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<http://hdl.handle.net/2324/2328410>

出版情報 : Evergreen. 6 (1), pp.92-97, 2019-03. Green Asia Education Center

バージョン :

権利関係 :



Effect of Polypropylene Plastic Waste as Co-feeding for Production of Pyrolysis Oil from Palm Empty Fruit Bunches

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(Received December 28, 2018; accepted March 26, 2019)

In this study, a pyrolysis oil product from slow co-pyrolysis of plastic waste (polypropylene, PP) with palm empty fruit bunches (EFB) was obtained using a fixed-bed reactor. The effect of EFB to PP mass ratio on the physical and chemical properties of pyrolysis oil product was studied. The effect of PP waste toward the properties for pyrolysis oil product yields a lesser amount of oxygenated species, where the pH is similar to a commercial fuel. Co-feeding of PP has a potential in improving the physical and chemical properties of the pyrolysis-oil product as a fuel by lowering its corrosiveness.

Keywords: slow co-pyrolysis, co-feeding, empty fruit bunches, polypropylene, pyrolysis oil

1. Introduction

Currently, the development of bioenergy as an alternative energy source is a key goal due to the decreasing availability of petrochemical fuels. One potential area of energy development is the utilization of biomass to produce bio-oil by the pyrolysis process. The pyrolysis method has economic advantages because it does not require pre-treatment of feedstock. Pyrolysis is one of the promising approaches to produce a renewable product and/or new chemicals ¹). It is a method of short-chain decomposition through a high-temperature heating process without the use of oxygen that provides products such as biochar, biogasoline, and bio-oil ^{1,2}). The product yield of pyrolysis affected by some parameters such as temperature, gas residence time, particle size, heating rate, and feedstock ³). By this method, reduced environmental pollution occurs and an increase in the value of waste to energy via conversion of agricultural biomass into bio-oil. Bio-oil production is very important

because of the need to diminish environmental pollution and to offset the limited global availability of fossil fuels, and the potential to achieve valorization of waste into fuel products ⁴). Techno-economic analysis of bio-oil production process from palm empty fruit bunches (EFB) via fast pyrolysis using a fluidized-bed process has been reported ⁴).

Palm EFB contains lignocellulose compounds, thus it represents a key resource for renewable energy production ⁵⁾⁶), especially for bio-oil products. EFB is an abundant waste biomass harvested in the tropic regions ⁷) that is increasingly more available due to the greater cultivation of palm. Although EFB can be used to produce a fertilized or burnt form to generate steam for electricity production ⁸), most of the EFB is disposed in landfills without proper treatment. Currently, EFB is used as compost or forage ³). Thus, a large amount of EFB can be used as a feedstock for bio-oil production ⁹). Biomass contains carbon, hydrogen and oxygen at levels that differ from conventional fossil fuel resources ⁶). This

feedstock is often in solid form and has low energy density. Thus, the storage and transport is not as efficient according to the higher cost, when compared to hydrocarbon liquid fuels⁶⁾. The quality of bio-oil is often determined by the nature of the biomass from which it is sourced¹⁰⁾.

EFB is a biomass source for bio-oil production but the bio-oil cannot be directly used as a fuel because has many undesirable properties such as low heating value, high acidity, high viscosity, high oxygen content, and high corrosiveness^{11) 12)}. Thus, bio-oil from this process needs further innovation and improvement its quality for upgrading its properties related the suitability as fuel in the fuel infrastructure.

