Bio-oil production from eucalyptus bark and palm empty fruit bunch using pyrolysis process

Susila Arita ^{a,*}, Marwan Asof ^b, Leily N Komariah^a, Syaiful^a,

Camelia Maharani^c, Yosua Aristides^c

Abstract Biomass is considered high potential to support the provision of renewable energy in Indonesia. Biomass has been used for various purposes in all sectors, so that the waste is produced in abundant quantities. Its waste can be used as raw materials for bio-oil production in many primary thermal processes, one of rising methods is pyrolysis. This study aims to test the biomass pyrolysis reactor and determine the effect of the type of raw materials and reaction temperature on the yield of pyrolysis products and the characteristics of the bio-oil produced. The reactor was set at temperatures of 300°C, 350°C, 400°C, 450°C, and 500°C. The raw materials used are wood biomass eucalyptus pellita (EP) and palm empty bunch (PEB). The pyrolysis process produced bio-oil, bio-char and gas. The yield of each component of the products is then compared. The bio-oil composition is detected with GC-MS, and its physical properties are observed in the parameters of density, viscosity and pH. During the test it was known, that pyrolysis took place at a heating rate of 7-14°C/min, where the main reaction of pyrolysis occurred at temperatures of 150°C to 270°C. It showed that reaction temperature have insignificant effect on the yield and the characteristics of bio-oil. The yield of product resulted from EP and PEB pyrolysis were 41.64%, and 46.72% respectively. Meanwhile, bio-oil from the pyrolysis EP performing density of 1.062 g/ml, viscosity of 2.175 cP, and pH 2-3. The characteristics of bio-oil from EFB pyrolysis showed a density of 1.043 g/mL, viscosity of 1.358 cP, and pH 3-4. The composition of bio-oil from EP pyrolysis is dominated by C7-C10 hydrocarbons, while bio-oil produced from EFB composed by C6-C19 hydrocarbons.

Keywords -(biomass eucalyptus pellita

Comment [e1]: Untuk judul, belum ada keterangan tentang indeks a, b dan c yang ada dalam bagian kepengarangan

Comment [e2]: Sebaiknya menceritakan apa yang telah dilakukan dalam riset ini. Dalam abstrak tidak perlu lagi menjelaskan apa itu biomass dsb.

Comment [e3]: Penulisan derajadnya di nilai akhir saja

Comment [e4]: Kalimat ini tidak perlu ada di dalam abstrak, sebaiknya dihapus saja karena kalau disambung dengan kalimat selanjutnya, akan membingungkan, apakah hasil ini hanya untuk bio oil, atau ternasuk juga bio-char dan gas?

Comment [e5]: Kalimat ini juga membingungkan. Apakah hasil ini hanya untuk bio oil, atau ternasuk juga bio-char dan gas.

Comment [e6]: Singkatan untuk gram itu adalah g bukan gr. Perbaiki untuk semua singkatan ini pada manuskrip

1. INTRODUCTION

Biomass is one of the potential alternative energy sources to replace the fossil energy. In line with biomass utilization in industry, the resources can be automatically generated from its waste. The pulp and paper industry produces a wide range of waste characteristics such as liquid waste and solid waste. Solid waste in the form of waste bark from wood that is used as raw material for pulp such as eucalyptus pellita wood species. Eucalyptus bark has a relatively high content of cellulose, therefore it has the potential to be converted to bio-oil. Eucalyptus pellita is one of the fastest growing forest species and has the potential to be developed in Industrial Plantation. Based on the analysis of EB and PFEB, all the feedstocks should be considered suitable for pyrolysis, gasification and combustion processes. It can be thermally cracked to produce bio-oil. The chemical composition of Eucalyptus wood residue and Palm Fruit Empty Bunch can be seen in Table 1 and Table

Tabel 1: Chemical Composition of Typical Eucalyptus Wood Residue

Component	Hemicellulose, wt. %	Cellulose, wt. %	Lignin, wt. %
Eucalyptus leaves	11,28	17,93	9,25
Eucalyptus bark	12,90	27,48	32,09
Eucalyptus sawdust	24,74	33,89	20,77

Source: (Chen et al., 2015)

Comment [e7]: Bagian introduction ini masih sangat lemah. Pada umumnya, beberapa Jurnal mensyaratkan hanya satu sub-bab saja, tidak ada anak sub-bab. Introduction harus mengandung beda isu dari peneliti sebelumnya.

