Non-Catalytic Co-pyrolysis of Empty Fruit Bunch of Palm and Solid Tire Waste Into Upgrade Bio-oil

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Abstract- Alternative fuel is needed in order to anticipate the petroleum depletion and environmental issues. The most abundant and inexpensive raw material for producing renewable fuel is biomass. One of the biomass that is potentially used as raw material for fuel production is empty fruit bunch (EFB) waste of the palm oil industry. EFB can be converted into bio-oil by pyrolysis process, but this product can not be used directly as a transportation fuel, as it needs to undergo a process of an upgrade to bio-oil. Co-pyrolysis is a biomass pyrolysis process with solid material that has a high hydrogen index at atmospheric pressure. One of the materials that have a higher hydrogen index than biomass is polymer, such as solid tire waste. The objectives of this research are to study the effects of EFB treatment, the mass ratio of solid tire waste to EFB, and temperature of co-pyrolysis to the yield and composition of the product. EFB that had been treated was mixed with the tire waste, with a weight ratio of (100:0; 75:25; 50:50; 25:75 and 0:100) between EFB and tire waste. The mixed raw material was put into the co-pyrolysis reactor and heated at 400 – 600 °C, the nitrogen gas was used as a carrier and flowed at a flow rate of 400 mL/min for 45 minutes. The results showed that the treatment of EFB as the raw material of pyrolysis could increase the yield of bio-oil and improve the quality of bio-oil. With the addition of 75% tire waste in the co-pyrolysis raw material, the composition of hydrocarbons in bio-oil became 59.55% with a bio-oil heating value of 33.1 MJ/kg.

Keywords: Bio-oil; co-pyrolysis; empty fruit bunch; solid tire waste.

1. Introduction

Growth in the world's population and the automobile industry spurs an increase in fuel consumption every year [1,2]. The world's energy resources are still dominated by fossil fuels such as petroleum, gas and coal [3,4]. The use of fossil fuels continuously will cause problems such as the depletion of fossil fuel reserves, rising fuel prices, global warming and other environmental problems [5,6]. Therefore, it is necessary to find an alternative for renewable and environmentally friendly sources of energy [7].

Biomass is an alternative for a renewable source of energy which promotes zero carbon dioxide emission and does not directly contribute to global warming [8,9]. EFB of the palm is an attractive raw material for fuel production due to its abundance, inexpensive and safe for food security [10]. EFB can be converted into liquid and gaseous fuels through a pyrolysis process. However, this process is operated at high temperature [11,12]. Pretreatment of biomass by the chemical method has more amorphous structures than the untreated biomass [13]. Pyrolysis of treated biomass is an alternative process. It is chosen due to a lower operating temperature, and generates more liquid products.

Bio-oil obtained from biomass pyrolysis has not been able to substitute transportation fuel since it contains a high proportion of oxygenated compounds (35-40%wt) [14,15]. These compounds are found in diverse chemical forms, such as aldehydes, alcohols, acids, esters, ketones, phenol, guaiacol, and derivatives. These oxygenated compounds caused various undesired properties on bio-oil, such as thermal instability, high viscosity, low heating value and corrosiveness [16]. Consequently, the effort to upgrade quality is needed. It can be implemented by reducing the oxygenated compounds which involve process such as co-pyrolysis [17,18].

Co-pyrolysis is the pyrolysis process of biomass with a high hydrogen-index solid material at atmospheric pressure with the temperature ranges from 350 to 600 °C [19,20]. Solid tire waste has a higher hydrogen-index polymer than empty fruit bunch (EFB) of palm. Solid tire waste is abundant in Indonesia. It has a hydrogen index of 0.995, while EFB has a hydrogen index of 0.26 [9,21]. Therefore, tire waste can be used to improve EFB bio-oil through co-pyrolysis.

Several studies of co-pyrolysis were conducted using biomass and polymer material in a single fixed bed reactor. Hossain et al. [21] studied co-pyrolysis with the composition of 50% solid tire waste and 50% rice husk at 450 °C. This process resulted in a bio-oil yield of 52%. Meanwhile, Alvarez et al. [22] investigated co-pyrolysis pinewood sawdust and waste truck-tire at 500 °C, which resulted in bio-oil with the composition of 33.4% oxygenated compounds, and 20.3% hydrocarbon, as well as containing the heating value of 28.9 MJ/kg. These researches generated a relatively high amount of oxygenated compounds with the use of untreated biomass as raw material.

