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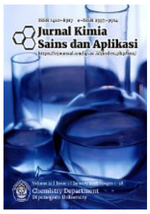

Conversion of Wood Waste to be a Source of Alternative Liquid Fuel Using Low Temperature Pyrolysis Method

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Abstract

Conversion of wood waste into bio-oil with low temperature pyrolysis method has been successfully carried out using tubular transport reactors. Pyrolysis carried out at temperatures of 250-300°C without using N_2 gas. Bio-oil purified by a fractionation distillation method to remove water and light fraction compounds. The materials obtained from different types of wood waste, namely: Randu wood (*Ceiba pentandra*), Sengon wood (*Paraserianthes falcataria*), Coconut wood (*Cocos nucifera*), Bangkirei wood (*Shorea laevis* Ridl), Kruing wood (*Dipterocarpus*) and Meranti wood (*Shorea leprosula*). Bio-oil products are analyzed for their properties and characteristics, namely the nature of density, acidity, high heat value (HHV), and elements contained in bio-oil such as carbon, nitrogen and sulfur content based on SNI procedures, while bio-oil chemical compositions are investigated using Gas Chromatography Mass Spectroscopy (GC-MS). The maximum yield of bio-oil products occurs at 300°C by 40%. Bio-oil purification by fractional distillation method can produce purity of 16-31% wt. The characterization results of the chemical content of bio-oil showed that bio-oil of methyl formate, 2,6-dimetoxy phenol, 1,2,3 trimethoxy benzene, levoglucosan, 2,4-hexadienedioic acid and 1,2- benzenediol.

1. Introduction

Biomass is a renewable resource with great potential as an alternative fuel source other than fossil. Biomass can be processed into hydrocarbons which can replace the role of fossil energy. Indonesia produces around 250 billion tons/year of biomass derived from forest biomass and agricultural waste [1]. One of the steps to convert biomass into renewable energy is pyrolysis [1-5]. Pyrolysis provides added value to wood as a biomass source.

Pyrolysis is the process for organic material decompose by oxygen-free heating methods. The heating rate of pyrolysis affects the composition and enhancement of the quality of hydrocarbons. If the heating rate becomes slow, then the pyrolysis product will tend to form charcoal. Meanwhile, the pyrolysis product is bio-oil, if the heating rate becomes fast [6].

Bio-oil is the result of biomass pyrolysis which contains several compounds, such as aldehydes, phenols, ketones, carboxylic acids, alcohols, ethers, esters, sugars, furans, nitrogen, and other oxygen compounds [4-6]. Bio-oil is more potential as a fuel than charcoal and gas. Bio-oil material can use on boilers, machines, gasoline and chemical raw materials [5, 7, 8].

In rural areas, wood waste (biomass) is only used as fuel in the kitchen or burned in a garden, so that it is economically less useful, it can even cause environmental pollution. Meanwhile, there is no special treatment to deal with the waste. Pyrolysis is one of the stages to convert biomass into renewable energy [7]. Şensöz [2] and Yorgun and Yıldız [8] have carried out slow pyrolysis in fixed-bed reactor methods. The maximum bio-oil yield from pyrolysis is 33.25% at 450°C [2] and 54.0% at 500°C [8].

The purpose of this study was to determine the potential of bio-oil from the six wood wastes. Therefore, liquid products from pyrolysis (bio-oil) studied for their properties and characteristics, such as density, acidity, high heat value (HHV), carbon, nitrogen, and sulfur content.

2. Method

2.1. Preparation of wood waste samples

Wood waste that used for pyrolysis experiments got from forest wood waste Indonesia. The samples used six types of wood waste such as Randu (*Ceiba pentandra*), Sengon wood (*Paraserianthes falcataria*), Coconut wood (*Cocos nucifera*), Bangkirei wood (*Shorea laevis* Ridl), Kruing wood (*Dipterocarpus*) and Meranti wood (*Shorea leprosula*). Wood waste cut into 2 cm^3 sizes, following by repeated washing with distilled water to remove dust and dirt. After that, the samples dried on an oven at 120°C for 4 hours to remove moisture. Samples are stored in containers.

2.2. Experiment setup

Figure 1 shows the homemade pyrolysis reactor that used for low temperature pyrolysis process of wood wastes. The design allows biomass to be in the heated zone when the desired temperature has reached. The pyrolysis device consists of a tubular reactor made from stainless steel. The reactor mounted on a heater and isolated to minimize heat loss. Thermocontrol equipment was outside the reactor to control the temperature of pyrolysis. The reactor is connected to a condenser to increase the efficiency of cooling the pyrolysis steam into bio-oil. This outlet connected to the bottle, where is the bio-oil sample collected. Meanwhile, Bio-char accumulates in the reactor.