Comment [e9]: Dalam semua Tabel, terdapat penulisan angka yang tidak sesual dengan cara penulisan angka dalam Bahasa inggris

Table 2: The Chemical Composition of PFEB

Elements	Composition, wt.% (Nurrohmi, 2011)	Composition, wt.% (Chang, 2014)	
Lignin	25,83	14.1-30.45	
Holocellulose	56,49	-	
α-cellulose	33,25	23.7-65.0	
Hemicellulose	23,24	20.58-33.52	
Extractive substances	4,19	3.21 - 3.7	

Comment [e10]: Tidak ada dalam referensi (apakah pengarangnya hanya satu, dua, atau lebih dari dua?), termasuk juga untuk Chang.

Comment [e8]: Dalam paragraf yang sepanjang ini, sebaiknya ada sitasi dari paper yang terkait dengan tujuan riset yang telah dilakukan.

Corresponding author;

Tel: +62 711 441543, Fax: +62 711 580147

E-mail: susilaarita@unsri.ac.id

^{*} Chemical Engineering Department Faculty of Engineering Universitas Sriwijaya, Jl. Srijaya Negara Bukit Besar, Palembang 30139, Indonesia. Laboratory of Energy Engineering and Waste Treatment Faculty of Engineering Universitas Sriwijaya, Jl. Raya Prabumulih Km 32, Indralaya 30660, Indonesia.

composition in the raw materials. Cellulose and hemicellulose contents in eucalyptus pellita bark is higher than that in the PFEB. Cellulose chain in eucalyptus pellita bark may longer than in PFEB. Longer cellulose chains require higher cracking energy, so pyrolysis of eucalyptus pellita bark produces less bio-oil than of PFEB.

The main reaction in pyrolysis produces condensable organic vapour formed at temperatures of 150-270°C (EP) and 120-230°C (PFEB), which is characterized by some exit gas and condensed bio-oil. At temperatures above 300°C, long-chain cellulose would certainly decompose into organic vapours. However, the decomposition of cellulose at 300°C has a very low reaction rate, that the amount of organic vapour is low. The organic vapour which supposed to be condensed was undergone with a secondary reaction due to the longer reaction time. The organic vapor then turned to non-condensable gas. It can be stated that temperature set affects the yield of pyrolysis products when gas carrier is used. Higher temperatures will lead to more pyrolysis products. However, when no carrier gas (inert) used, it may cause the product yield become constant due to the organic vapor may be condensed at close interval of temperature.

3.1 Effect of Set Temperature and Raw Material on the Density, Viscosity, and pH of Bio-oil

The characteristics of bio-oil measured include the density, viscosity, and pH. The measured density and viscosity indicate the composition/content of the bio-oil produced from both raw materials.

Figure 4a shows bio-oil density from pyrolysis of eucalyptus pellita bark and PFEB with set temperature variations.

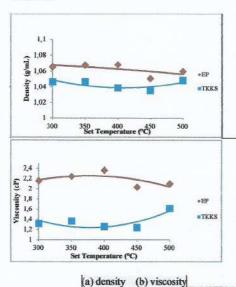


Figure 4: Physical Properties of Bio-oil Produced as a Function of Set Temperature

It can be seen that the density of bio-oil produced from eucalyptus pellita bark is higher than that from PFEB. The mean value of bio-oil density resulting from eucalyptus pellita bark pyrolysis is 1.0624 g/mL, whilst the mean value of bio-oil density from pyrolysis of PFEB is 1.0432 g/mL. Meanwhile, density of bio-oil is influenced by the composition in the bio-oil. If the content of bio-oil has compound with high molecular weight, the density will be large. This is influenced by the composition of the raw material, with cellulose content in the eucalyptus pellita bark higher than in the PFEB, so that cellulose decomposition from eucalyptus pellita bark produces bio-oil with hydrocarbon of higher molecular weight resulting from cellulose cracking of longer chain. This density yield is not much different from the bio-oil produced from pyrolysis of bagasse which ranging at 1.06-1.08 g/mL, as studied by (Zulkania, 2016).

