxylation of acids and decarbonylation reactions of carbonyls and sugars.

© 2021 The Author(s). Published by Elsevier B.V. on behalf of King Saud University. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

# 1. Introduction

\* Corresponding author.

E-mail address: chazmier@usm.my (M.A. Ahmad). Peer review under responsibility of King Saud University.



The total capacity of fossil fuel-based power plants is enlarging dramatically as a consequence of rapid population growth and faster industrialization, which has resulted in an immense demand for limited fossil fuel resources such as oil, natural gas and coal in the majority of power plants around the world (Alsobaai, 2013; Karmaker et al., 2020). Moreover, fossil fuels are the main contributor to the increase in greenhouse gases that is the main cause for increasing average global temperatures and climate change (Leonard et al., 2020). Due to the depletion of fossil fuel reserves and gas emissions, clean renewable

https://doi.org/10.1016/j.arabjc.2021.103282

1878-5352 © 2021 The Author(s). Published by Elsevier B.V. on behalf of King Saud University. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

energy sources are increasingly required to meet the energy demand and mitigate the global warming and environmental pollution (Ryu et al., 2020; Balachandar et al., 2013).

Biomass is one of the major future sustainable energy resources which is abundant in all continents, where the global biomass production hits about 100 billion tons per year (Systems, 2017; Wang et al., 2017). Biomass covers a wide range of plentiful agricultural wastes, animal wastes and algae (Papari and Hawboldt, 2015; Ahmad et al., 2021). Moreover, biomass is considered as a carbon-neutral energy source, since the emitted  $CO_2$  is originally absorbed from atmosphere during photosynthesis process. Using biofuels as an alternative fuels can prevent the emission of approximately 2.1 giga- tons (Gt) of CO<sub>2</sub> into the atmosphere per a year by 2050 (Ojha and Vinu, 2018). Also, emissions of CO, CO<sub>2</sub> and SO<sub>2</sub> from biofuels is insignificant compared to the conventional fossil fuels (Jiménez-Cruz et al., 2021). These features of biomass have encouraged researchers to develop technologies capable of converting biomass into high valuable forms of biofuels such as thermochemical technologies, including pyrolysis, liquefaction, gasification and combustion (Zhao et al., 2020).

In pyrolysis process, the bio-oil derived from biomass is not suitable for direct use as a fuel due to high acidity and high levels of oxygen and water, which cause low heating value, and thermal instability (Ryu et al., 2020). On the other hand, co-pyrolysis of biomass with hydrogen-rich materials, such as plastic, is a promising way to upgrade the production and quality of pyrolytic bio-oil thru synergistic reactions between formed intermediates (Hassan et al., 2020). The synergetic effect is defined as an effect resulting from co-processing of two of more components that generate an effect greater than the sum of their separate effects (Onay and Koca, 2015). Co-pyrolysis of biomass and plastics increases the vield of bio-oil with more homogeneous composition compared to that collected from blending of the individual oils which tend to separate after a period of time (Gunasee et al., 2017). Co-pyrolysis is a technology that is simple to design and operate without any catalysts or solvents for producing high quality bio-oil from two or more materials as feedstock (Abnisa and Wan-Daud, 2015). Co-pyrolysis improves the quality of the produced bio-oils, since the synergistic effects enhance the oil stability, promote formation of hydrocarbons and reduce reactive oxygenated compounds (Navarro et al., 2018; Gin et al., 2021).

Malaysia is the world's second largest producer of palm oil, contributing about 25.8% of world production and 34.3% of world exports (Zubaidah, 2021; Council, 2020). Among the agricultural biomass, oil palm wastes are the attractive pyrolysis feedstock that can be utilized as liquid fuel. The critical problem facing the oil palm sector is the proper disposal of solid waste such as empty fruit bunches (EFB) and palm frond (PF) (Ong et al., 2020; Uemura et al., 2013). In addition, the disposal of end-life plastics has become a major annoying environmental issue due to the massive increase in plastic consumption (Xue et al., 2017). Significantly, Malaysia annually generates more than 0.94 million tons of mismanaged plastic wastes (Chen et al., 2021). The utilization of plastics and oil palm wastes as biofuels reduces both amount of solid wastes dumped in the landfill (Gu et al., 2019).

Co-pyrolysis is supposed to upgrade pyrolytic oil as a result of the synergistic impact between plastics and biomass intermediates (Hassan et al., 2020; Mu et al., 2020). Previous studies (Ephraim et al., 2018; Deng, 2017; Sfakiotakis and Vamvuka, 2018) focused mainly on the effect of co-pyrolysis temperature and heating rate on the synergistic effect. However, Özsin and Pütün (2018) proved the synergistic effects depended strongly on biomass-polymer pair. They found that the co-pyrolysis of polystyrene (PS) with walnut shells and with peach stones caused a positive synergistic effect on bio-oil yields. Moreover, Aboulkas et al. (2012) reported that co-pyrolysis of lignite-LDPE mixtures enhanced significantly the oil yields. However, there still remains a need to study the effect of biomass-plastic pair on the quantity and quality of co-pyrolytic bio- oil, as well as co-processing PF:LDPE and PF:PP pairs which have not been studied before.

The aim of this study was to investigate the synergistic effect of biomass-plastic pair on the yield and composition of bio-oil. Each of EFB and PF was co-pyrolyzed mutually with LDPE and PP in a fixed bed reactor. The chemical compositions of bio-oil were analyzed using gas chromatography mass spectroscopy (GCMS) technique to gain more insight into the effect of biomass-plastic pair. The thermogravimetric analysis (TGA) has been carried out to investigate the thermal behavior of biomass-plastic blends during co-pyrolysis process.