This research aims to study the effect of the EFB treatment, the ratio of EFB to tire waste and temperature on the yield and composition of the product in co-pyrolysis. EFB as raw material was treated with 0.1 M sodium hydroxide solution. The EFB immersion in NaOH solution can reduce the potassium element in EFB. It is necessary to reduce the potassium element in EFB as the process can increase the yield of bio-oil. The potassium element acts as a catalyst in the secondary reaction which is breakdown the bio-oil into gas. Likewise, the addition of tire waste can increase the hydrocarbon content in bio-oil so that the heating value of bio-oil can increase.

2. Materials and Methods

2.1. Materials

Materials consists of EFB of palm, tire waste and sodium hydroxide. EFB contains 32.2% hemicellulose, 58.5% cellulose and 9.4% lignin. Ash content in EFB and tire waste are 2% and 2.6% respectively. The elemental analysis of EFB and tire waste can be seen in Table 1.

Table 1. The Elemental analysis of EFB and tire waste

Element	EFB (%)	tire waste (%)	tire waste (%), Erliyanti et al. [23]
Carbon (C)	47.54	82.44	81.93
Hydrogen (H)	7.11	7.92	6.27
Nitrogen (N)	0.62	0.75	0.0
Sulfur (S)	nd	2.5	2.34
Oxygen (O)	39.82	4.8	3.95

2.2. Instruments

The experiment instuments consist of tube reactor (inner diameter of 30 mm and lenght of 300 mm), condensor, separator, temperature controller, nitrogen cylinder and flowmeter. The scheme of equipment was presented in Fig. 1.

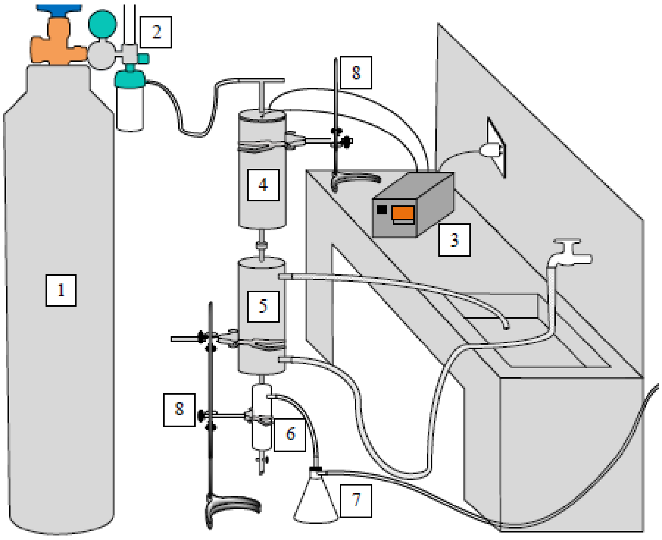

Fig. 1. Schematic diagram the experimental for co-pyrolysis. (1)-nitrogen cylinder; (2)-flowmeter; (3)-temperature controller; (4)-reactor; (5)-condensor; (6)-separator 1; (7)-separator 2; (8)-stative & clamp

2.3. Procedures

2.3.1 Pretreatment of EFB

Before processing, EFB was treated by physical and chemical methods. EFB taken from PTPN V Riau, Indonesia was washed with water, then dried in the sun. The drying EFB was cut into 1 cm size and soak into 0.1 M NaOH solution with a weight ratio of EFB and sodium hydroxide solution of 1:5. The treatment process is carried out at 30 °C for 24 hours. Treated EFB was filtered and washed with distilled water, then dried using an oven at 110 °C for 24 hours. Treated EFB was subsequently analyzed for lignocellulosic content and tested with pyrolysis at 400 °C for 45 minutes.

