

Characterization of Bio-Oil from Fast Pyrolysis of Palm Frond and Empty Fruit Bunch

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Abstract. As the world's biggest producer of palm oil, 109 million tons of palm frond and 46 million tons of empty fruit bunch (EFB) were produced annually in Indonesia. These two kinds of palm biomass were still in low-application and could be potentially used as future energy resources such as biofuel. One of the promising methods to convert palm frond and EFB into biofuel, as a dense and easy to transport material, is fast pyrolysis. Before pyrolysis, biomass feedstock was characterized their component and elemental compositions, moisture content and higher heating value (HHV). Fast pyrolysis processes were conducted at a temperature of 350°C using thermal oil heater as a heat carrier. The gas phase from pyrolysis was condensed and produced a dark color and water soluble liquid called bio-oil. As GC-MS data shows, the bio-oil from both feed stocks was dominated by acetic acid, furans, phenols, aldehydes, and ketones. The HHV was reported 12.19 and 26.49 MJ/kg, while water content was 41.91 and 11.54 wt% for bio-oil from palm frond and EFB, respectively. The high content of lignin in EFB effects to the low content of water, high content of phenolic compound, and high calorific value in the bio-oil from EFB.

1 Introduction

The increasing of global energy demand and the depletion of fossil fuel reserves has forces study on new energy resources. Biomass has become favorable as a potential renewable energy source because of its abundance, making it easy to obtain, especially in countries with high agricultural activity. Waste generated in general has not been well utilized to address problems in the environment [1].

Indonesia is the largest palm oil producing country in the world has a palm oil plant of more than 10.5 million hectares [2] which can produce 4.4 tons·ha⁻¹·y⁻¹ of palm empty bunches and 10.4 tons·ha⁻¹·y⁻¹ of palm frond [3]. Currently, empty bunches and palm frond is partly utilized for composting, and animal feed and the rest was left on the ground. Instead of being piled up as waste, it can be converted into biofuel that more dense and easy to transport material.

The process of converting biomass into fuel can be through two paths, namely biochemical pathways and thermochemistry. The biochemical process is done through anaerobic fermentation or digestion process using microbes [4] while the thermochemical process is considered more efficient because it



produces solid, liquid, and gas products under thermal conditions. This process can be pursued through pyrolysis pathways, gasification, liquefaction, and combustion [5].

Pyrolysis is one of the most promising processes for converting biomass that produces bio-oil, biochar and noncondensable gas [5]. This process generally occurs at high temperatures and in the absence of oxygen. Both exothermic and endothermic reactions involved in pyrolysis process. Exothermic reactions occur at low temperatures in the early stages when the pyrolysis process begins, including the breaking of the bonds of organic compounds into small fractions. As temperatures increase, some primary products vaporize and break into secondary products; this stage is called endothermic reaction [6].

Bio-oil, as the main product of biomass pyrolysis, is a high-density oxygenated compound that forms of thick dark brown or black liquid that is easy flowing and smelling sharp [5]. The chemical composition in bio-oil depends on the biomass feedstock used. Because it comes from decomposition and depolymerization of cellulose, hemicellulose, and lignin, the main composition of the bio-oil consists of water, acids, alcohols, ketones, aldehydes, phenols, ether, esters, sugars, furans, nitrogen compounds, and various other compounds. These components make bio oil corrosive, unstable, has high water content, and has a low calorific value for direct use as fuel [7]. Therefore, characterizations of bio-oil are required to determine further upgrading process to improve its quality.

In this research, the raw material of palm empty fruit bunches (EFB) and palm frond has been converted into bio-oil through fast pyrolysis process at 350°C. Characterization of bio-oil was conducted to determine the water content, pH, calorific value, and characterization of its components using GC-MS.

2 Materials and Methods

2.1 Materials

Palm Frond used in this experiment was collected from a palm tree in PUSPIPTEK, South Tangerang, Indonesia. The leaves were removed from the frond before chopping and powdering until the size of 16 – 30 mesh. Palm EFB was collected from a local palm oil mill in Lebak Regency, Indonesia. Before pyrolysis process, EFB was chopped and powdered into the same size as palm frond. The moisture content of palm frond and EFB was 13.06 and 12.73%, respectively.

2.2 Bio-oil Productions

Bio-oil productions were conducted using a reactor describes in Solikhah et al.[8] operated at 350°C using thermal oil as a heat carrier. Bio-oil as the liquid product was collected from the condenser in the form of dark color and water soluble liquid.

2.3 Characterizations

Analysis of cellulose, hemicellulose, and lignin in the palm frond and EFB was conducted using an HPLC (Waters Corp, USA) according to the method developed by Sluiter et al. [9].

The bio-oils were qualitatively analyzed using a gas chromatograph mass spectrometer of Shimadzu GC/MS QP 2010 (Shimadzu Corp, Tokyo, Japan). In the analysis, a column of DB1 (dimethyl polysiloxane, 30 m x 0.32 mm x 1 µm capillary column) obtained from Agilent, USA was used. Helium gas on GCMS grade (Air Liquide, Indonesia) was used for gas carrier. A 0.8 µL sample was injected on the column that was started at 40 °C then hold for 4 minutes, after that, ramped at 5 °C/minute until 250 °C and then hold for 10 minutes.

