41. Rizki-zen ijfac 2019-41

by Susila Arita

IJFAC

Indonesian Journal of Fundamental and Applied Chemistry

Article http://ijfac.unsri.ac.id

Breakdown of Water-in-Oil Emulsion on Pyrolysis Bio-Oil

Muhammad Rizky Zen[1], Susila Arita[2]*, Leily Nurul Komariah[2]

[1]Chemical Engineering Master Program, Faculty of Engineering, Universitas Sriwijaya
[2]Chemical Engineering Department, Faculty of Engineering, Universitas Sriwijaya

**Corresponding author: susilaarita@ft.unsri.ac.id*

Abstract

The pyrolysis bio-oil which has been studied by many researchers has typically contained a high amount of water, around 20-30%. In this research, the effective bio-oil purification using chemical demulsification method has been studied to reduce the amount of water by breaking down the water-in-oil emulsion on pyrolysis bio-oil. A various dosage of chemical demulsifier (100 ppm, 150 ppm, 200 ppm, and 250 ppm) has been added into the pyrolysis bio-oil and the water separation over time also been observed. The temperature of bio-oil (30, 40, 50, 60, and 70 °C) was also studied as a factor that could have a significant effect on the demulsification process of pyrolysis bio-oil. After the injection of 250 ppm of demulsifier at 30 °C, the water separation reached a maximum of 72% in 60 minutes and could reduce the water content from 25% to 8.5%. At the temperature of 60ºC and 250 ppm of demulsifier, the water separation reached a maximum of 96% in 35 minutes, and successfully reduced the water content from 25% to 1.3%. Finally, it has been concluded that this bio-crude purification using chemical demulsification method could be applied to effectively reduce the amount of water from pyrolysis bio-oil product.

Keywords: Pyrolysis Bio-Oil, Water Content, Emulsion, Demulsifier, Chemical Demulsification

Abstrak (Indonesian)

Pyrolysis bio-oil yang telah dipelajari oleh banyak peneliti biasanya mengandung jumlah air yang tinggi, sekitar 20-30% dari kadar air. Sehingga dalam penelitian ini, pemurnian bio-oil yang efektif menggunakan metode demulsifikasi kimia telah dipelajari untuk mengurangi jumlah air dengan memecah emulsi air-dalam-minyak pada pyrolysis bio-oil. Berbagai dosis demulsifier kimia (100 ppm, 150 ppm, 200 ppm, dan 250 ppm) telah ditambahkan ke dalam pirolisis bio-oil dan pemisahan air dari waktu ke waktu juga telah diamati. Dan kemudian suhu bio-oil (30, 40, 50, 60, dan 70 °C) juga dipelajari sebagai faktor yang dapat memiliki efek signifikan pada proses demulsifikasi pyrolysis bio-oil. Dari hasil yang diperoleh, setelah injeksi 250 ppm demulsifier pada 30 °C, pemisahan air mencapai maksimum 72% dalam 60 menit dan dapat menurunkan kadar air dari 25% menjadi 8,5%. Kemudian pada suhu 60ºC dan 250 ppm demulsifier, pemisahan air mencapai maksimum 96% hanya dalam waktu 35 menit, dan berhasil menurunkan kadar air dari 25% menjadi 1,3%. Akhirnya, telah disimpulkan bahwa pemurnian bio-oil dengan menggunakan metode demulsifikasi kimia dapat diterapkan untuk secara efektif menurunkan kadar air dari pyrolysis bio-oil.

Kata Kunci: Pyrolysis Bio-Oil, Kandungan Air, Emulsi, *Demulsifier*

Article Info

Received 14 January 2019
Received in revised 21 February 2019
Accepted 27 February 2019
Available online 10 June 2019

INTRODUCTION

Nowadays, the efforts to search for alternative energy sources that can reduce dependence on fossil energy, especially fuel oil, attract many researchers in the world to be able to find alternative energy sources. The problems caused by the use of fossil energy sources such as the diminishing oil resources are not comparable with the increasing of public demand for fuel oil. Moreover, environmental issues arising from the use of fossil fuels such as global warming, air pollution, etc. [1] causes the use of fossil energy as if it has a very broad negative impact when compared to its benefits. Concern of these problems, nowadays there are many technologies and innovations produced by researchers to be able to produce oil fuels that are more environmental friendly. As for Biofuel, it is fuel oil produced from the processing of energy sources derived from biomass or biomass waste which is expected to be able to replace the role of fuel oil derived from fossil energy.