2.3.2 Co-pyrolysis Process

Treated EFB was mixed with the pieces of cut-up tire waste with a weight ratio of (100:0; 75:25; 50:50; 25:75 and 0:100). The mixed raw materials were put into the co-pyrolysis reactor and heated at 450 °C as well as the nitrogen gas was flowed at a flow rate of 400 mL/min for 45 minutes. The experiment was repeated at temperatures of 400, 500, 550 and 600 °C. The vapour produced was condensed in a water-cooled condenser, while liquid product was collected in the Erlenmeyer flask. Finally, the bio-oil and char product were weighed separately. Non-condensable gas was stored in the gas storage bottle and analyzed to calculate the composition of each constituent.

2.4. Product Analysis

The bio-oil yield determined by weighing the bio-oil and char obtained. The bomb calorimeter was used to measure the heating value of the bio-oil. The chemical composition of the product determined using the gas chromatography-mass spectroscopy (GC-MS, Shimadzu series QP2010S). The GC-MS using Restek RxiR-5MS; 30 m; 0.25 mm ID column and helium as the carrier gas for analyzing the bio-oil. The temperature of the column was set to 50 °C for 5 min and then increased to 280 °C at 5 °C/min heating rate. The injection and detection temperatures were set at 280 °C with the total flow of 40.0 mL/min and pressure of 12 kPa. The composition of the gas product obtained determined using gas chromatography (GC) (Shimadzu series GC 8A). The porapak-Q column and helium as a gas carrier were used to analyze CH_4, CO and CO_2 content at a column temperature of 40 °C and injection and detection temperatures of 60 °C. The molecular sieve (MS 5A) column and nitrogen as a gas carrier were used to analyze H_2 gas, at column temperature of 60 °C and injection and detection temperatures of 70 °C. Morphology and element composition of char obtained was investigated using SEM-EDX (Scanning Electron Microscope–Energy Dispersive X-ray). The yield of bio-oil, char and gas calculation were done using equatioans as follows:

$$Y_{bio-oil} = \frac{W_{bio-oil}}{W_{raw-material}} x100\% \tag{1}$$

$$Y_{char} = \frac{W_{char}}{W_{raw-material}} x100\% \tag{2}$$

$$Y_{gas} = \frac{W_{raw-material} - W_{bio-oil} - W_{char}}{W_{raw-material}} x100\% \tag{3}$$

Where $Y_{bio-oil}$ is the yield of the bio-oil product; $W_{bio-oil}$ is the weight of the bio-oil product; $W_{raw-material}$ is the weight of raw-material; Y_{char} is the yield of char; W_{char} is the weight of char; Y_{gas} is the yield of gas.

3. Results and Discussion

3.1. Effect of EFB treatment on the yields of product

The effect of soaking treatment using 0.1 M NaOH for 24 hours on EFB of palm was studied by comparing the bio-oil, char and gas yield of treated and untreated EFB. The results can be seen in Fig. 2. It is showed that co-pyrolysis at 400 °C the treated EFB resulting in higher bio-oil yield and lower char and gas yield. It appears that through the EFB treatment, increased bio-oil yield to 40.3% and decreased the char and gas yield to 8.4% and 51.3% respectively. The increase of bio-oil yield due to the soaking process increase the amorphous structure and reduce the lignin content in the EFB. Comparison of lignin content of treated and untreated EFB can be seen in Table 2.

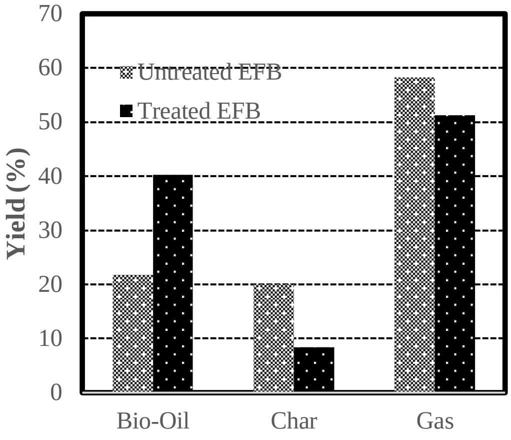

Fig. 2. Effect of EFB treatment on the yield of product

Table 2. The composition of lignocellulose compounds on EFB

Lignocellulose compounds	Composition of untreatment EFB (%)	Composition of treatment EFB (%)
Hemicellulose	32.4	32.1
Cellulose	51.4	58.5
Lignin	16.2	9.4

Furthermore, the soaking process also decreases the potassium in EFB. The comparison of mineral content analyzed using SEM-EDX in char product of untreated and treated EFB can be seen in Table 3.