#### 2. Methodology

#### 2.1. Materials

In this study, biomasses of empty fruit bunch (EFB) and palm fond (PF) were obtained from United Oil Palm Mill, Nibong Tebal, Penang, Malaysia. Low-density polyethylene (LDPE) and polypropylene (PP) obtained from Lotte Chemical Titan (M) Sdn Bhd, Pasir Gudang, Johor, Malaysia. EFB and PF were dried, grinded and screened to achieve particle size of 1–2 mm. Nitrogen and helium gases (purity of 99.9%) supplied by Araztech Engineering, Penang, Malaysia were used as a carrier gas.

#### 2.2. Biomass characterization

The ultimate analysis was conducted using CHNS/O analyzer (Model: Perkin-Elmer 2400, USA). The oxidation furnace temperature was set to 975 °C. The reduction furnace temperature was set to 500 °C. The proximate analysis was conducted using Perkin-Elmer TGA 7 connected to Thermal Analysis Controller TAC7/DX. The thermal gravimetric analysis (TGA) was done according to American Society for Testing and Materials method (ASTM D 7582-10). The sample was heated from 30 °C to 110 °C at 10 °C/min with nitrogen gas flow of 20 mL/min and held at 110 °C for 10 min. Then the sample was heated from 110 °C to 850 °C at 10 °C/min and held at 850 °C for 10 min followed by switching from nitrogen to oxygen atmosphere at similar gas flowrate (Dewayanto et al., 2016). Thermal behavior of pure materials and their corresponding blends was evaluated in order to find the maximum degradation temperature. The thermal behavior was estimated by measuring the weight loss of the sample as a function of temperature with time. In each experimental run, the samples were heated from 30 °C to 800 °C at 10 °C/min and held at that temperature for 10 min with nitrogen  $(N_2)$  purge of 20 mL/min.

## 2.3. Pyrolysis experiments

The aim of these experiments was to study the effect of biomass-plastic pair on the yield and composition of bio-oil as a main product. Co-pyrolysis was conducted in a vertical stainless steel fixed-bed reactor with an internal diameter of 25 mm and height of 700 mm. The reactor was installed in an electric furnace which by necessary heat was provided. For each batch, 3 g of biomass and 3 g of plastic (weight ratio of 1:1) were mixed and inserted into the reactor through glass funnel. Nitrogen gas was fed into the reactor at flowrate of 250 mL/min for 10 min to create inert condition as well as to push the vapor products toward the condenser during the co-pyrolysis step.

The co-pyrolysis process was performed at optimum temperature,  $T_{opt}$  with heating rate of 10 °C/min, nitrogen flow rate of 250 mL/min and holding time of 45 min (Hassan

et al., 2019) in order to achieve maximum degradation of the materials and maximize the bio-oil yields. Initially, pure LDPE, PP, EFB and PF were pyrolyzed separately as basis for the calculation of potential co-pyrolysis yield (theoretical yield). Then biomass-plastic blend (EFB:PP, PF:PP, EFB: LDPE or PF:LDPE) with weight ratio of 1:1 were pyrolyzed at the corresponding  $T_{opt}$  obtained from TGA analysis at the same heating conditions. The liquid products from the condenser and wax trap were collected and weighted. Noncondensed gases were collected by gas bags through the vent valve after the condenser. When the reactor was cooled to room temperature, the solid char recovered and weighted. The yield of the oil (Y<sub>o</sub>), solid char (Y<sub>c</sub>) and gas (Y<sub>g</sub>) were calculated using the Eq. (1a-1c):

$$Y_{o} = \frac{W_{o}}{W} * 100 \tag{1.a}$$

$$Y_c = \frac{W_c}{W} * 100 \tag{1.b}$$

$$Y_g = 100 - (Y_o + Y_c)$$
 (1.c)

where Wo and Wc are respectively the weight of the obtained oil and char, while W is the initial weight of the feed (Chandran et al., 2020).

In order to evaluate the synergy effects during co-pyrolysis process, the experimental co-pyrolytic yields were compared with the predicted co-pyrolytic yields. Predicted yields were calculated based on the individual pyrolysis yields of PP, EFB, LDPE and PP according to Eq. (2) (Cao, 2019; Zhao et al., 2020):

Predicted Yield = 
$$(X_1.W_1 + X_2.W_2)$$
 (2)

where  $W_1$  and  $W_2$  are the of pyrolytic yields of individual pyrolysis of plastic and biomass, respectively.  $X_1$  and  $X_2$  are the mass ratios of plastic and biomass in the blend samples, respectively. All experiments were replicated for 3 times and the variations between the yields of each experiment were found smaller than 1%.

## 2.4. Bio-oil characterization

The chemical compound distribution in bio-oil product was characterized by gas chromatography mass spectroscopy (GCMS) (Model: Perkin Elmer Clarus 600/600 T, USA) (Hassan et al., 2019). The analysis was performed using a capillary column of Elite-5MS with a length of 30 m, inner diameter of 0.25 mm and a film thickness of 0.25  $\mu$ m. Highly pure helium was used as the carrier gas with a constant flow rate of 1.0 mL/min. The analysis was conducted by heating the column at 50 °C and was kept for 2 min, the temperature was then ramped to 280 °C at a rate of 5 °C/min and was held at this condition for 20 min. The injected sample was 1  $\mu$ L volume.