Figure 4b shows the dynamic viscosity values measured from bio-oil resulting from the biomass pyrolysis. Similar to density, the viscosity of bio-oil from pyrolysis of eucalyptus pellita bark is higher than that of PFEB due to some factors. The mean value of bio-oil dynamic viscosity of eucalyptus pellita bark pyrolysis amounted to 2.1749 cP, whereas the mean value of bio-oil dynamic viscosity of PFEB pyrolysis is 1.3582 cP.

As per density, the viscosity is also influenced by bio-oil composition. Component with high molecular weight contributed by the existance of higher molecular weight distribution. It leads to a higher viscosity which indicates an occurance of polymerization reaction (Gomez, 2018). It can be accepted as the cause of the viscosity of bio-oil from pyrolysis of EP bark is higher than palm empty fruit bunches.

The pH of bio-oil measured from both feedstocks has value of 2-3 for bio-oil from eucalyptus pellita bark and 3-4 for bio-oil from PFEB. This acid value of pH is due to the presence of acetic acid and other acids due to pyrolysis processes that breaks down cellulose, lignin and acidic extractive substances [13] (Wibowo, 2015). Low pH of bio-oil is in accordance with the results from Guo [12](2015) with pyrolysis pH of quite acidic, at 2-3. Guo provides recommendations for handling and storage of bio-oil using stain-resistant materials, such as stainless steel, glass, plastic, and fiberglass. High acidity levels cause untreated bio-oils to be used only as direct fuel such as for boiler fuel. The use for other fuels can cause the engine to rust.

The temperature set of biomass pyrolysis for both feedstocks does not affect the measured density, viscosity, and pH values. This is caused by the condensed of bio-oil found in the temperature range of 150°C to 270°C, it means that the bio-oil produced gives a same composition as

Comment [e14]: Cari referensi yang lain dari paper berbahasa Inggris di mana density yield nya hampir sama

Comment [e12]: Untuk semua gambar, gunakan software yang cocok atau lebih baik untuk gambar, Software tersebut diantaranya adalah Origin.

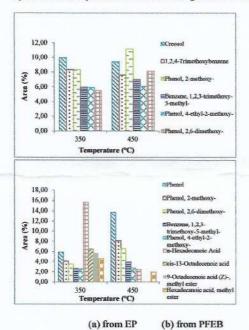
Comment [e15]: Cari referensi yang lain dari paper berbahasa Inggris di mana ada keterangan nilai keasaman dapat membreak down cellulose, lignin dan yang lain.

Comment [e13]: Indeks (a) dan (b) sebaiknya di dalam gambar. Kemudian dalam keterangan gambar (Caption) ditunjukkan bahwa (a) itu apa...dan (b) itu juga apa...

product resulted from reaction occurred at the same temperature. The pyrolysis reaction occurred at low temperatures due to the low heating rate at the reactor. The pH value of bio-oil from pyrolysis of EP is 2-3, while of PFEB is 3-4.

3.2 Effect of Set Temperature and Raw Material on Bio-oil Composition

The content of bio-oil produced from pyrolysis of the biomass was analyzed using Gas Chromatography-Mass Spectrometry. Samples that have highest bio-oil volume difference between the two raw materials were analyzed. The bio-oil analyzed is bio-oil produced from both raw materials at temperatures of 350 °C and 450 °C. The hydrocarbon composition can be seen in Figure 5a and 5b.