Table 3. Comparison of element composition in char product of untreated and treated EFB

Element	Composition in char of untreated EFB (%)	Composition in char of treatment EFB (%)
C	59.07	69.04
O	9.05	11.61
Si	2.35	2.55
Al	nd	4.26
Na	nd	2.74
K	22.75	2.15
Ca	nd	3.69

Based on Table 3, by soaking EFB in 0.1 M NaOH solution, the potassium element in char decreased by 90.5%. The element potassium catalyzed the secondary reaction of the pyrolysis process [9]. With a decrease in potassium, it increased the bio-oil yield. This result was in line with the work of Banks et al. [24] who stated that by adding potassium to biomass, bio-oil yield was lower as well as higher yields of non-condensable gases and char.

The morphology of char obtained from untreated and treated EFB pyrolysis can be seen in Fig. 3. Char obtained from untreated EFB pyrolysis had less porosity compared to char of treated EFB. It is showed that untreated EFB was more difficult to be degraded into bio-oil compared to treated EFB. The EFB treatment decreased the degree of polymerization and crystallinity of the lignocellulose in EFB and increased the internal surface area of the lignocellulose [10,13].

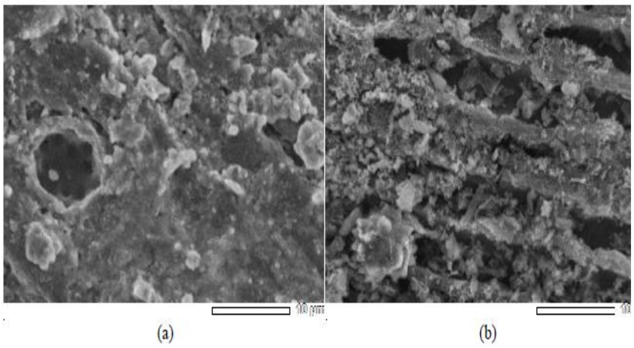

Fig. 3. SEM char analysis, (a) product of pyrolysis untreated EFB, (b) product of pyrolysis treated EFB

Treatments on EFB also affected the composition of compounds in bio-oil. Fig. 4 shows the comparison of the composition of bio-oil from the results of the pyrolysis of treated and untreated EFB. With the EFB treatment, the acetic acid content in bio-oil decreased, while the methanol and hydrocarbon content increased by 19.65% and 1.69 %, respectively.

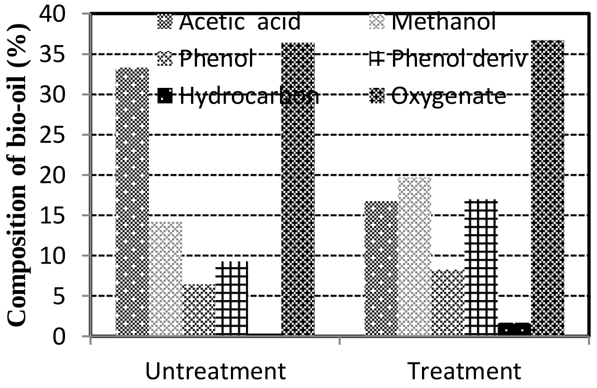

Fig. 4. Effect of treated EFB on the composition of the product

3.2. *Effect of treated EFB and tire waste ratio on the yields and composition of product*

The experiments to study the effect of treated EFB and tire waste ratio on product yield was carried out at 450 °C for 45 minutes. The EFB and tire waste ratio variables were 0:100; 25:75; 50:50; 75:25 and 100:0 with product yields presented in Fig. 5. With the reduced EFB and tire waste ratio, the bio-oil yield tended to decrease, while the char yield was likely to rise. EFB pyrolysis produced higher bio-oil yields than pyrolysis of the tire waste. This was because the ash content in EFB was lower than the ash content in the tire waste. Raw materials that had higher ash content result in higher char yields [22]. This result was strengthened by the results of the thermo-gravimetric analyzer (TGA), as shown in Fig. 6.