In order to reduce the oxygen compounds and increase the caloric value of pyrolysis oil from EFB, polypropylene (PP) plastic waste was added to the bio-oil production stream via slow co-pyrolysis. PP is the largest type of plastic waste in the world, one of the major components of municipal solid waste, and it contains about 14 wt.% hydrogen atoms, thus it is appropriate as hydrogen source for co-pyrolysis process^{13) 14)}. PP is classified as cheap hydrogen donor atoms because the hydrogen/carbon ratio is about 1 – 2¹⁵⁾. PP is also simply changed into liquid and gas hydrocarbons by pyrolysis process¹¹⁾. As we know that the pyrolysis of PP can be done by the presence of a catalyst or absence of a catalyst. These process is composed by four steps, namely initiation, transfer, decomposition and termination¹⁶⁾. A key goal of this study was to utilize EFB to produce pyrolysis oil with the addition of PP plastic waste as the initiator for the reaction. This type of plastic waste was selected because previous research indicated that such materials produce quality products in the form of pyrolysis oil. The utilization of biomass for bio-oil production has been achieved using the fast pyrolysis method without any additive mixing, but the produced bio-oil tends to have elevated oxygen levels¹⁷⁾. Co-pyrolysis is a process of combining two types of raw materials into the pyrolysis process, where numerous studies indicate that such co-pyrolysis can improve the quality and quantity of bio-oil products^{11) 15)}.

In particular, the addition of plastics in biomass pyrolysis increase yield and the bio-oil caloric value, as compared to pyrolysis of biomass alone. The effect is caused by the presence of paraffin-containing hydrocarbon polymers, isoparaffin, olefin, naphtha and aromatic systems¹⁸⁾.

In this study, we produced pyrolysis oil from EFB mixed with PP waste using slow co-pyrolysis at 500°C with a fixed bed reactor.

2. Experimental

The Materials

Raw materials in the form of PP plastic waste and EFB. PP waste was obtained from the waste contained in the greater Jakarta area. All PP and EFB are oven dried at 80°C, to yield materials with moisture content below

10%. After that, raw materials were chopped with an auxiliary grinder machine up to a size of ± 3 -5 cm.

Preparation of pyrolysis oil product

The reactor design for the slow co-pyrolysis method and preparation of pyrolysis oil product was adapted from the reports by Supramono et al.¹⁹⁾ and Kusriani et al.²⁰⁾. Slow co-pyrolysis was done in a stainless steel reactor in the cylindrical type with a length of 25 cm and a diameter of 6 cm. A feedstock composed of EFB and PP were put in a boat made of a half cylinder size with a length of 11 cm and diameter of 5 cm. 20 g feeds from EFB and PP wastes were used for each experiment. The mass ratio of feedstock PP waste to EFB was varied to be 0:100, 25:75, 50:50, 75:25 and 100:0. The boat was located horizontally inside in the cylindrical reactor. Nitrogen flow is adjusted to be 3 L/h in an up-flow reactor configuration to fulfil the maximum residence time of 7–10 seconds to avoid by-products and/or secondary reaction of plastic. Prior to pyrolysis, the reactor was flushed with nitrogen gas for 15 min with a flow rate of 750 mL/min. The heating rate of the pyrolysis process was maintained and set at 5 °C/min to heat nitrogen gas at 500 °C. After reaching 500 °C, the temperature was maintained for 30 min for each run to produce greater yield of pyrolysis oil product. Then, the vapours were delivered to the condenser by cooling water at 10 °C to allow condensation of the pyrolysis oil. The pyrolysis oil was collected in a bottle for quantitative and qualitative analysis of the identified compounds. Schematic representation of the production of pyrolysis oil is shown in Fig. 1.

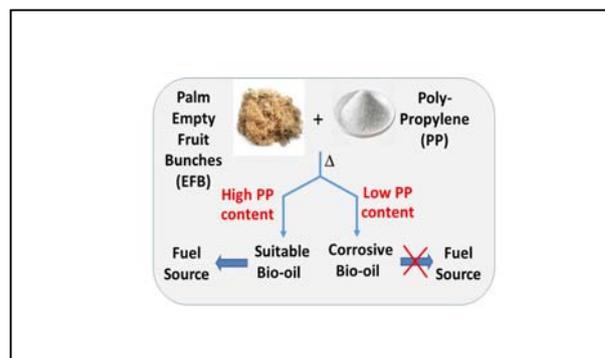


Figure 1. Schematic process for production of pyrolysis oil from EFB and PP plastic waste