## 3. Results and discussion

#### 3.1. Characterization of materials

Table 1 displays the proximate and ultimate compositions of the plastics and biomasses. It is obvious that LDPE, PP, EFB and PF were rich in volatile matter thus can be source for production of bio-oil (Boubacar Laougé and Merdun, 2020; Onay, 2007). From elemental analysis, EFB and PF have significant oxygen content which was the prominent factor for the release of volatile oxygenates, leading to the acidity of bio-oil (Ojha and Vinu, 2018). On the other hand, LDPE and PP with high hydrogen content and lower oxygen content could serve as a hydrogen donor to the biomass intermediates, hence promoting the transformation of oxygenates to hydrocarbon compounds (Hassan et al., 2020) (see Table 2).

#### 3.2. Thermal degradation of individual components and blends

Figs. 1 and 2 present the thermogravimetric (TG) and differential thermogravimetry (DTG) curves, respectively for individual and blended samples. In case of individual materials, TG curves illustrate that EFB and PF have low thermal stability, and begin to break down at a lower temperature compared to plastics. At 150 °C EFB and PF lose their moisture about 4.5% and 7.5%, respectively. The next degradation stage of EFB and PF occurred from 150 °C to 470 °C with a maximum degradation rate happen at 390 °C. The maximum mass loss of 62% and 58% for EFB and PF, respectively were due to the thermal overlapped degradation of hemicelluloses and cellulose (Shafaghat, 2019). The next degradation occurs in the range of 470-800 °C with a mass loss of 8% and 15% for EFB and PF, respectively which due to the lignin decomposition (Parthasarathy and Narayanan, 2014). On the other hand, LDPE and PP decompose in a single step. This can be related to the homogeneous structure of plastic unlike biomass that contains different compounds including hemicellulose, cellulose, and lignin (Gunasee et al., 2017). LDPE and PP lose the major parts of their mass approximately 97% and 96%, respectively in a range (440-545 °C). DTG curves illustrated that the maximum degradation rate for both plastics occurred around Topt of 540 °C. Based on the maximum volatiles loss range, LDPE and biomass of DTG curves were overlapped at range of 440-470 °C. Therefore, interactions between them are to be expected when they are utilized as a co-feed during the co-pyrolysis process.

The degradations of the blends are more complex and complicated. The samples lose their moisture up to approximately 150 °C. The first degradation stage started from approximately 150-390 °C for EFB:LDPE, PF:LDPE and EFB:PP and from 150 °C to 410 °C for PF:PP. The second stage occurred in the range of 440-530 °C for PF:LDPE, 450-535 °C for EFB: LDPE, 480-550 °C for EFB:PP and 490-560 °C for PF:PP. According to Fig. 2(b), each of blends revealed two decomposition peaks between 200 °C and 550 °C. The first peak is attributed the major part of biomass decomposition, while the second peak indicated to the decomposition of plastic and remaining biomass (Tsamba et al., 2006). The interactions between plastics and biomass shows slightly decrease in T<sub>opt</sub> for blends than that for individual plastics. This biomassderived char was act as a catalyst that promotes the degradation of plastics (Uzoejinwa, 2020). On the other hand, shapes of TG curves for plastic-biomass blends indicate that there is a clear wide area separated the degradation of biomass and plastic which in, the loss of volatiles particles was very less. Accordingly, the optimum temperatures were determined in order to use them in the next pyrolysis process. It can be concluded from Fig. 2(a) that the optimum reaction temperature

	22							
	PF	EFB	LDPE	РР				
Proximate analysis $(\%p p)$								
Moisture	7.51	4.52	0.0	0.0				
Volatile matter	73.32	71.35	100	100				
Fixed carbon	14.11	20.43	0.0	0.0				
Ash	5.06	3.71	0.0	0.0				
Elemental/Ultimate analysis (%p/p) <sup>a</sup>								
Carbon	39.1	45.3	79.4	77.0				
Hydrogen	6.74	7.86	14.1	12.2				
Nitrogen	2.30	2.30	1.90	1.90				
Oxygen	50.76	43.45	2.10	6.70				
Sulfur	1.10	1.09	2.50	2.20				

<sup>a</sup> Dry and ash free basis.

Table 2 Experimental and predicted composition of bio-oil obtained from co-pyrolysis of biomass an plastic blends.

Compounds	GSCM area %									
	PF-LDPE		EFB-LDPE		EFB-PP		PF-PP			
	Pred	Exp	Pred	Exp	Pred	Exp	Pred	Exp		
Aromatic Hydrocarbons	3.94	0.23	1.61	0.74	1.60	0.0	3.94	0.0		
Aliphatic Hydrocarbons	36.64	70.45	40.92	61.24	13.7	40.57	9.42	39.86		
Alcohols	10.74	13.52	12.71	13.71	24.51	12.38	22.53	4.96		
Phenols	11.30	0.0	2.91	2.06	2.60	0.0	10.90	0.0		
Carbonyls	10.90	4.73	4.17	4.61	2.70	2.22	9.41	3.50		
Esters	15.83	11.10	25.30	15.90	42.38	39.04	32.96	44.36		
Nitrogenates	0.76	0.0	0.57	0.0	0.57	0.0	0.76	0.0		
Sugars	0.87	0.0	0.0	0.0	0.0	0.0	0.87	0.0		
Acids	8.90	0.0	11.80	2.70	12.14	5.80	9.30	7.30		

for EFB and PF was 390 °C, while for LDPE and PP was 540 °C. On the other hand, Fig. 2(b) shows that the optimum reaction temperature was 510 °C, 520 °C, 540 °C and 540 °C for PF:LDPE EFB:LDPE, EFB:PP and PF:PP, respectively.