Figure 1. The pyrolysis reactor on the experimental.

2.3. Low temperature pyrolysis method

Pyrolysis of wood waste is carried out at a temperature of 300°C for 3 hours. The next step is to purify bio-oil by fractionation distillation at a temperature of 95-100 ° C for 2-3 hours, to remove water and get pure bio-oil.

2.4. Characterization of bio-oil

Bio oil characterized physically and chemically. Physical analysis carried out consisted of the determination of the density used pycnometer bottles, acidity used a pH meter (SNI 06-6989.11-2004), and high heating value (HHV) used a calorimeter bomb (basic C2000 IKA). The analysis of its constituent elements includes carbon and nitrogen content used the Kjeldahl micro method, while analysis of sulfur content used the gravimetric method (SNI 06-6989.20-2004). The analysis of the chemical compounds was carried out with the Shimadzu QP 2010 Gas Chromatography-Mass Spectroscopy (GC-MS) equipment..

3. Result and Discussion

3.1. Pyrolysis results

Woods of Randu, Sengon, and Coconut are examples of softwood types that contain lignin and high hemicellulose. Meanwhile, Bangkirei, Meranti, and Kruing wood are examples of hardwood types. Hardwood has high cellulose content when compared to softwood. So, hardwood can produce more bio-oil than softwood [9]. The bio-oil yield obtained from the pyrolysis process of six wood species ranged from 32.97-40% wt (Table 1). The yield value depends on the type of feed (wood waste) and the condensation system. In this study, water used as a cooler to speed up the condensation process.

The research result shows that Kruing wood converted to 40 %wt of bio-oil. The large bio-oil yield obtained from Kruing wood due to the highest of its celloluse content too. It compares to the other hardwoods such as Bangkirei and Meranti wood. According to Mohan and coworkers [10], wood which higher cellulose content can produce a large amount of bio-oil. Meanwhile, the pyrolysis at lower temperatures tends toward the formation of a large amount of charcoal. A maximum yield of charcoal which is equal to 80 %wt, obtained at 300°C [7]. Meanwhile, the wood type that produces a large amount of bio-char is Coconut wood. The difference of the bio-char content obtained from the pyrolysis process, caused by differences in the decomposition mechanism of each wood waste. Different things happened to the gas product amount. The gas amount produced by the pyrolysis reaction is not affected by the type of wood. The presence of gas products is possibly caused the imperfect cooling process so that the gas formed cannot be fully condensed.

Table 1. Low temperature pyrolysis results of soft wood waste and hardwood.

Parameter (wt%)	Sample					
	Randu*	Sengon*	Coconut*	Bangkirei**	Meranti **	Kruing **
Bio-oil	35.56	36.98	35.76	32.97	38.76	40
Bio-char	37.93	21.07	43.47	35.81	38.18	32.45
Gas	26.51	41.95	20.77	31.22	23.06	27.55

*= Softwood, ** = Hardwood

Figure 2. shows the results of bio-oil purification from six types of wood waste using the fractionation distillation method. The condensate produced is a yield of 16-31%. The largest amount of condensate was found in Meranti wood bio-oil 31% while the smallest amount of condensate was Coconut wood 16%. Based on previous research, the type of wood affects the results of bio-oil [4, 11]. This possible because each wood has different properties and content so that when given the same treatment will produce different products. Okorogwei and coworkers [11] pyrolyzed some tropical biomass in a bench scale screw reactor at 450°C. The highest bio-oil yield of 66wt% (Neem wood) and bio-oil yield at least 53wt% (Tropical Almond wood).

Bio-oil produced from pyrolysis contains up to 85% of water and other components that dispersed in bio-oils such as phenol, carbonyl, acid, furans, and polycyclic aromatic hydrocarbons [2, 3, 8]. The water content can cause corrosion in the engine, low heating value and unstable heating [8], so must be removed. After the fractionation distillation process, the bio-oil is thicker and brownish red. It is indicated that the water has successfully separated.

Bio-oil from Meranti wood has the highest purity, while bio-oil from Coconut wood has the lowest purity. This is estimated because Meranti wood is one type of hardwood which has a lignin content greater than Coconut wood which is softwood. The results of this study are according to previous research [2, 3, 10, 12]. Based on these results, bio-oil from Meranti wood has more potential as fuel than other types of wood. However, further analysis of the physical and chemical properties of each bio-oil is needed. It aim to ensure the potential of the bio-oil as an alternative source of environmentally friendly liquid fuels.