Characterization

Volatile matter was measured in accordance with ASTM standard no. 3175, where the size of EFB is near 1-3 cm and a weight of 2 g. The sample was placed in a porcelain crucible and kept in a furnace at 550 °C for 10 min and weighted after cooling at room temperature, then stored at desiccator. The composition of pyrolysis oil product was analyzed by gas chromatography-mass spectrometry (NIST GCMS-QP1010 Ultra Shimadzu,

UK). The pyrolysis-oil was extracted using diethyl ether solvent and concentrated with nitrogen gas. Thermal analysis of EFB and PP wastes were determined by thermogravimetric analysis (Perkin Elmer STA 6000). The viscosity of pyrolysis oil was determined using a Saybolt universal viscometer at 40°C. The results were compared against with those of commercial fuels.

3. Results and Discussion

Characterization

The proximate analysis was conducted to determine the water content, ash, solid carbon, heating value, and volatile matter in the feed. The ultimate test was performed to determine the contents of C, N, O, and S, where the results of the proximate and ultimate analysis of EFB are shown in Table 1.

Table 1. Proximate and ultimate analysis of EFB and PP

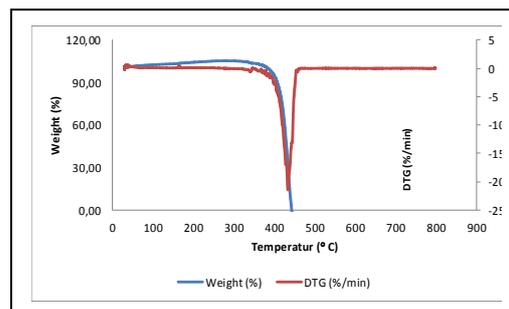
Parameter	EFB	PP
Proximate Test (wt.%)		
Water content	13.64	10.00
Ash content	4.88	0.09
Volatile matter	65.86	89.70
Fixed carbon	15.56	0.21
Ultimate Test (wt.%)		
Carbon	45.94	83.10
Hydrogen	5.64	11.77
Nitrogen	3.99	0.14
Sulfur	0.14	0.16
Oxygen	24.84	4.83

The water content in EFB and PP are 13.64 and 10%, respectively. The presence of water can reduce the heat value, especially the low heating value and combustion temperature. Water can increase the ignition delay or burning delay, and also lower the combustion rate when compared to commercial fuel²¹. Water can also reduce the viscosity of pyrolysis oil product, thus making it more feasible to be used as a fuel. The oxygen content for EFB is high enough to reach 24.84%, and contributes to higher levels of oxygenated species in pyrolysis oil with lower caloric value.

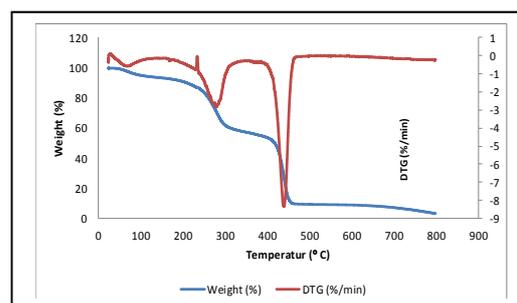
The volatile matter is the amount of substance that evaporates during the combustion process. The higher volatile matter in biomass can result in higher bio-oil yields²². The volatile matter of EFB and PP are 65.86 and 89.70 %, respectively. PP has very low ash content (0.02%), thus it has utility as a precursor in pyrolysis oil production. High levels of ash content can cause pyrolysis oil to be more corrosive and lower its durability. Diebold²³ reported that the compounds produced from high ash levels often contain alkali (Na, K), (Mg, Ca), and other species such as S, Cl, N, P, Si, Al, along with heavy metals such as Cd, Zn, As, Pb, Cu, and Hg.