#### 3.3. Product yields and synergistic effect

#### 3.3.1. Pyrolysis of pure materials

In order to optimize bio-oil yields, the pyrolysis process was performed at optimum temperature of 390 °C for EFB and PF, and 540 °C for LDPE and PP. In terms of plastic pyrolysis, LDPE and PP have completely converted into liquid and gas products with negligible portion of char (Almeida and Marque, 2015; Anuar Sharuddin et al., 2016). In addition, the plastic chemical structure consists mainly of volatile materials as shown in Table 1. Fig. 3(a) shows that the plastic generated the highest bio-oil yields compared to those from biomass. The bio-oil with vield of 82.6% was the key fraction of LDPE pyrolysis which was significantly higher than that produced from pure PP (75.3%). Low bio-oil yield of PP and the formation of more gaseous products were due to the high oxygen content of PP compared to LDPE which led to produce more non-condensable gases such as CO and CO<sub>2</sub> (Anene et al., 2018; Miandad et al., 2017). On the other hand, the bio-oil yields from the EFB and PF pyrolysis was about 44% and 40%, respectively. Biomass generated large amounts of char compared with plastics due to the fact that biomass has

lower volatile matters and higher fixed carbon content than the plastic as shown in Table 1 which favors char yields (Stančin, 2021).

#### 3.3.2. Co-pyrolysis synergistic effect on bio-oil yield

The co-pyrolysis experiments were performed at the corresponding optimum temperature for PF:LDPE (510 °C), EFB:LDPE (520 °C), EFB:PP (540 °C) and PF:PP (540 °C). The biomass-plastic blending ratio and holding time were fixed at 1:1 and 45 min. Fig. 3(b) shows that the yields of bio-oil from co-pyrolysis of LDPE and biomass blends was dramatically higher than those for blends of PP and biomass, meanwhile bio-oil vields generated from EFB and plastic blends were higher than those generated from PF and plastic blends. Co-pyrolysis of EFB:LDPE yielded higher bio-oil (67.1%), than PF:LDPE (65%). On the other hand, PF:PP gave lower bio-oil yield (54.7%) than EFB:PP (59.8%). For byproducts, the char residues were not significantly affected among all feedstock since the plastic decomposition shared negligible amount of solid residue. Regarding gas yields, PF:PP and EFB:PP generated large amounts of non-condensable gases such as CO, CO<sub>2</sub>, and C2-C3 hydrocarbons (Ojha and Vinu, 2018), since the optimum temperatures of them higher than LDPE:biomass pairs.

In order to evaluate the synergistic effect for each plasticbiomass blend on bio-oil yield, the predicted yields were compared with experimental co-pyrolysis yields as shown in Fig. 4.



**Fig. 1** Thermogravimetric (TG) graphs for (a) individual PF, EFB, LDPE and PP and (b) their biomass-plastic blends.

It can be seen that the obtained results demonstrate different synergy effects on bio-oil production among biomass-plastic pairs. EFB:LDPE blend shows a significant positive synergy with 4% increase in the oil yield, compared to the predicted values. Similarly, significant positive synergistic effect was also observed in co-pyrolysis of LDPE and PF blend with 3.7% increase in the experimental yield. These synergetic effect was attributed to the radical secondary reactions, which cause condensation reactions of non-condensable fragments (Özsin and Pütün, 2018). In addition to the role of LDPE as hydrogenation medium for biomass (Aboulkas et al., 2012), which could prohibit polymerization and cross-linking reactions of biomass, resulting in higher biomass weight loss (Yuan et al., 2018).

On the other hand, Fig. 4 also revealed that there was no additive synergistic interaction between the PP and biomass blends in the case of the PP and EFB combination. Meanwhile, PP and PF blend gave negative synergy of -2.9%. This was due to the higher PF:PP optimum temperature than other biomass-plastic blends which promoted the formation of non-condensable gases. The ash content in PF higher than EFB which reduces the production of the bio-oil. Moreover, the biomass-PP curves are sharper compared with those of biomass-LDPE. This means that biomass-PP radical mechanism is very rapid which favored breaking of C – C bond of PP rather than breaking C – H bond, resulting in a lower hydrogen in the atmosphere (Burra and Gupta, 2018).



**Fig. 2** Differential thermogravimetry (DTG) graphs for (a) individual PF, EFB, LDPE and PP and (b) their biomass-plastic blends.

# 3.4. Characterization of bio-oil

Chemical composition analysis of the co-pyrolytic oil is the most helpful tool to evaluate the synergistic interaction between biomass intermediates and plastics. The components detected in pyrolysis oil can be classified into aromatic hydrocarbon, aliphatic hydrocarbon (alkane and alkene), alcohol, phenol, carbonyl (aldehyde and ketone), ester, sugar, acid, and nitrogenated compounds. Hydrocarbons and alcohols were classified as a high-value organic chemical in the biooil. On the other hand, oxygenated compounds such as acids, ketones, aldehydes, esters and ethers and nitrogenated compounds were undesirable products, because they mainly contribute to corrosiveness, instability and lower heating value of bio-oil (Hassan et al., 2020). The abundances of compounds are compared by the means of their percentage area obtained by GCMS.