(a) nom Er (b) nom 11 EE

Figure 5: Hydrocarbon Composition in Bio-oil Produced from EP and PFEB

As mentioned previously, the bio-oil product is condensed at temperature range of 150-270°C at all set of temperatures. This is shown in Figure 6, where the composition of bio-oil with different temperature set does not have much difference from each other. The composition of both samples is C7 to C10 hydrocarbons. The component of highest carbon content of bio-oil with temperature set of 350°C is creosol ($C_8H_{10}O_2$) with percent area of 9.96%, whilst at temperature set of 450°C is phenol, 2-methoxy-($C_7H_8O_2$) with percent area of 11.13%.

Different things happened in the analysis of bio-oil composition from pyrolysis of PFEB. The components contained in bio-oil from PFEB have a considerable difference composition. It is influenced by the different temperature sets in the reactor. The composition of bio-oil with temperature set of 350°C consists of C6 hydrocarbon compound (phenol) and C16 to C19, whilst the bio-oil composition produced at 450°C temperature set is C6 to C10 hydrocarbon component. The longest carbon chain component of bio-oil with temperature set of 350°C is n-hexadecanoic acid (C₁₆H₃₂O₂) with percent area of 15.68%, whilst at 450°C temperature set is phenol (C₆H₆O) with area percent of 13.73%.

The density and viscosity of bio-oil from PFEB and EB were respectively 1.03559 g/mL and 1.23905 cP. It is not in line with the composition indicated by GCMS analysis. Components in the bio-oil with longer chain hydrocarbons (C16 to C19) should promote a higher density and viscosity. The tars content much depends on the process conditions and the reactor construction, type and moisture of the feedstock, as well as on the refining system of the pyrolysis gases [14] (Lugovoy et al., 2018).

The low viscosity of bio-oil is mainly due to high water content in bio-oil produced. As known, viscosity of the bio-oils is related to fatty acid chain length and number of saturated bonds. In general, the density of bio-oil is higher than that of water confirms that it contains heavy fractions. The lignin content of original feedstock has good influence to the molecular weight and viscosity of bio-oil.

Difference in raw materials used cause different bio-oil composition, with most components of bio-oil from EP are of C7-C8 hydrocarbons, whilst from PFEB is dominated by C6 hydrocarbons with percent area of 13.73%. This is because the cellulose content in the raw feedstock of EP is higher than of PFEB. The result of long chain cellulose cracking will produce bio-oil with longer chains as well.

4. CONCLUSION

The configuration of equipments used in the experiment affects the heat transfer and residence time of the pyrolysis process. The pyrolysis process in this work can be categorized as moderate pyrolysis. Biomass with shorter cellulose chains (fewer cellulose compositions) will result in higher bio-oil yields than biomass with longer cellulose chains, where pyrolysis of PFEB produce higher bio-oil yields than of Eucalyptus pellita bark. The temperature set affects the yield of pyrolysis product when a gas carrier is used during pyrolysis process. The condensation of organic vapour into bio-oil has relatively short temperature range (150-270 °C), so that the temperature set of biomass pyrolysis for both feedstocks does not affect the value of density, viscosity, pH, and measured composition. Raw materials affect the density and viscosity of the product, where bio-oil from pyrolisys of EP has higher density and viscosity than PFEB's. The longest hydrocarbon chain in bio-oil produced from pyrolysis EP is of C7-C10. The major components in bio-oil produced from pyrolysis of PFEB are of C6-C19 hydrocarbons.