One of the technologies currently being developed to convert biomass into an energy source is pyrolysis. Pyrolysis makes it possible to produce three different products namely Bio-Oil/Pyrolysis Oil, Bio-Char, and Syngas which are expected to contribute to the development of alternative fuels because they are efficient and environmentally friendly [2]. Bio-oil produced from the pyrolysis process of biomass itself is known as a dark brown liquid, slightly thick, and smells of smoke. However, Bio-oil is currently only an intermediate product which still requires processing technology to eventually be able to produce quality fuel oil products.

Furthermore, bio-oil products have so far been reviewed from the literature that has a characteristic that is relatively high water content. The water content in bio-oil products ranges from 15 to 30 wt%, depending on the water content found in the raw material and also the pyrolysis operating conditions. This relatively high water content is not only derived from the water content in the biomass feedstock but also comes from the dehydration process that occurs during the pyrolysis process takes place [3]. This high water content and one of the factors is the low heating value of bio-oil as a fuel besides its high oxygen level. High water content not only reduce the heating value of bio-oil but also consume large amounts of latent heat [4]. For example, Fast Pyrolysis Bio-oil (FPBO) products from pine woodchips produced by BTG Biomass Technology Group B.V (Enschede, Netherlands) have a water content of 25.5 wt% [5]. So that when viewed from the energy value or heating value, the bio-oil product has a relatively lower value when compared to other oil fuels produced from petroleum processing. The heating value of bio-oil products is usually lower than 20 MJ/kg, much lower than that found in fuel oil. In addition, another problem that can be caused by the high water content of bio-oil is increasing ignition delay, decreasing combustion rate and adiabatic flame temperatures during the combustion process, and also complicating the injection process [6].

To process bio-oil into a high-quality fuel oil product, the purification process is very much needed after the production process. One of the most concern parameters is the water content. In fuels derived from petroleum, the water content is regulated in such a way and is very limited because it can reduce the quality of the fuel itself. Besides being able to cause a separate phase, the water content in fuel oil can also cause corrosion, problems in the burner or even the formation of emulsions [6]. For bio-oil itself, with high water content, it is very important to regulate because it can affect other characteristics and also the phase stability of bio-oil itself. High water and oxygen content cause non-volatility, high acidity, corrosiveness, and aging during storage. So that with the reduction of water content can increase stability and viscosity, reduce the acidity of bio-oil, but certainly requires expensive and appropriate techniques [7]. In bio-oil, water is an emulsion form and cannot be removed using physical methods such as centrifugation [8]. Moreover, bio-oil also contains low boiling (below 100 °C) and water-soluble compounds. So, conventional drying methods or xylene distillation (ASTM D 95) cannot be used without significant loss of low molecular weight chemical components and the chemical components of the reaction secondary from the bio-oil liquid itself [9,10].

As a comparison, before processing crude oil in a refinery unit and turning it into a quality fuel product that can eventually be used, crude oil produced from production wells undergoes several purification processes. One of them is the separation of water which is produced along with the crude oil, because if this water content is not handled, it can disrupt the subsequent process of processing crude oil such as corrosion. The method commonly used to separate the water content from crude oil is chemical demulsification using an injection of chemicals, namely oil demulsifier. This type of chemical is specially designed to break the emulsion between water and oil so that the water can be separated from crude oil. This method has been widely used by oil producers and has proven effective in reducing the water content of crude oil but it never been tested in pyrolysis bio-oil. The use of oil demulsifier is expected to help accelerate and simplify the separation of water from crude oil so that water itself mixed with crude oil can separate into two layers, namely crude oil in the top layer and water in the bottom layer. Given the high water content in bio-oil, the use of chemical demulsification as bio-oil purification method becomes interesting to be studied and expected to be very helpful in developing bio-oil products produced from biomass pyrolysis.