#### 3.4.1. Chemical composition of individual pyrolysis bio-oil

Initially, the compositions of pyrolytic oil, derived from pure materials, were specified in order to calculate the predicted bio-oil compositions from the co-pyrolysis of biomass-plastic blends. Fig. 5 reveals the bio-oil product composition from pyrolysis of PF, EFB, LDPE and PP. The components in bio-oil are very different among these feedstocks. In general, the biomass-derived bio-oil has large amount of undesirable oxygenated products compared to the plastic-derived bio-oil which is rich in hydrocarbons. The abundance of oxygenated compounds could be ascribed to the lignin and cellulose in



Fig. 3 Products yield of (a) individual substances pyrolysis and (b) corresponding blends co-pyrolysis.

the structure of the biomass (Kabir et al., 2017; Özsin and Pütün, 2018). With regard to the bio-oil derived from biomass, EFB showed slightly less oxygenated content compared to PF. Fig. 5 showed that the major compounds from PF pyrolysis were ester (25.92%), phenols (21.74%), carbonyls (18.66%), acids (17.96%), and (11.96%) of hydrocarbons (aromatic and aliphatic), while the pyrolysis of EFB exhibited (44.37%) of esters, phenols (5.09%) carbonyls (5%) and acids (23.7%), and (15.85%) hydrocarbons. However, the largest involved classes in both biomass-derived oil are oxygenated compounds. This is due to the elemental composition of the EFB and PF, which appears to have a higher oxygen content and less carbon. In contrast, plastic-derived bio-oil contains a large amount of hydrocarbons and alcohol with little amounts of oxygenated compounds except significant amount of esters in PP-derived bio-oil. LDPE-derived bio-oil is rich of aliphatic hydrocarbons compounds (69.18%) and has significant portion of alcohols (20.96%) and share small amount (5.74%) of esters with traces of phenols and carbonyls. On the other hand, the PP derived bio-oil exhibited high portions of alcohol and esters 44.55% and 40% respectively, in addition to significant amount of hydrocarbons (14.74%).



Fig. 4 Evaluation of synergistic effect for biomass/plastic pair on bio-oil yield.



Fig. 5 Chemical compositions of bio-oil produced by pyrolysis of individual materials.

# 3.4.2. Co-pyrolysis synergistic effect on bio-oil composition

The predicted compositions of co-pyrolytic oil were compared with those results obtained from co-pyrolysis experiments. Fig. 6 and Table 1 show the theoretical and experimental bio-oil chemical compositions for the copyrolysis of biomass and plastic blends (with the weight ratio 1:1). As expected from the research literature, synergies between plastics and biomass are obvious in the results of bio-oil composition analyses (Özsin and Pütün, 2018; Stančin, 2021; Dewangan et al., 2016). However, it can be seen that degree of synergy depends on biomassplastic pairs.



**Fig. 6** Effect of biomass-plastic pair on the relative experimental and theoretical yields in the bio-oil, (a) high-value components and (b) undesired components.

3.4.2.1. High-value chemical compounds. Fig. 6(a) presents the effect of biomass-plastic pair on the distribution of high-value compounds in bio-oil. By comparing the predicted composition distribution calculated based on pyrolysis of individual pyrolysis with those obtained from experimental copyrolysis, we can first conclude that co-pyrolysis of biomassplastic blends enhance the total high-value chemical compounds in oils, depending on biomass-plastic pairs. PF:LDPE bio-oil promote greatly the formation of aliphatic hydrocarbons and alcohols where the experimental value was 70.45% for aliphatic hydrocarbons and 13.52% for alcohols, meanwhile predicted values were 36.64% and 10.74% for aliphatic hydrocarbons and alcohols, respectively. For EFB:LDPE, aliphatic hydrocarbons also increased from 40.91% value to

61.24%, and alcohol increased slightly from 12.71% to 13.71%. However, both biomass-LDPE pairs promoted aliphatic and reduced aromatic hydrocarbons. This was due to the availability of more hydrogen radicals, which converted the aromatics to aliphatic products (Ahmed et al., 2020). This is in agreement with Dewangan et al. (Dewangan et al., 2016) who reported that the liquid produced from co-pyrolysis LDPE with sugarcane bagasse (SCB) consists mainly of significant amount of aliphatic hydrocarbons with smaller amounts of aromatics. On the other hand, the average of desirable (hydrocarbons and alcohols) compounds obtained by PP with biomass co-pyrolysis is considerably lower compared with those from LDPE with biomass. However, in case of PF:PP, aliphatic hydrocarbon increased from 9.43% to 39.86 while alcohols decreased sharply from 22.53% to 4.96%. Similarly, EFB:PP shows increase in aliphatic hydrocarbons from 13.69% to 40.57% and sharp reduction in alcohols from 24.51% to 12.38%. TGA biomass-PP curves are sharper than biomass-LDPE, which means that biomass-PP reaction is very rapid, favoring breaking of C - C bonds rather than breaking C - H bonds (Burra and Gupta, 2018) thus prohibit the synergistic effect of hydrocarbons production. In addition, Fig. 5 suggests that the abundant alcohols derived from PP were interacted with the acids abundant in the biomass, resulting in formation of more esters and reduction of alcohols (Molinero et al., 2013).

3.4.2.2. Undesired chemical compounds. Concerning undesired components, Fig. 6(b) displays the experimental oxygenated and nitrogen-contain composing bio-oil resulted from copyrolysis process and the predicted composition. In general, co-pyrolysis of biomass-plastic blends reduce the content of oxygenated compounds, compared with bio-oil obtained from biomass alone which reveals large quantities of oxygencontaining compounds. For PF:LDPE, positive synergic effects were observed regarding diminishing phenols and acids, as well as reduction of esters and carbonyls respectively from 15.83% and 10.9% to 11.1% and 4.73%. EFB:LDPE blend reduces the esters and acids respectively from 25.3% and 11.8% to 15.9% and 2.7%. The reduction in oxygenated compounds in bio-oil derived from biomass:LDPE blends was ascribed to the efficiency of LDPE as a hydrogen donor compared to PP which has lower hydrogen and higher oxygen content (Hassan et al., 2020). For EFB:PP, it was seen that synergistic effects led to insignificant reduction in esters and carbonyls. Acids and phenols dropped respectively from 12.14% and 2.6 to 5.8% and zero. During co-pyrolysis of PF:PP, negative synergistic effects elevated esters content greatly from 32.96% to 44.36% while other major oxygenates such as acids, carbonyls and phenols respectively reduced from 9.3%, 9.41% and 10.9% to 7.3%, 3.5% and zero. This increase in esters in bio-oil derived from biomass:PP blends was attributed to esterification of the acids derived from biomass and abundant alcohols generated from PP (Molinero et al., 2013).