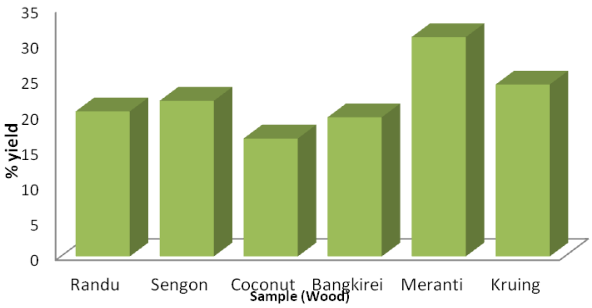

Figure 2. Yield percentage of pure bio-oils.

3.2. Physical and chemical properties of bio-oil

Bio-oil from Mohan and Coworkers [10] has high acidity, so it is poor for further applications. Bio-oil which high acidity properties can cause corrosion and crust. Meanwhile, our bio-oil is relatively more alkaline (Table 2) than previous research. Based on acidity properties, our bio-oil is better than Mohan's bio-oil [10].

Table 2. Physical and chemical properties of the bio-oils

Bio-oil	Density (g/cm^3)	pH	HHV (MJ/kg)	Elemental analysis (%)		
				C	N	S
Randu *	1.13	3.72	15.74	44.90	0.27	7.01
Sengon *	1.24	3.58	18.62	41.37	0.21	6.41
Coconut *	1.06	3.66	14.68	42.15	0.33	8.97
Bangkirei **	1.23	3.75	18.29	47.56	0.22	7.73
Meranti **	1.12	3.59	17.13	48.26	0.33	8.97
Kruing **	1.08	3.62	18.23	41.97	0.14	7.15
Conventional Bio-oil [13]	-	2.5	16-19	54-58	0 – 0.2	-
Petroleum oil [13]	-	-	40	85	0.3	-

*= Softwood, ** = Hardwood

Bio-oil has lower HHV than petroleum oil because bio-oil contains oxygenated compounds, water, and high density [10]. Meanwhile, HHV of our bio-oil is almost the same value as conventional bio-oil from the previous study. The nitrogen and sulfur content in bio-oil is higher than petroleum oil. So bio-oil requires special treatment to be used as fuel. Although bio-oil has poor properties as fuel. However, bio-oil has advantage as a high-value raw material for chemical [13]. Therefore, further analysis is needed to determine the composition of each bio-oil.

3.3. Components of bio-oil

Bio-oil was identified using Gas Chromatography-Mass Spectroscopy (GC-MS) to determine the chemical components. Bio-oil has a very complex mixture that contains hundreds of chemical compounds in different molecular weights. In this study, only the main peak shows a higher percentage of the area. This observation may be related to the partial degradation of biomass components that provide larger molecules, such as sugar derivatives which are consistent with the results shown in Table 3.

Table 3. shows the compounds identified type from chemicals in each of bio-oil. Each compound has been classified into acid (2,4 hexadienedioic acid), phenol (2,6-dimethoxy phenol and 1,2-Benzenediol), ether (1,2,3 trimethoxy benzene), sugar (levoglucosan), ester (methyl formate) respectively. Table 3 shows that levoglucosan is the main product for low-temperature pyrolysis of wood waste. Meanwhile, Meranti wood has the highest levels of levoglucosan. Levoglucosan produced from cellulose decomposition [3]. Meanwhile, hardwood has higher cellulose than softwood. So it produces more yield of levoglucosan than softwood. This research result is according to Mohan *et.al.* [10] and McKendry [12]. The other hand, the content of levoglucosan also influenced by the age factor of the

wood. Based on its physical and chemical properties, bio-oil can directly use as fuel on boilers, gas turbines and diesel engines, and the other hand, bio-oil storage as same as petroleum products.