MATERIALS AND METHODS

Materials

Pyrolysis bio-oil used in this research was produced from Palm Empty Fruit Bunch (PEFB) as biomass feedstock and the chemical demulsifier was kindly donated by Eonchemicals as one of oilfield chemical supplier in Indonesia. Table 1 shows the chemical product identification of chemical demulsifier used in this research.

Table 1. Chemical product identification.

Company Name	PT Eonchemicals Putra
Trade Name	Eonbreak DM 9801 Demulsifier
Chemical Family	Ethoxylates Compound
Composition	-Hydrocarbon Solvent < 60 %wt. -Formaldehyde, polymers with branched 4-nonyl phenol, ethylene oxide, and propylene oxide > 20%wt -Solvent naphtha, petroleum, heavy aromatic > 3 %wt. -1,2,4-Trimethylbenzene > 0.5 %wt. -Naphthalene > 0.2 %wt. -Oxirane > 0.0001 %wt.
Appearance	Yellow to brown liquid
Specific gravity	0.90
Solubility in water	Insoluble

Methods

Pyrolysis Bio-Oil Production

The pyrolysis bio-oil production has been carried out using a pyrolizer unit which has been developed by the Energy and Environmental Engineering Laboratory at Universitas Sriwijaya with an operating temperature of 450 °C and atmospheric pressure. At first, size reduction was carried out and then continued with the drying process. Next, the sieving process is carried out to get the appropriate size distribution. The prepared raw material was then fed into the pyrolysis reactor which has been preheated. Finally, the heating process was continued until the temperature of 450 °C was reached and maintained. Condensed bio-oil liquid during the pyrolysis process was then accommodated using a receiver.

Initial Characterization of Pyrolysis Bio-Oil Product

The bio-oil products were then characterized to determine the initial parameters of bio-oil including bio-oil composition using GC-MS ISQ Series Trace™ 1300.

Emulsion preparation in pyrolysis bio-oil samples

To study the performance of the demulsifier in reducing the water content in the bio-oil pyrolysis product, water-in-oil emulsion was prepared for bio-oil. Based on the procedure carried out by Hajivand et al [11], mixing was carried out between bio-oil and produced water by comparison (3:1 v/v) to obtain 25% (v/v) water content. Then proceed with constant stirring for 2 hours using a magnetic stirrer at medium speed at room temperature (30 °C) to disperse the water droplets into bio-oil until the liquid is homogeneous and a stable emulsion is formed.

Application of chemical demulsification method to the pyrolysis bio-oil

The chemical demulsification was carried out using a bottle-test method based on references from Hajivand et al [11]. Varied amounts of demulsifiers were added to measuring cylinders such as test tubes or centrifuge tubes which contained 10 ml of bio-oil. Moreover, this test was also carried out with temperature variations from bio-oil to determine the optimum condition of bio-oil and the demulsifier used. Then after the addition of demulsifier, followed by a shaking process for 30 seconds to get a good mixing between demulsifier and emulsion on bio-oil. Furthermore, the separation of water is monitored based on the position of the water and bio-oil interfaces and then recorded based on the function of time to ensure the amount of water that is separated every 5 minutes for 60 minutes separation time. A bottle containing bio-oil without treatment is used as a reference (blank). The amount of water separation from bio-oil based on time is included in the graph which is defined as:

$$\left(\% \, {}^{V}\!/_{V}\right) = {}^{V_1}\!/_{V_2} \times 100 \quad (1)$$

Where V_1 is a volume of separated water and V_2 is the initial volume of the water in emulsion [11,12,13].

RESULTS AND DISCUSSION

Initial Characterization of Pyrolysis Bio-Oil Product

From Figure. 1, it appears a dark, slightly thick oily liquid which is characteristic of bio-oil products themselves.