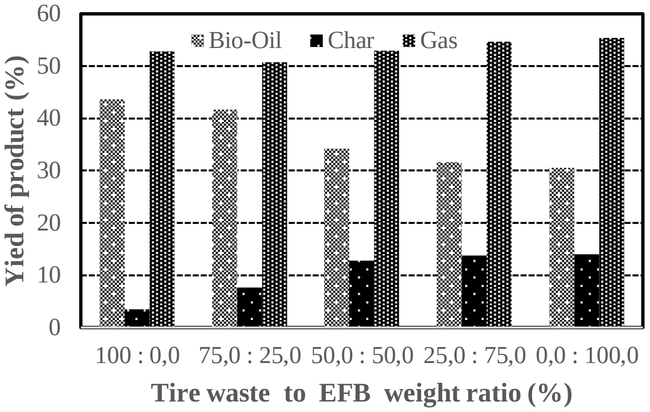

Fig. 5. Effect of EFB treatment and tire waste ratio on yield of product

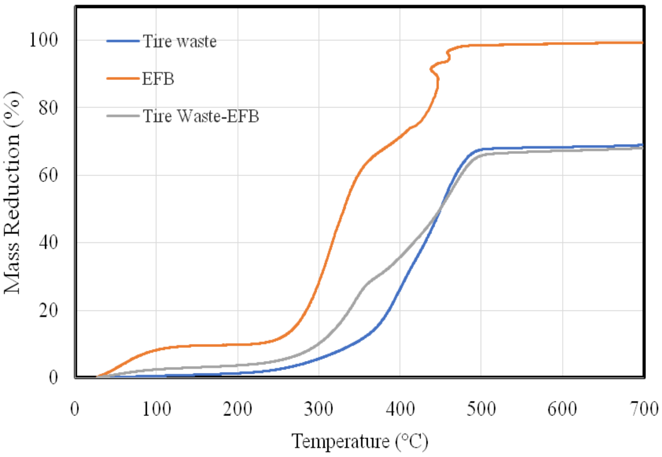

Fig. 6. Effect of temperature on raw material mass reduction

Fig. 6 shows that at temperatures below 300 °C the reduction in mass of EFB, mixture of EFB and tire waste as well as the tire waste were relatively slow. This was because in the temperature range there was the evaporation of water and volatile compounds. Whereas from 300 to 500 °C the mass reduction from the raw material was very fast, this was due to the temperature of the compound in the EFB and the tire waste began to decompose into compounds that had shorter carbon chains. In Fig. 6 it appeared that the reduction in mass from the EFB was greater than tire waste. This was because the carbon content and ash in EFB was less than in tire waste.

The effect of the EFB and tire waste ratio on the composition of bio-oil products can be seen in Fig. 7. As the amount of tire waste in the raw material mixture increased, the amount of acetic acid and phenol in bio-oil inclined to decrease, while the amount of hydrocarbon in bio-oil was likely to increase. For the addition of 75% tire waste in the co-pyrolysis raw material, the composition of hydrocarbons in bio-oil became 59.55%. With the increase of hydrocarbons in bio-oil, it increased the heating value of bio-oil. Fig. 8 shows that with the addition of 75% used tires, the heating value of bio-oil was increased to 33.01 MJ/kg. As a comparison, the heating value of bio-oil products in this study was notably higher than the heating value of bio-oil via the catalytic upgrading of bio-oil using silica alumina catalyst (22.36 MJ/kg) performed by Jamilatun et al. [25].