## 4. Conclusion

The EFB:LDPE has a significant synergy effect on bio-oil yield, as well as PF:LDPE. Concerning bio-oil chemical composition, although they differ in the degree of effect, all feedstocks shown a positive synergistic effect for the formation of aliphatic hydrocarbons. Furthermore, all feedstocks decreased the overall oxygenated compounds of fuel substitute. The hydrogen generated from plastic promoted the decarboxylation of acids and decarbonylation reactions of carbonyls and sugars, meanwhile, oxygen was removed as  $CO_2$  and CO. It can be concluded that the quantity and quality of bi-oil highly depended on biomasspolymer pairs. Consequently, selection of feedstock can be an efficient way to maximize and improve bio-oil product.

## **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

# Acknowledgement

The authors thankfully acknowledge the support obtained from the Lotte Chemical Titan (M) Sdn Bhd, Pasir Gudang, Johor, Malaysia and Universiti Sains Malaysia (Grant Number: 304/PJKIMIA/6050422/L128) in the form of research grant and facilities.

#### References

- Abnisa, F., Wan-Daud, W.M.A., 2015. Optimization of fuel recovery through the stepwise co-pyrolysis of palm shell and scrap tire. Energy Convers. Manag. 99, 334–345. https://doi.org/10.1016/j. enconman.2015.04.030.
- Aboulkas, A., Makayssi, T., Bilali, L., El Harfi, K., Nadifiyine, M., Benchanaa, M., 2012. Co-pyrolysis of oil shale and plastics: Influence of pyrolysis parameters on the product yields. Fuel Process. Technol. 96, 209–213. https://doi.org/10.1016/ j.fuproc.2011.12.001.
- Ahmad, A.A., Ahmad, M.A., Yahaya, N.K.E.M., Karim, J., 2021. Adsorption of malachite green by activated carbon derived from gasified Hevea brasiliensis root. Arab. J. Chem. 14, (4). https://doi. org/10.1016/j.arabjc.2021.103104 103104.
- Ahmed, M.H.M., Batalha, N., Mahmudul, H.M.D., Perkins, G., Konarova, M., 2020. A review on advanced catalytic co-pyrolysis of biomass and hydrogen-rich feedstock: insights into synergistic effect, catalyst development and reaction mechanism. Bioresour. Technol. 310 (March), 123457. https://doi.org/10.1016/j. biortech.2020.123457.
- Almeida, D., Marque, M. de F., 2015. Thermal and catalytic pyrolysis of polyethylene plastic waste in semi. Polimeros 26 (1), 1–8. https:// doi.org/10.1590/0104-1428.2100.
- Alsobaai, A.M., 2013. Thermal cracking of petroleum residue oil using three level factorial design. J. King Saud Univ. - Eng. Sci. 25 (1), 21–28. https://doi.org/10.1016/j.jksues.2011.06.003.
- Anene, A.F., Fredriksen, S.B., Sætre, K.A., Tokheim, L.A., 2018. Experimental study of thermal and catalytic pyrolysis of plastic waste components. Sustain. 10 (11), 1–11. https://doi.org/ 10.3390/su10113979.
- Anuar Sharuddin, S.D., Abnisa, F., Wan Daud, W.M.A., Aroua, M. K., 2016. A review on pyrolysis of plastic wastes. Energy Convers. Manag. 115, 308–326. https://doi.org/10.1016/j. enconman.2016.02.037.
- Balachandar, G., Khanna, N., Das, D., 2013. Biohydrogen Production from Organic Wastes by Dark Fermentation. Elsevier B.V, Ny.
- Boubacar Laougé, Z., Merdun, H., 2020. Pyrolysis and combustion kinetics of Sida cordifolia L. using thermogravimetric analysis. Bioresour. Technol. 299 (Cotober 2019), 122602. https://doi.org/ 10.1016/j.biortech.2019.122602.
- Burra, K.G., Gupta, A.K., 2018. Kinetics of synergistic effects in copyrolysis of biomass with plastic wastes. Appl. Energy 220

(February), 408–418. https://doi.org/10.1016/j. apenergy.2018.03.117.

