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Submission date: 03-Jun-2023 04:57PM (UTC+0700)
Submission ID: 2107991888
File name: -_Agustina_2020_IOP_Conf._Ser.__Mater._Sci._Eng._845_012016.pdf (378.81K)
Word count: 4897
Character count: 22928

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To cite this article: T. E. Agustina *et al* 2020 *IOP Conf. Ser.: Mater. Sci. Eng.* **845** 012016

The extraction of oil from cooling pond wastewater as a raw material for biodiesel

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Abstract. The environmental pollution caused by the waste and the strict regulations of waste were currently a major concern for industries, such as the palm oil industry. Constraints experienced today are the difficulty of degradation process of the waste due to the high quantity and the content of contaminants in the waste. One of the efforts that can be prepared to reduce the negative impact is by using the waste as a raw material for biodiesel. Among the potential wastes to become a raw material for making the biodiesel is the wastewater from the cooling pond as a part of the wastewater treatment in palm oil industry. The objectives of this research are to study the process of oil separation from wastewater cooling pond by liquid-liquid extraction method to recover oil and use it as a raw material for making biodiesel. Extraction was carried out at room temperature. The solvent type, wastewater sample to solvent ratio, and extraction time were varied. Based on the results, the highest oil yield of 90% was reached by using n-hexane solvent, the wastewater sample to solvent ratio of 2: 3, and extraction time of 72 hours, while the acid number of 78.49 mg KOH/g oil was obtained. The separated oil can be used as a raw material for making biodiesel through the esterification and transesterification processes. The biodiesel produced has been met the standard of SNI 0471822006 for kinematic viscosity (0.83 cSt), acid number (0.54 mg KOH/g), methyl ester (99.40%), free glycerol (0.01%), and total glycerol (0.13%).

1. Introduction

The palm oil industry has significant benefits, yet it causes negative impacts, both to the quality and quantity of the natural resources and environment. The waste cause pollution and therefore should be treated before they are disposed to the environment. The waste in this regard refers to the by-products of the palm oil industry, usually in the liquid and solid forms. Generally, the solid wastes are directly released without being processed, and this is harmful to the environment. However, the study on utilization of waste from oil palm industry (empty fruit bunch) mixed with waste oil (used engine oil and used cooking oil) to produce solid fuel product have been reported [1]. Whereas the wastewater is often treated in moderation before being released to the water body.

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The wastewater should be treated to meet the required standards of the Ministry of Environment before discharged to the environment. Table 1 shows the quality of wastewater based on the environmental parameter set by the Ministry of Environment of Republic of Indonesia [2].

Table 1. The general quality of wastewater released from palm oil mill

No.	Environmental Parameter	Wastewater	
		Estimation (mg/L)	Average (mg/L)
1.	BOD	8,200-35,000	21,280
2.	COD	15,103-65,100	34,720
3.	TSS	1,330-50,700	31,170
4.	pH	3.3-4.6	4
5.	Total of nitrogen	12-126	41
6.	Oil and fat	190-14,720	3,075

The waste derived from the palm industry might be used after being processed. Importantly, these wastes, especially from the cooling ponds, have the potential to be used as raw materials for biodiesel. The waste comes from a fat pit pond flowed to the cooling pond meant to cool the hot wastewater to a temperature which activates the bacteria. Essentially, the cooling process is vital in preparing the life of bacteria needed in the waste processing [3], apart from precipitating the sludge. Also, the wastewater from the cooling pond flows to the anaerobic pond for the next biological processing [4].

The cooling pond wastewater contains oil and fat of around 6000 mg/L and should be extracted. This is due to the fact that it is classified as the low rank of oil and a high fatty acid content, apart from being cheaper and readily available [5]. Several methods have been used to separate the oil waste, such as the method of biological and chemical adsorption and extraction. Ahmad et al., (2008) conducted a study on the recovery process of oil and carotene from the POME waste by extracting the solvent to retake the oil left in the palm waste. The result showed that the oil derived from the solvent extraction of n-hexane was higher than petroleum ether, which was about 3280 mg/L using n-hexane solvent and 1710 mg/L with petroleum ether [6]. This finding showed that the more solvent used in the extraction process, the more oil would be obtained.

The purpose of this study, therefore, was to obtain the oil from the cooling pond which would be utilized as the primary material of biodiesel. The effect of solvent type, the ratio of raw material (wastewater sample) to the solvent, and the duration of the extraction of the oil from cooling pond wastewater were also studied.