Thermal analysis

Thermal behavior of EFB, PP and EFB-PP were evaluated using thermogravimetric analysis (TGA). The thermal degradation of EFB and PP bound with the complex chemical reaction and their composition. This data can be used to investigate its thermal properties and the reaction kinetics. It can be accomplished from TGA curve that show the mass loss at increasing temperature and a fixed heating rate²⁴. The high temperature thermal decomposition of the EFB, PP and EFB with ratio 50:50 (wt.%) are presented in Figures 2(a) and (b).



(a)



(b)

Figure 2. TG and DTG curves of (a) PP and (b) EFB and PP waste with mass ratio of 50:50

The first stage of EFB decomposed is from room temperature to 200°C. The main thermal decomposition stage of EFB starts near 200°C to 490°C²⁰. This TGA profiles is also similar with reported for EFB by Lee et al.²⁴ with peak decomposition at 66, 295 and 356°C. The final decomposition stage occurs between 490 to 730°C. For EFB, it can be seen that an event at higher temperature up to 782°C. It can be inferred that carbonaceous residues are present at approximately 28% of the total sample as a residue that remain in the crucibles, in agreement with TGA profiles reported for coal waste by Mohamed et al.²⁵. On the other hand, the main thermal decomposition of PP occurs between 373°C to 452°C (see Fig. 2(a)) in line with the trend observed for Miscanthus biomass²⁶.

The experimental analysis of thermal degradation of EFB:PP with a weight ratio of 50 wt.% occurs firstly at

23 – 83°C, with a second event at 200 – 315°C, and a third event at 375 – 490°C (see Fig. 2(b)). This thermogram is combined from both EFB and PP. The strong peak at 375 – 490°C is indicated by the decomposition of PP.

Effect of co-feeding PP towards Yield of Pyrolysis-oil

The effect of the addition of PP wastes on the yield of the solid, liquid and gas fraction products depicted in Fig. 3. PP has a low methyl fraction that affects each carbon atom of its main chains, causing PP to have a smaller tensile strength. The total mass of solid and liquid fractions was analyzed to examine the effects of co-feeding of EFB and PP. The results showed that increasing the total mass of PP and EFB up to 100 wt.% resulted in pyrolysis oil products of 17.4 and 5.05 wt.%, respectively. The increasing PP waste to EFB weight ratios of 10:90, 25:75, 50:50 and 75:25 wt.% produce a variable yield of pyrolysis oil products at 9.0, 7.8, 6.8 and 6.3 wt.%, respectively (see Fig. 4). In this study, when PP increase the yield of pyrolysis oil decrease because of the PP degradation involved the four steps reactions, namely initiation, transfer, decomposition and termination¹⁶⁾, however, their reaction of PP is not total and perfect occurred thus it effected the pyrolysis oil product.

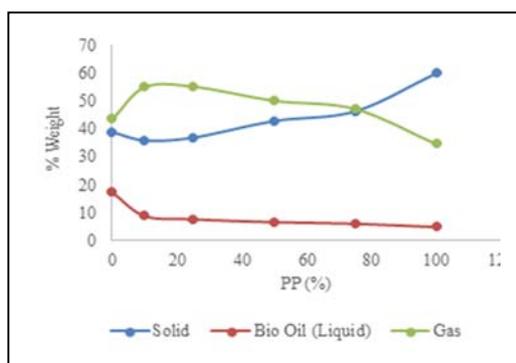


Figure 3. Comparison of solid, liquid and gas fractions with different weight ratios of EFB and PP

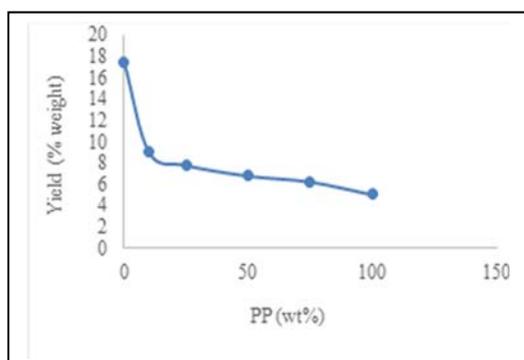


Figure 4. Comparison of % yield of pyrolysis oil product with different weight ratios of PP plastic waste