Figure 1. Pyrolysis Bio-Oil Products from Palm Empty Fruit Bunch.

The chemical composition obtained from GC-MS analysis of bio-oil products shown in Table 2:

Table 2. The chemical composition of pyrolysis bio-oil from palm empty fruit bunch.

Compound	Area (%)
Aromatic/Aliphatic	20.44
Phenolic	34.73
Organic Acids	22.85
Esters	18.73
Alcohols	1.56
Ketone	1.00
Others	0.68

Based on the literature review that has been done previously and from the results of the composition analysis carried out on bio-oil products, it is known that organic acids such as carboxylic acid contained in bio-oil products. Those compounds were actually emulsifying agents whose presence could be a cause of the stability of water-in-oil emulsion and finally resulting in high water content. Emulsifying agents could form an interfacial layer that surrounds the droplets of water dispersed into bio-oil and causes stability of the water-in-oil emulsion resulting in high-water content on the bio-oil product.

In addition, the content of phenolic compounds which causes a low pH of bio-oil so that it helps promote the stability of the emulsion. Through this chemical demulsification method, the addition of oil demulsifier was able to break down water-in-oil emulsions so that the water contained in bio-oil can be effectively separated.

Effect of demulsifier dose variation against water separation from pyrolysis bio-oil products

This experiment was conducted with the aim to determine the ability of demulsifiers to break down water-in-oil emulsions present in bio-oil and to see the relationship between demulsifier doses to demulsification efficiency so that the optimum dosage for the demulsification process can be known. When the demulsifier works, the interfacial layer surrounding the droplets of water is thinning and then breaks causing the water droplets to separate from bio-oil and over time they will join each other and form a layer of water which is then under the bio-oil layer. The formation of these two layers is due to the difference in density between water and bio-oil itself. Two different conditions of bio-oil products as shown in Figure 2, namely before and after the demulsification process.

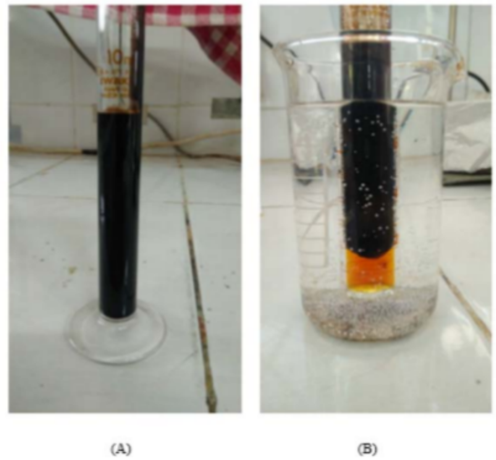

Figure 2. Pyrolysis Bio-Oil: (2a) before and (2b) after demulsification process.

As explained earlier, the success of the demulsifier works to break down the water-in-oil emulsion that is present in bio-oil. The liquid is water that has been separated from bio-oil. The yellow color can be due to the presence of a water-soluble compound that follows the water layer. But in terms of the level of clarity, the water layer looks clear. This indicates that the type of demulsifier used is suitable for application to bio-oil pyrolysis products from palm empty fruit bunches.

The relationship between demulsifier dose variations against the percentage of water separation as shown in Figure 3, shows that there was a different percentage of water separation at each dose of the demulsifier given. This shows that the addition of a certain dose of demulsifier had an effect on the separation of water from bio-oil.

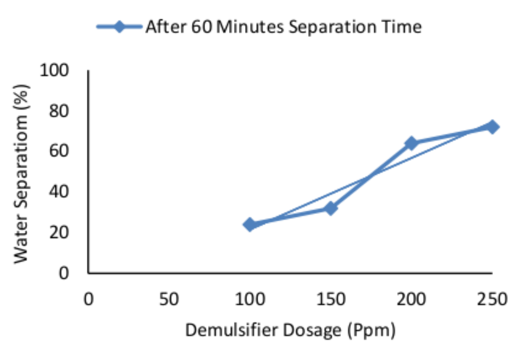

Figure 3. Effect of demulsifier dose variations on the percentage of water separation.