References

- Bridgwater, AV., Meier, D., Radlein, D., 1999, An overview of fast pyrolysis of biomass, Org Geochem 30(12), 1479-93.
- [2] Chen, Z., Zhu, Q., Wang, X., Xiao, B., Liu, S., 2015, Pyrolysis behaviors and kinetic studies on Eucalyptus residues using thermogravimetric analysis, Energy Conversion and Management, 105, 251–259
- [3] Goyal, H.B., Seal, D., Saxena, R.C., 2008, Bio-fuels from thermochemical conversion of renewable resources: a review, Renew. Sustain. Energy Rev, 12, 504-517.
- [4] Guedes, RE., Luna, AS., Torres, AR., 2018, Operating parameters for bio-oil production in biomass pyrolysis: A review, Journal of Analytical and Applied Pyrolysis, 129, 134–149
- [5] Balasundrama, V., Ibrahim, N., Kasmania, R. M., Abd. Hamid, M. K., Ishac, R., Hasbullah, H., Rasit Alie, R., 2017, Catalytic Pyrolysis of Coconut Copra and Rice Husk for Possible Maximum Production of Bio-Oil, Chemical Engineering Transactions, 56
- [6] Sukiran, MA., Chow, MC., Abu Bakar, NK., 2009, Bio-oils from pyrolysis of oil palm empty fruit bunches. Am J Appl Sci, 6(5), 869-875.
- [7] Pareek, V., Sharma, A., dan Zhang, D., 2015, Biomass Pyrolysis—A Review of Modelling, Process

- Parameters and Catalytic Studies. Renewable and Sustainable Energy Reviews, Volume 50, 1081-1096
- [8] Zulkania, A., 2016, Pengaruh Temperatur dan Ukuran Partikel Biomassa terhadap Bio-oil Hasil Pirolisis Ampas Tebu/Baggase, Jurnal Teknoin, 22(5), 328-336.
- [9] Folgueras, MB., Fernández, F.J. Ardila, C.R., Alonso, M., Lage, S., 2017, Fast Pyrolysis of Guadua angustifolia-Kunth, Energy Procediia, 01036 (2(021071) 70, 060–065)
- [10] Gaurav, K., Panda, AK., Singh, K., 2010, Optimization of process for the production of bio-oil from eucalyptus wood, Journal of Fuel Chemistry and Technology, Volume 38, 162-167
- [11] Charusiri, W., 2015, Fast of Pyrolysis of Residues from Paper Mill Industry to Bio-oil and Value Chemicals: Optimization Studies, Energy Procedia, 74, 933-941.
- [12] Guo, M., Song, W., and Buhain, J. 2015. Bioenergy and Biofuels: History, Status, and Perspective, Bioenergy and Biofuels, 42, 712-725.
- [13] Wibowo, S., and Hendra, D., 2015, Karakteristik Biooil dari Rumput Gelagah (Saccharum spontaneum Linn.) Menggunakan Proses Pirolisis Cepat, Jurnal Penelitian Hasil Hutan, 33(4), 347-363.
- [14] Lugovoy, YV., Chalova, KV., Sulmana, EM., Kosivtsov, Y Y., 2018, Thermocatalytic Refining of Gaseous Products Produced by Fast Pyrolysis of Waste Plant Biomass, Chemical Engineering Transactions, Vol. 70.

Comment [e16]: Referensi sebaiknya mengacu pada paper yang terbit dalam jurnal internasional yang menggunakan Bahasa Inggris. Beberapa reviewer sering mengecek sitasi sesuai dengan referensi yang tertulis. Oleh karena itu, sebaiknya referensi atau sitasi yang diacu adalah paper yang berbahasa Inggris.

Comment [e20]: Untuk referensi ini dan [13], sebaiknya menggunakan paper yang berbahasa Inggris agar dapat dicek oleh reviewer dan mudah dicari di Google.

Comment [e21]: Perbaiki kesalahan penulisan nama Jurnal

Comment [e22]: Penulisan referensi tidak sama dengan nomor [11]

Comment [e17]: Ada

ketidakkonsistenan dalam penulisan Jurnal yang diacu. Silakan lihat GFA jurnal target, dan tuliskan nama Jurnal secara konsisten. Apakah nama jurnal disingkat, atau ditulis seluruhnya.

Comment [e18]: Penulisan referensi tidak lengkap dan tidak konsisten dengan yang lain

Comment [e19]: Ada banyak ketidakkonsistenan dalam penulisan referensi ini. Silakan dicek ulang