Table 3. Chemicals compounds from bio-oil of softwood and hardwood

Compound	% Sample					
	Randu*	Sengon*	Coconut*	Bangkirei**	Meranti**	Kruing**
Methyl formate	6.01	3.93	5.34	-	2.72	3.52
2,6-dimetoxy phenol	7.23	7.21	9.53	3.87	4.47	5.88
1,2,3 thrimethoxy benzene	4.50	3.95		2.24	2.57	-
Levoglucosan	29.73	29.22	17.57	32.08	45.76	30.05
2,4 hexadienedioic Acid	6.54	5.35	4.37	4.48	1.92	4.37
1, 2-Benzenediol	-	-	7.67	5.04	6.92	6.37

*= Softwood, ** = Hardwood

4. Conclusion

Wood waste has been conversion into bio-oil successfully that using tubular reactors. Low-temperature pyrolysis produces 40% bio-oil with pyrolysis temperature of 300°C. Bio-oil purification is carried out using the fractionation distillation method to produce bio-oil with a purity of 16-31%. Bio-oil produced has density properties, acidity values of heat value and element content. Meanwhile, the results of GC-MS bio-oil showed the components contained in bio-oil in the form of methyl formate, 2,6-dimethoxy phenol, 1,2,3 trimethoxy benzene, levoglucosan, 2,4-hexadienedioic acid and 1, 2- benzenediol which could be used as an alternative source of ingredients. liquid fuel and chemicals.

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References

[1] Aryadi Suwono, Indonesia's Potential Contribution of Biomass in Sustainable Energy Development, Asian Pacific Confederation of Chemical Engineering congress program and abstracts, Japan, (2004).

[2] Sevgi Şensöz, Slow pyrolysis of wood barks from Pinus brutia Ten. and product compositions, *Bioresource Technology*, 89, 3, (2003) 307-311 https://doi.org/10.1016/S0960-8524(03)00059-2

[3] O. K. Mahadwad, D. D. Wagh and P. L. Kokil, Formation, analysis and characterization of wood pyrolyzed oil, *IOP Conference Series: Materials Science and Engineering*, 206, (2017) 012012 http://doi.org/10.1088/1757-899x/206/1/012012

[4] Q. M. K. Waheed, M. A. Nahil and P. T. Williams, Pyrolysis of waste biomass: investigation of fast pyrolysis and slow pyrolysis process conditions on product yield and gas composition AU - Waheed, Q M K, *Journal of the Energy Institute*, 86, 4, (2013) 233-241 http://doi.org/10.1179/1743967113Z.00000000067

[5] Mohammad Amir Firdaus Mazlan, Yoshimitsu Uemura, Noridah B. Osman and Suzana Yusup, Fast pyrolysis of hardwood residues using a fixed bed drop-type pyrolyzer, *Energy Conversion and Management*, 98, (2015) 208-214 https://doi.org/10.1016/j.enconman.2015.03.102

[6] Y. L. Tan, A. Z. Abdullah and B. H. Hameed, Fast pyrolysis of durian (Durio zibethinus L) shell in a drop-type fixed bed reactor: Pyrolysis behavior and product analyses, *Bioresource Technology*, 243, (2017) 85-92 https://doi.org/10.1016/j.biortech.2017.06.015

[7] George W. Huber, Sara Iborra and Avelino Corma, Synthesis of Transportation Fuels from Biomass: Chemistry, Catalysts, and Engineering, *Chemical Reviews*, 106, 9, (2006) 4044-4098 http://doi.org/10.1021/cr068360d

[8] Sait Yorgun and Derya Yıldız, Slow pyrolysis of paulownia wood: Effects of pyrolysis parameters on product yields and bio-oil characterization, *Journal of Analytical and Applied Pyrolysis*, 114, (2015) 68-78 https://doi.org/10.1016/j.jaap.2015.05.003

[9] Laidy E Hernandez-Mena, Arai AB Pécoraa and Antonio L Beraldob, Slow pyrolysis of bamboo biomass: Analysis of biochar properties, *Chemical Engineering Transactions*, 37, (2014) 115-120 http://doi.org/10.3303/CET1437020

[10] Dinesh Mohan, Charles U. Pittman and Philip H. Steele, Pyrolysis of Wood/Biomass for Bio-oil: A Critical Review, *Energy & Fuels*, 20, 3, (2006) 848-889 10.1021/ef0502397

[11] Edmund C Okoroigwe, Zhenglong Li, Shantanu Kelkar, Christopher Saffron and Samuel Onyegegbu, Bio-oil yield potential of some tropical woody biomass, *Journal of Energy in Southern Africa*, 26, 2, (2015) 33-41

[12] Peter McKendry, Energy production from biomass (part 1): overview of biomass, *Bioresource Technology*, 83, 1, (2002) 37-46 https://doi.org/10.1016/S0960-8524(01)00118-3

[13] P. M. Mortensen, J. D. Grunwaldt, P. A. Jensen, K. G. Knudsen and A. D. Jensen, A review of catalytic upgrading of bio-oil to engine fuels, *Applied Catalysis A: General*, 407, 1, (2011) 1-19 https://doi.org/10.1016/j.apcata.2011.08.046