Component Analysis of Pyrolysis oil Product

GC-MS was used to analyze the chemical components of the pyrolysis oil product after the pyrolysis oil was extracted using a diethyl ether solvent was along with concentration by nitrogen gas. The chemical compounds contained in the pyrolysis oil product are identified based on the relative peak area values (%) in the GC-MS chromatogram. Based on the obtained results, it can be concluded that various compounds are present in the pyrolysis oil product. The aromatic and aliphatic compounds called non-oxygenated compounds, and furans, ketones, aldehydes, acids, phenols, and ketones, referred to as oxygenated compounds were identified in the pyrolysis-oil (see Fig. 5). The results showed that an increase of the total mass of PP and EFB up to 100 wt.%, yielded pyrolysis oil products at 17.4 and 5.05 wt.%, respectively. Further, an increase of the PP plastic waste to EFB ratios of 10:90, 25:75, 50:50 and 75:25 wt.% produced pyrolysis oil products of 9.0, 7.8, 6.8 and 6.3 wt.%, respectively. The pyrolysis oil product is composed of aromatic, aliphatic, phenol, furan, alcohol, aldehyde, ketone and acid compounds. In addition to these compounds, there are also complex hydrogenated compounds.

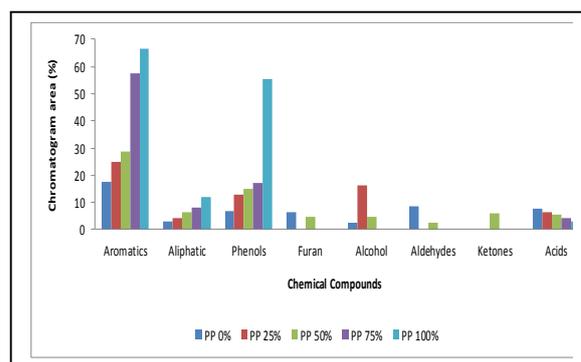


Figure 5. The composition of pyrolysis oil product that produced from the PP:EFB with weight ratio of 0 : 100

Viscosity Test and pH of Pyrolysis oil Product

The viscosity and pH test of the pyrolysis oil was measured to test whether pyrolysis oil can be further utilized as a commercial fuel source. As a fuel, pyrolysis oil should not have a low pH, because it can cause pyrolysis oil to be corrosive. Viscosity analysis is required as a physical property of the fluid that represents the rapid or slow fluid flowability. If the fuel has a viscosity that is too high, it will be hard to flow causing mechanical damage.

In this study, the pyrolysis oil product with variable PP weight ratios of 0: 100, 50:50, and 100: 0 (wt.%) were investigated. For samples with variable PP and EFB, it is seen that the viscosity of diesel is very close to the pyrolysis-oil product in the absence of EFB. The properties of pyrolysis oil are further listed in Table 2

The viscosity of pyrolysis oil products are higher (4.2 to

7) than that found for the commercial fuels (4). The presence of very high lignin compounds in EFB causes the pyrolysis oil to become more viscous, and the pyrolysis oil product becomes unstable ²⁷⁾.

Tabel 2. Comparison properties of pyrolysis oil product vs commercial fuel

Properties	EFB (100 wt.%)	EFB:PP ratio of 50:50 wt.%)	PP (100 wt.%)	Diesel fuel	Gas fuel
viscosity (cSt)	7	4.8	4.2	4	1.17
pH	3	3	5	5	5