The higher the demulsifier dose, the higher the percentage of water separation. Higher doses of 250 ppm was more effective and able to break down the interfacial layer surrounding the water droplets found in bio-oil so as to accelerate the coalescence of the water droplets. In industrial applications, the higher the dosage used means the faster the separation time will be obtained but the costs for the demulsifier used will be also higher, but vice versa, the lower the dose used, the lower the cost for demulsifier, but it will take longer time for separation and greater equipment capacity.

Effect of bio-oil temperature on demulsifier performance

From the first observations made, it was found that at a dose of 250 ppm the highest separation results were compared with other dosage variations which reached 72% within 60 minutes. The second experiment was conducted to determine the factors that can affect the performance of demulsifiers so that they can be more effective in the process of demulsification, especially in terms of the percentage of water separation and also the time of separation. The second observation was done to see the effect of bio-oil temperature variations in terms of the percentage of water separation, with an injection of 250 ppm of demulsifier.

As shown in Figure 4, it could be seen that with the increase of bio-oil temperature for the demulsification process, there was a significant increase in the percentage of water separation from bio-oil. In addition, it was also seen from the time of separation, the separation process occurs in a shorter time. The maximum water separation was reached after 35 minutes, faster than before which is 60 minutes.

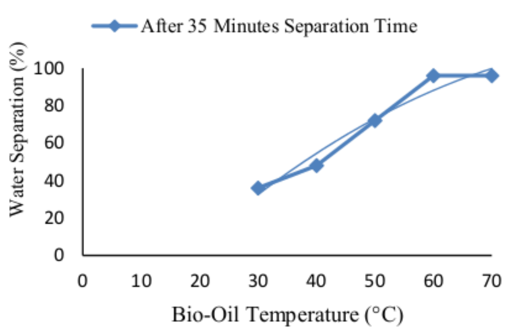

Figure 4. Effect of bio-oil temperature variations on the percentage of water separation.

At 40 °C, the 48% of water separation was achieved after 35 minutes, higher than before at 30 °C which is 36%. The increase also occurred at bio-oil temperatures of 50, 60, and 70 °C which reached 64%, 92%, and 96% of water separation. This shows that control of the bio-oil temperature greatly influences the performance of the demulsifier in the demulsification process. The higher the temperature of bio-oil for the demulsification process, the more the percentage of water separation will be increased. This is because the higher temperatures help accelerate the movement of the water droplets contained in bio-oil, thus increasing the frequency of coalescence these droplets which has a positive impact on the shorter separation time [14].

In addition, it also had a destabilizing effect on the interfacial layer because the interfacial viscosity decreases with increasing temperature. But it should keep in mind that the increase of bio-oil temperature was limited due to low boiling compound that might be lost in higher temperature.

CONCLUSION

The chemical demulsification method can be applied as a purification method in reducing the water content of the bio-oil pyrolysis product and has provided good and effective results. Pyrolysis bio-oil contains a number of carboxylic acids and other chemical components which act as emulsifying agents that cause water-in-oil emulsion stability in bio-oil. In addition, the phenolic compound content also helps promote the stability of water-in-oil emulsions because it causes low pH of bio-oil. Oil demulsifier can work well to break the interfacial layer that surrounds the water droplets so that the water droplets can join each other to form a separate layer of bio-oil and then finally can be separated.

ACKNOWLEDGEMENT

Authors express gratitude to the Energy and Environmental Engineering Laboratory Universitas Sriwijaya for the valuable technical support and the laboratory analysis provided by Mathematical and Science Laboratory of the Universitas Sriwijaya and Coal Testing Laboratory of Politeknik Negeri Sriwijaya.

REFERENCES

[1] B. Dudley, "BP Statictical Review of World Energy," London, 2018. Available: https://www.bp.com/content/dam/bp/en/corporate/pdf/energy-economics/statistical-review/bp-stats-review-2018-full-report.pdf [Jan. 13, 2019]

[2] P. Badger, S. Badger, M. Puettmann, P. Steele, and J. Cooper, “Techno-Economic Analysis: Preliminary Assessment of Pyrolysis Oil Production Costs and Material Energy Balance Associated with a Transportable Fast Pyrolysis System,” *BioResources*, vol. 6, no. 1, pp. 34–47, 2011.