Water content on bio-oil was analyzed using Karl Fisher KF200 (Mitsubishi Chemical Analytech Co.,Ltd., Kanagawa, Japan). The heating value of bio-oil was measured using Automatic Calorimeter

AC500 (Leco Corp., Saint Joseph, USA). The pH analysis was performed on bio-oil using 848 Titrino plus (Metrohm AG, Switzerland).

3 Results and Discussions

3.1 Celluloses and Lignin

The analysis shows that the cellulose, hemicellulose, and lignin composition in palm frond were 36.67, 18.71, and 27.38% while in EFB were 23.83, 15.90, and 39.51%, respectively. This result shows that palm frond is dominated by cellulose which is in accordance previous studies by Abnisa et al. and Kabir et al. [3,10]. On the other hand, EFB is dominated by lignin. This result differs from the study of Abnisa et al. [7] but similar to the analysis of softwood mentioned by Kan et al. [11].

3.2 Water Content

Based on Table 1, it can be seen that the bio-oil from palm frond (41.91%) has higher water content than the bio-oil from EFB (11.54%). The water content of bio-oil is influenced by the water content of raw materials used and water formation generated during pyrolysis process [11]. The lower water content in bio-oil from EFB also affected by higher lignin content in the biomass, as mentioned by Fahmi et al. [12].

3.3 pH

The identification of pH is required because low pH can cause corrosion at the time of storage. The measurement results in Table 1 show that pH value in both bio-oil from palm frond and EFB was low/acidic. This indicates that the decomposition of lignin and hemicellulose compounds was occurred at the pyrolysis to form acid compounds, as mentioned by Kanet al. [11].

Table 1. Water content, pH, and Heating Value of Bio-oil

Parameter	Bio-oil from EFB	Bio-oil from Palm Frond
Water content, % mass	11.54	41.91
pH	2.8	3.1
Heating Value (HHV), MJ/kg	26.49	12.19

3.4 GC-MS Analysis

Details compositions of bio-oil from palm frond and EFB can be seen in Table 2 and 3. Based on the table, both bio-oils are dominated by acetic acid, furan, phenol, aldehyde, and ketone compounds. Bio-oil from palm frond shows a high content of acetic acid and phenolic compounds at 35 and 40%, respectively. On the other hand, acetic acid in bio-oil from EFB is less than that from a palm frond. This result is in accordance with the result by Wang et al. [13] that acetic acid and 2-furfural are the major products obtained from hemicellulose and that the presence of lignin in EFB becomes an inhibitory effect on the formation of acetic acid. Table 3 shows that bio-oil from EFB contains phenolic compounds as much as 47%. The high content of the phenolic compound in bio-oil from EFB is affected by the high content of lignin that decomposed into the phenolic compound, as mentioned by Wang et al. [14].

Table 2. Major Components of Bio-oil from Palm Frond

Component	Area, %
Acetic acid	35.79
Chloroform	2.26
2-Propanone, 1-hydroxy-	3.93
2-Propanone	0.90
2-Furancarboxaldehyde	2.68
Phenol	5.78
Phenol, 2,6-bis(1,1-dimethylethyl)-4-methyl-	34.18

Table 3. Major Components of Bio-oil from EFB

Component	Area, %
Acetic acid	4.07
2-Propanone, 1-hydroxy-	1.95
2-Furancarboxaldehyde	1.19
2-Furanmethanol	1.64
Phenol	24.64
2-Furanmethanol, tetrahydro-	1.37
2-Cyclopenten-1-one, 2-hydroxy-3-methyl	1.44
Phenol, 2-methoxy-	3.25
2-Methoxy-4-methylphenol	0.99
Phenol, 2-(1,1-dimethylethyl)-	3.97
Phenol, 4-ethenyl-2-methoxy-	1.51
Phenol, 2,6-dimethoxy-	7.76
Benzaldehyde, 4-hydroxy-3-methoxy	0.95
Benzene, 1,2,3-trimethoxy-	1.50
Benzoic acid, 4-hydroxy-, methyl ester	0.93
Phenol, 2-methoxy-4-(2-propenyl)-	1.84
Benzene, 1,2,3-trimethoxy-5-methyl	1.90
Benzaldehyde, 6-hydroxy-4-methoxy-2,3-dimethyl	1.76
Phenol, 2,6-dimethoxy-4-(2-propenyl)-	3.18
1H-Purin-6-amine, [(2-fluorophenyl)methyl]	1.40

3.5 Calorific Value

Calorific value is an important parameter in fuel characterization. The calorific value of bio-oil is represented by higher heating value (HHV). The result on Table 1 shows that bio-oil from palm frond has a lower heating value than the one of the EFB. This result is affected by the water content in both bio-oil. The higher moisture content of the bio-oils causes the lower heating value since the presence of water will influence the combustion process. As mentioned above, the water content in bio-oil is affected by lignin content in biomass so that higher content of lignin in EFB results lower water content. On the other hand, calorific value also affected by chemical composition of the bio-oil as mentioned by Zhao et al. [15]. Pyrolysis reaction of lignin produced phenolic compound that gives bio-oil with heating value of 20.4 to 24.5 MJ/kg [16]. Therefore, higher content of lignin in biomass produced a higher calorific value of its bio-oil.