The pH of pyrolysis oil product without PP and 50 wt.% of PP have a similar pH value of 3. However, for pyrolysis-oil products with the weight ratio of PP is 100 wt.%, the pH increased and reached to pH 5. The pH of pyrolysis oil product with EFB at 100 wt.% is pH 3 and indicates that the pyrolysis oil is more acidic than the bio-oil product with PP at 100 wt.%. Thus, pyrolysis oil product from pure of EFB contained more oxygenated compounds that favour facile oxidization over carbonaceous materials such as industrial coal waste ²¹⁾. Oxidation reactions that occur not only change the color of pyrolysis oil product to a black colour but it also produced acidic radical compounds. Therefore, the pyrolysis-oil product using EFB of 100 wt.% is acidic. With its high acid content, the pyrolysis-oil product from 100 wt.% biomass cannot be used as a fuel source due to considerations of corrosiveness ^{11) 12)}.

The effects are caused by the role of PP plastics in reducing the content of oxygenated species in the pyrolysis oil product, where it can inhibit the occurrence of oxidation reactions which result in pyrolysis oil with greater acidity. The higher the proportion of PP waste in the precursor led to the yield of a pyrolysis oil product with lesser oxygenated compounds. Increasing the weight ratio of PP waste can produce pyrolysis oil product with less oxygenated products.

The pH of pyrolysis oil produced by PP waste (100 wt.%) is pH 5, which is a weakly acidic in nature. This is due to the lack of oxygen content in PP waste and the greater hydrogen content, so it has a lesser tendency to oxidize. Therefore, the color of pyrolysis oil product with PP (100 wt.%) is more stable than the product derived from EFB at 100 wt.%.

Comparison of the color of pyrolysis oil products for PP (100 wt.%), EFB (100 wt.%) and EFB:PP ratio (50:50 wt.%) is shown in Fig. 6. All color is yellowish and clear. For pyrolysis oil product with PP (100 wt.%) is yellow more thick. Both EFB (100 wt.%) and EFB:PP ratio (0:50 wt.%) are not significant different from each other.

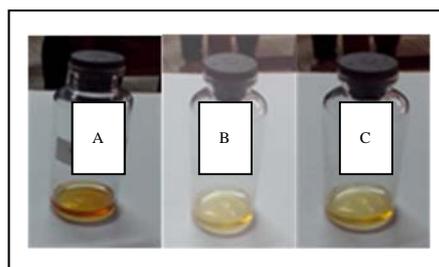


Figure 6. Color of pyrolysis oil products for A. PP waste (100 wt.%), B. EFB (100 wt.%), and C. with EFB:PP weight ratios of 50:50 wt.%)

4. Conclusion

We have investigated the pyrolysis oil properties that resulted from mixtures of EFB and PP by using slow co-pyrolysis. The physical and thermal properties of EFB and PP were characterized using a proximate ultimate test and TGA. In the case of EFB, it can be seen that a thermal event at high temperatures (up to 782°C) that yields residues of approximately 28% of the sample weight that remain in the crucibles. The characteristics of the pyrolysis oil was analyzed by GC-MS. The slow co-pyrolysis process was conducted at a heating rate of 5°C/min at 500°C in the presence of 750 mL/min N₂ gas, with total weight of EFB:PP of 20 g for 30 minutes. The total mass of solid fraction and liquid fraction were analyzed to assess the effects of co-feeding of PP. The effect of PP waste towards the properties for pyrolysis-oil product has lower levels of oxygenated compounds, where the pH is similar with that of commercial fuels. Pyrolysis oil products with PP waste of 100 wt.% was demonstrated to be less acidic due to the presence of aromatic and aliphatic compounds. PP lowers the corrosivity of pyrolysis oil so that it can be utilized further as a suitable fuel source.

Acknowledgment

The authors greatly acknowledge the Universitas Indonesia.

This article's publication is partially supported by the United States Agency for International Development (USAID) through the Sustainable Higher Education Research Alliance (SHERA) Program for Universitas Indonesia's Scientific Modeling, Application, Research and Training for City-centered Innovation and Technology Project, Grant No. AID-497-A-1600004, Sub Grant No. IIE-00000078-UI-1.

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