[3] A. V. Bridgwater, “Review of fast pyrolysis of biomass and product upgrading,” *Biomass and Bioenergy*, vol. 38, pp. 68–94, Mar. 2012.

[4] A. V. Bridgwater, “Review of fast pyrolysis of biomass and product upgrading,” *Biomass and Bioenergy*, vol. 38, pp. 68–94, Mar. 2012.

[5] A. de R. Pinho, M. B. B. de Almeida, F. L. Mendes, V. L. Ximenes, and L. C. Casavechia, “Co-processing raw bio-oil and gasoil in an FCC Unit,” *Fuel Process. Technol.*, vol. 131, pp. 159–166, Mar. 2015.

[6] Q. Lu, W.-Z. Li, and X.-F. Zhu, “Overview of fuel properties of biomass fast pyrolysis oils,” *Energy Convers. Manag.*, vol. 50, no. 5, pp. 1376–1383, May 2009.

[7] G. Kabir and B. H. Hameed, “Recent progress on catalytic pyrolysis of lignocellulosic biomass to high-grade bio-oil and bio-chemicals,” *Renew. Sustain. Energy Rev.*, vol. 70, pp. 945–967, Apr. 2017.

[8] A. Oasmaa, E. Leppämäki, P. Koponen, J. Levander, and E. Tapola, “Physical characterisation of biomass-based pyrolysis liquids,” Espoo, 1997. [On-line]. Available: http://www.vtt.fi/inf/pdf/publications/1997/P306.pdf [Jan. 13, 2019]

[9] A. Oasmaa, C. Peacocke, S. Gust, D. Meier, and R. McLellan, “Norms and Standards for Pyrolysis Liquids. End-User Requirements and Specifications,” *Energy Fuels*, vol. 19, no. 5, pp. 2155–2163, 2005.

[10] Q. Lu, X. Yang, and X. Zhu, “Analysis on chemical and physical properties of bio-oil pyrolyzed from rice husk,” *J. Anal. Appl. Pyrolysis*, vol. 82, no. 2, pp. 191–198, Jul. 2008.

[11] P. Hajivand and A. Vaziri, “Optimization of Demulsifier Formulation for Separation of Water from Crude Oil Emulsions,” *Brazilian J. Chem. Eng.*, vol. 32, no. 01, pp. 107–118, 2015.

[12] A. M. Alsabagh, M. E. Hassan, S. E. M. Desouky, N. M. Nasser, E. A. Elsharaky, and M. M. Abdelhamid, “Demulsification of W/O emulsion at petroleum field and reservoir conditions using some demulsifiers based on polyethylene and propylene oxides,” *Egypt. J. Pet.*, vol. 25, no. 4, pp. 585–595, Dec. 2016.

[13] A. Abdurahman, H. Nour, R. M. Yunus, and Z. Jemaat, “Chemical Demulsification of Water-in-Crude Oil Emulsions,” *J. Appl. Sci.*, vol. 7, no. 2, pp. 196–201, Feb. 2007.

[14] A. M. Al-Sabagh, N. M. Nasser, E. A. Khamis, and M. Abd-El-Raouf, “Resolution of water in crude oil emulsion by some novel aromatic amine polyesters,” *Egypt. J. Pet.*, vol. 24, no. 3, pp. 363–374, Sep. 2015.

41. Rizki-zen ijfac 2019-41

ORIGINALITY REPORT

1%	0%	1%	2%
SIMILARITY INDEX	INTERNET SOURCES	PUBLICATIONS	STUDENT PAPERS

MATCH ALL SOURCES (ONLY SELECTED SOURCE PRINTED)

1%

★ Submitted to University of Western Australia

Student Paper

Exclude quotes	On	Exclude matches	< 1%
Exclude bibliography	On		