- Cao, B. et al, 2019. Synergistic effects of co-pyrolysis of macroalgae and polyvinyl chloride on bio-oil/bio-char properties and transferring regularity of chlorine. Fuel 246 (January), 319–329. https://doi. org/10.1016/j.fuel.2019.02.037.
- Chandran, R., Kaliaperumal, R., Balakrishnan, S., Britten, A.J., MacInnis, J., Mkandawire, M., 2020. Characteristics of bio-oil from continuous fast pyrolysis of Prosopis juliflora. Energy 190,. https://doi.org/10.1016/j.energy.2019.116387 116387.
- Chen, H.L., Nath, T.K., Chong, S., Foo, V., Gibbins, C., Lechner, A. M., 2021. The plastic waste problem in Malaysia: management, recycling and disposal of local and global plastic waste. SN Appl. Sci. 3 (4), 1–15. https://doi.org/10.1007/s42452-021-04234-y.
- Council, M.P.O., 2020. Malaysian Palm Oil Industry. Malaysian Palm Oil Counc. [Online]. Available: http://mpoc.org.my/malaysianpalm-oil-industry/.
- Deng, S. et al, 2017. Investigation on the fast co-pyrolysis of sewage sludge with biomass and the combustion reactivity of residual char. Bioresour. Technol. 239, 302–310. https://doi.org/10.1016/j. biortech.2017.04.067.
- Dewangan, A., Pradhan, D., Singh, R.K., 2016. Co-pyrolysis of sugarcane bagasse and low-density polyethylene: influence of plastic on pyrolysis product yield. Fuel 185, 508–516. https://doi. org/10.1016/j.fuel.2016.08.011.
- Dewayanto, N., Azman, A.N., Ahmad, N.A., Mohd Shah, M.S.H., 2016. Study of thermal degradation of biomass wastes generated from palm oil milling plant. Chem. J. Tek. Kim. 3 (2), 31. https:// doi.org/10.26555/chemica.v3i2.5860.
- Ephraim, A., Pham Minh, D., Lebonnois, D., Peregrina, C., Sharrock, P., Nzihou, A., 2018. Co-pyrolysis of wood and plastics: Influence of plastic type and content on product yield, gas composition and quality. Fuel 231 (April), 110–117. https://doi.org/10.1016/ j.fuel.2018.04.140.
- Gin, A.W., Hassan, H., Ahmad, M.A., Hameed, B.H., Mohd Din, A. T., 2021. Recent progress on catalytic co-pyrolysis of plastic waste and lignocellulosic biomass to liquid fuel: the influence of technical and reaction kinetic parameters. Arab. J. Chem. 14, (4). https://doi. org/10.1016/j.arabjc.2021.103035 103035.
- Gu, J., Fan, H., Wang, Y., Zhang, Y., Yuan, H., Chen, Y., 2019. Copyrolysis of xylan and high-density polyethylene: product distribution and synergistic effects. Fuel 267 (August), 2020. https://doi. org/10.1016/j.fuel.2019.116896.
- Gunasee, S.D., Danon, B., Görgens, J.F., Mohee, R., 2017. Copyrolysis of LDPE and cellulose: synergies during devolatilization and condensation. J. Anal. Appl. Pyrolysis 126 (May), 307–314. https://doi.org/10.1016/j.jaap.2017.05.016.
- Hassan, H., Lim, J.K., Hameed, B.H., 2019. Catalytic co-pyrolysis of sugarcane bagasse and waste high-density polyethylene over faujasite-type zeolite. Bioresour. Technol. 284 (January), 406–414. https://doi.org/10.1016/j.biortech.2019.03.137.
- Hassan, H., Hameed, B.H., Lim, J.K., 2020. Co-pyrolysis of sugarcane bagasse and waste high-density polyethylene: synergistic effect and product distributions. Energy 191,. https://doi.org/10.1016/j.energy.2019.116545 116545.
- Jiménez-Cruz, F., Marín-Rosas, C., Castañeda-Lopez, L.C., García-Gutiérrez, J.L., 2021. Promising extruded catalyst for palm oil transesterification from LiAlH4 hydrolysates. Arab. J. Chem. 14 (5). https://doi.org/10.1016/j.arabjc.2021.103141.
- Kabir, G., Mohd Din, A.T., Hameed, B.H., 2017. Pyrolysis of oil palm mesocarp fiber and palm frond in a slow-heating fixed-bed reactor: a comparative study. Bioresour. Technol. 241, 563–572. https://doi. org/10.1016/j.biortech.2017.05.180.
- Karmaker, A.K., Rahman, M.M., Hossain, M.A., Ahmed, M.R., 2020. Exploration and corrective measures of greenhouse gas emission from fossil fuel power stations for Bangladesh. J. Clean. Prod. 244,. https://doi.org/10.1016/j.jclepro.2019.118645 118645.