4 Conclusions

Characterization of bio-oil from fast pyrolysis of palmfrond and empty fruit bunch has been conducted to determine the water content, pH, calorific value, and characterization of its components using GC-MS. As GC-MS data shows, the bio-oil from both feed stocks was dominated by acetic acid, furans, phenols, aldehydes, and ketones. The HHV was reported 12.19 and 26.49 MJ/kg, while moisture content was 41.91 and 11.54 wt% for bio-oil from palm frond and EFB, respectively. The high content of lignin in EFB effects to the low content of water, high content of phenolic compound, and high calorific value in the bio-oil from EFB.

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References

- [1] Bridgwater A. Fast pyrolysis processes for biomass. *Renew Sustain Energy Rev* 2000;4:1–73. doi:10.1016/S1364-0321(99)00007-6.
- [2] BPS-Statistics Indonesia. Indonesian Oil Palm Statistics 2015. BPS-Statistics Indonesia; 2016.
- [3] Abnisa F, Arami-Niya A, Wan Daud WMA, Sahu JN, Noor IM. Utilization of oil palm tree residues to produce bio-oil and bio-char via pyrolysis. *Energy Convers Manag* 2013;76:1073–82. doi:10.1016/j.enconman.2013.08.038.
- [4] Bridgwater A V. Review of fast pyrolysis of biomass and product upgrading. *Biomass and Bioenergy* 2012;38:68–94. doi:10.1016/j.biombioe.2011.01.048.
- [5] Cardoso CAL, Machado ME, Caramão EB. Characterization of bio-oils obtained from pyrolysis of bocaiuva residues. *Renew Energy* 2016;91:21–31. doi:10.1016/j.renene.2015.11.086.
- [6] Xu Y, Hu X, Li W, Shi Y. Preparation and Characterization of Bio-oil from Biomass. *Prog. Biomass Bioenergy Prod., InTech*; 2011. doi:10.5772/16466.
- [7] Abnisa F, Arami-Niya A, Daud WMAW, Sahu JN. Characterization of Bio-oil and Bio-char from Pyrolysis of Palm Oil Wastes. *BioEnergy Res* 2013;6:830–40. doi:10.1007/s12155-013-9313-8.
- [8] Solikhah MD, Raksodewanto AA, Kismanto A, Karuana F, Heryana Y, Riza, et al. Development of bio-fuel from palm frond via fast pyrolysis. *IOP Conf Ser Earth Environ Sci* 2017;65:12014. doi:10.1088/1755-1315/65/1/012014.
- [9] Sluiter A, Hames B, Ruiz R, Scarlata C, Sluiter J, Templeton D, et al. Determination of Structural Carbohydrates and Lignin in Biomass. vol. 2011. National Renewable Energy Laboratory; 2012.
- [10] Kabir G, Mohd Din AT, Hameed BH. Pyrolysis of oil palm mesocarp fiber and palm frond in a slow-heating fixed-bed reactor: A comparative study. *Bioresour Technol* 2017;241:563–72. doi:10.1016/j.biortech.2017.05.180.
- [11] Kan T, Strezov V, Evans TJ. Lignocellulosic biomass pyrolysis: A review of product properties and effects of pyrolysis parameters. *Renew Sustain Energy Rev* 2016;57:1126–40. doi:10.1016/j.rser.2015.12.185.
- [12] Fahmi R, Bridgwater AV, Donnison I, Yates N, Jones JM. The effect of lignin and inorganic species in biomass on pyrolysis oil yields, quality and stability. *Fuel* 2008;87:1230–40. doi:10.1016/j.fuel.2007.07.026.
- [13] Wang S, Guo X, Wang K, Luo Z. Influence of the interaction of components on the pyrolysis behavior of biomass. *J Anal Appl Pyrolysis* 2011;91:183–9. doi:10.1016/j.jaap.2011.02.006.
- [14] Wang S, Dai G, Yang H, Luo Z. Lignocellulosic biomass pyrolysis mechanism: A state-of-the-art review. *Prog Energy Combust Sci* 2017;62:33–86. doi:10.1016/j.pecs.2017.05.004.
- [15] Zhao C, Jiang E, Chen A. Volatile production from pyrolysis of cellulose, hemicellulose and lignin. *J Energy Inst* 2017;90:902–13. doi:10.1016/j.joei.2016.08.004.
- [16] Bu Q, Lei H, Wang L, Wei Y, Zhu L, Zhang X, et al. Bio-based phenols and fuel production from catalytic microwave pyrolysis of lignin by activated carbons. *Bioresour Technol* 2014;162:142–7. doi:10.1016/j.biortech.2014.03.103.