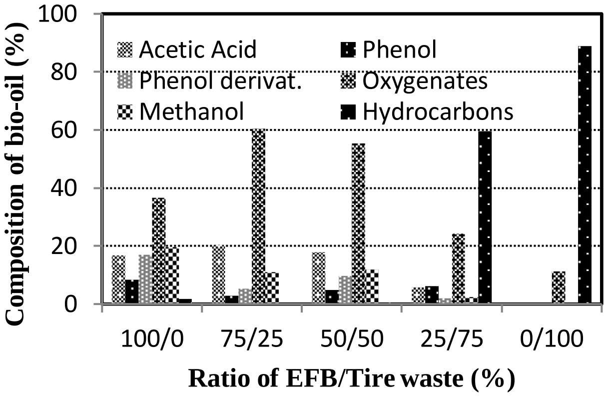

Fig. 7. Effect of EFB treatment and tire waste ratio on bio-oil composition

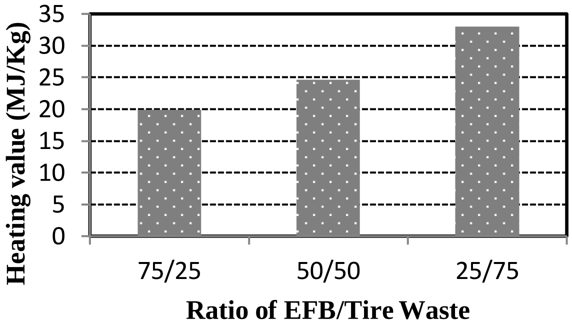

Fig. 8. Effect of EFB treatment and tire waste ratio on the bio-oil heating value

3.3. *Effect of co-pyrolysis temperature on the yields of product*

The raw material with EFB and tire waste ratio of 25:75 at 400-600 °C was used to study the effect of co-pyrolysis temperature on product yield. Fig. 9 shows that with an increase in temperature from 400 to 500 °C, the yield of bio-oil increased, but at temperatures above 500 °C decreased. This shows with an increase in temperature up to 500 °C raw material decomposed into bio-oil, but at temperatures above 500 °C, the formed bio-oil decomposed into gas. Bio-oil yield at EFB and tire waste ratio 25: 75 and temperature of 500 °C were of 44.3%. The effect of co-pyrolysis temperature on the composition of gas product can be seen in Fig. 10. With the increase of co-cracking temperature, the concentration of carbon monoxide in gas product decreased. On the contrary, for the concentration of carbon monoxide, with increasing temperature, the concentration of carbon dioxide showed an increase. This means that with increasing of co-pyrolysis temperature, the reaction of decarboxylation increased, while decarbonylation reaction decreased.

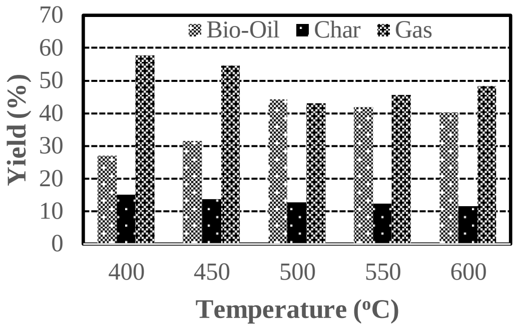

Fig. 9. Effect of co-pyrolysis temperature on product yield

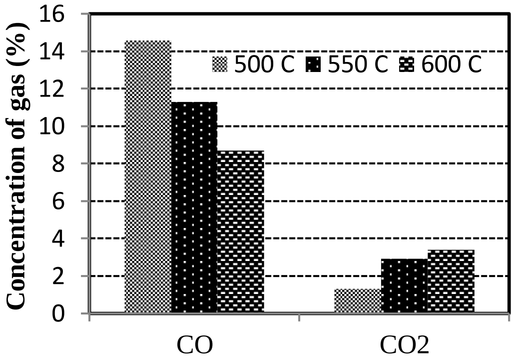

Fig. 10. Effect of co-pyrolysis temperature on the composition of gas product

4. Conclusion

The EFB treatment, the ratio of EFB to tire waste and temperature of co-pyrolysis affected the yield and composition of the product. Treatment of EFB could increase the yield of bio-oil and improve quality of bio-oil. Reducing EFB and tire waste ratio, the bio-oil yield tended to decrease, but the concentration of hydrocarbon would increase. The addition of 75% tire waste in the co-pyrolysis results in the composition of hydrocarbons in bio-oil of 59.55% and a bio-oil heating value of 33.1 MJ/kg. With the raw material EFB to tire waste ratio of 25 : 75 at a temperature of 500 °C, it was resulted bio-oil yield of 44.3%.

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