- Leonard, M.D., Michaelides, E.E., Michaelides, D.N., 2020. Energy storage needs for the substitution of fossil fuel power plants with renewables. Renew. Energy 145, 951–962. https://doi.org/10.1016/j. renene.2019.06.066.
- Miandad, R., Barakat, M.A., Aburiazaiza, A.S., Rehan, M., Ismail, I. M.I., Nizami, A.S., 2017. Effect of plastic waste types on pyrolysis liquid oil. Int. Biodeterior. Biodegrad. 119, 239–252. https://doi. org/10.1016/j.ibiod.2016.09.017.
- Molinero, L., Ladero, M., Tamayo, J.J., Esteban, J., García-Ochoa, F., 2013. Thermal esterification of cinnamic and p-methoxycinnamic acids with glycerol to cinnamate glycerides in solventless media: a kinetic model. Chem. Eng. J. 225, 710–719. https://doi. org/10.1016/j.cej.2013.04.016.
- Mu, M., Han, X., Jiang, X., 2020. Interactions between oil shale and hydrogen-rich wastes during co-pyrolysis: 1. Co-pyrolysis of oil shale and polyolefins. Fuel 265 (December 2019), 116994. https:// doi.org/10.1016/j.fuel.2019.116994.
- Navarro, M.V., López, J.M., Veses, A., Callén, M.S., García, T., 2018. Kinetic study for the co-pyrolysis of lignocellulosic biomass and plastics using the distributed activation energy model. Energy 165, 731–742. https://doi.org/10.1016/j.energy.2018.09.133.
- Ojha, D.K., Vinu, R., 2018. Copyrolysis of Lignocellulosic Biomass with Waste Plastics for Resource Recovery. Elsevier B.V..
- Onay, O., 2007. Influence of pyrolysis temperature and heating rate on the production of bio-oil and char from safflower seed by pyrolysis, using a well-swept fixed-bed reactor. Fuel Process. Technol. 88 (5), 523–531. https://doi.org/10.1016/j.fuproc.2007.01.001.
- Onay, O., Koca, H., 2015. Determination of synergetic effect in copyrolysis of lignite and waste tyre. Fuel 150, 169–174. https://doi. org/10.1016/j.fuel.2015.02.041.
- Ong, T.K., Choo, H.L., Lee, S.M., Kong, K.Y., 2020. Oil palm wastes as sustainable sound absorbing particleboard. IOP Conf. Ser. Mater. Sci. Eng. 815 (1). https://doi.org/10.1088/1757-899X/815/1/ 012010.
- Özsin, G., Pütün, A.E., 2018. A comparative study on co-pyrolysis of lignocellulosic biomass with polyethylene terephthalate, polystyrene, and polyvinyl chloride: synergistic effects and product characteristics. J. Clean. Prod. 205, 1127–1138. https://doi.org/10.1016/ j.jclepro.2018.09.134.
- Papari, S., Hawboldt, K., 2015. A review on the pyrolysis of woody biomass to bio-oil: focus on kinetic models. Renew. Sustain. Energy Rev. 52, 1580–1595. https://doi.org/10.1016/j. rser.2015.07.191.
- Parthasarathy, P., Narayanan, S.K., 2014. Effect of hydrothermal carbonization reaction parameters on. Environ. Prog. Sustain. Energy 33 (3), 676–680. https://doi.org/10.1002/ep.
- Ryu, H.W., Kim, D.H., Jae, J., Lam, S.S., Park, E.D., Park, Y.K., 2020. Recent advances in catalytic co-pyrolysis of biomass and plastic waste for the production of petroleum-like hydrocarbons. Bioresour. Technol. 310, (May). https://doi.org/10.1016/j.biortech.2020.123473 123473.
- Ryu, H.W., Kim, D.H., Jae, J., Lam, S.S., Park, E.D., Park, Y.K., 2020. Recent advances in catalytic co-pyrolysis of biomass and plastic waste for the production of petroleum-like hydrocarbons. Bioresour. Technol. 310. https://doi.org/10.1016/j. biortech.2020.123473.
- Sfakiotakis, S., Vamvuka, D., 2018. Study of co-pyrolysis of olive kernel with waste biomass using TGA/DTG/MS. Thermochim. Acta 670 (May), 44–54. https://doi.org/10.1016/j.tca.2018.10.006.
- Shafaghat, H. et al, 2019. In-situ and ex-situ catalytic pyrolysis/copyrolysis of empty fruit bunches using mesostructured aluminosilicate catalysts. Chem. Eng. J. 366 (February), 330–338. https://doi. org/10.1016/j.cej.2019.02.055.
- Stančin, H. et al, 2021. Co-pyrolysis and synergistic effect analysis of biomass sawdust and polystyrene mixtures for production of highquality bio-oils. Process Saf. Environ. Prot. 145, 1–11. https://doi. org/10.1016/j.psep.2020.07.023.
- Systems, B., 2017. Bioenergy Systems for the Future.

- Tsamba, A.J., Yang, W., Blasiak, W., 2006. Pyrolysis characteristics and global kinetics of coconut and cashew nut shells. Fuel Process. Technol. 87 (6), 523–530. https://doi.org/10.1016/ j.fuproc.2005.12.002.
- Uemura, Y., Omar, W., Othman, N.A., Yusup, S., Tsutsui, T., 2013. Torrefaction of oil palm EFB in the presence of oxygen. Fuel 103, 156–160. https://doi.org/10.1016/j.fuel.2011.11.018.
- Uzoejinwa, B.B. et al, 2020. Co-pyrolysis of seaweeds with waste plastics: modeling and simulation of effects of co-pyrolysis parameters on yields, and optimization studies for maximum yield of enhanced biofuels. Energy Sources Part A Recover. Util. Environ. Eff. 42 (8), 954–978. https://doi.org/10.1080/ 15567036.2019.1602209.
- Wang, S., Dai, G., Yang, H., Luo, Z., 2017. Lignocellulosic biomass pyrolysis mechanism: a state-of-the-art review. Prog. Energy Combust. Sci. 62, 33–86. https://doi.org/10.1016/j. pecs.2017.05.004.

- Xue, Y., Johnston, P., Bai, X., 2017. Effect of catalyst contact mode and gas atmosphere during catalytic pyrolysis of waste plastics. Energy Convers. Manag. 142, 441–451. https://doi.org/10.1016/j. enconman.2017.03.071.
- Yuan, H., Fan, H., Shan, R., He, M., Gu, J., Chen, Y., 2018. Study of synergistic effects during co-pyrolysis of cellulose and high-density polyethylene at various ratios. Energy Convers. Manag. 157 (October 2017), 517–526. https://doi.org/10.1016/j. enconman.2017.12.038.
- Zhao, Y., Yang, X., Fu, Z., Li, R., Wu, Y., 2020. Synergistic effect of catalytic co-pyrolysis of cellulose and polyethylene over HZSM-5. J. Therm. Anal. Calorim. 140 (1), 363–371. https://doi.org/10.1007/ s10973-019-08633-7.
- Zubaidah, S. et al, 2021. Oil palm empty fruit bunch valorization for activated and non-activated carbon nanoparticles and its heavymetal-removal efficiency. Water Sci. Technol., 2652–2668 https:// doi.org/10.2166/wst.2021.166.