2. Experimental

2.1 Sample Preparation

The wastewater sample of the cooling pond used in this study was obtained from one of PTPN Plantation in South Sumatra. The samples and solvent (n-Hexane, ethyl acetate, and methanol) were measured and put in the beaker glass in the volume ratio of 1:1, 3:2, 2:3, and 2:1 with the mixed volume of sample and solvent of 300 ml. The mixture was stirred with a magnetic stirrer for 1 hour and put in the separating funnel for 24 hours, 48 hours, and 72 hours. The products formed layers which were separated by opening the faucet under the separating funnel for the impurities to be released. And only the mixture of oil and solvent remained, which is separated by a simple distillation method. The oil from distillation was measured and weighed, while the solvent separated was quantified to determine the amount recovered.

2.2 Extraction Process

In this study, the extraction was conducted at the room temperature to prevent the excessive evaporation of the solvent and involved stirring using a magnetic stirrer. The stirring process was done to prevent

the solvation of the waste preventing the solvent from penetrating the material and draw the oil since the waste used enormously. Additionally, the stirring was also carried out to fasten the balance of solvent and sample, broaden the contact wide, and equalize the extraction process.

This study was conducted to determine the effect of a solvent in the extraction process, the volume ratio of the cooling pond wastewater to the solvent, along with the duration of extraction, on the quantity and quality of the oil produced. Importantly, the quantity of the oil was determined by the yield, while the acid number indicated the quality. The solvent used was chosen based on its characteristics, such as cheap and readily available, low boiling point, and inertness. The solvent had low boiling point about 68.73^{o}C (n-hexane), 77^{o}C (ethyl acetate), and 64.7^{o}C (methanol). The low boiling point aimed to ease the evaporation process without using high temperatures. The solvent did not have a low boiling point as this would sharply decrease the solvent during the evaporation process. The solvent should also be inert, which meant it should not react with the cooling pond wastewater. According to Krisyanti and Sukandar (2011), temperature was one of the factors affecting the extraction process. A higher temperature produced more oil and vice versa. However, the quality of the oil produced in this process was declining due to the heating process [7]. The acid number determined the quality of the oil. In general, the oil with a very high acid number was the one hydrolyzed and oxidized. The free fatty acid content was generated in the hydrolysis and oxidation process of the oil [8]. Moreover, the hydrolysis reaction occurred due to the excessive amount of water in the oil and the reaction cause a rancidity of the oil. The oil in the hydrolysis process was then changed into free fatty acid and glycerol.

3. Results and discussion

3.1. The effect of solvent type on the yield of oil and acid number

The variation in solvent was meant to determine the effect of solvent on the quantity and quality of the oil obtained. Additionally, the variation was also meant to establish the best solvent used in the production stage of the biodiesel material. The yield of oil obtained by using different solvent during 24-72 hours of extraction is shown in Figure 1. Evidently, the solvent type used affected the yield of oil, where the highest yield of 71.67%, was achieved using n-hexane solvent in the sample to solvent volume ratio of 2:3, while the lowest yield of 47.00%, was obtained using methanol using the sample to solvent volume ratio of 2:1, during 24 hours of extraction as can be seen in Figure 1 (a). Since methanol is a polar solvent, it was not fit in recovering the oil from the cooling pond wastewater and is often used to extract plants [9]. This is because the polar solvent dissolved in water and was also hard to be recovered and re-used in the subsequent extraction process.

N-hexane produced a high yield of oil than methanol and ethyl acetate since they were non-polar solvents. h-hexane is a non-polar solvent that is most widely used for oil extraction because it has high susceptibility, ability to dissolve high oil, and low boiling point so that it is easy to recover [10]. It dissolved the oil, and it was easy to recover and use in the next extraction process. The use of n-hexane yielded a higher yield of oil compared to ethyl acetate because n-hexane had a smaller dielectric constant compared to ethyl acetate. The smaller the dielectric constant of a solvent led to the more non-polar of a solvent [11]. For this reason, n-hexane had a high rate of dissolved and dissolved the oil more than ethyl acetate.

The yield of oil achieved after 48 and 72 hours of extraction are shown in Figure 1 (b) and (c). The effect of the solvent type on the yield of oil showed the same tendency with a 24 hours of extraction, where the n-hexane solvent had higher yield of oil than methanol and ethyl acetate. Based on Figure 1 (b) and (c), the lowest yield of oil of 56.50% was found using methanol with the sample to solvent volume ratio of 2:1, while the highest yield of oil of 90.00%, was obtained using n-hexane with the sample to solvent volume ratio of 2:3.

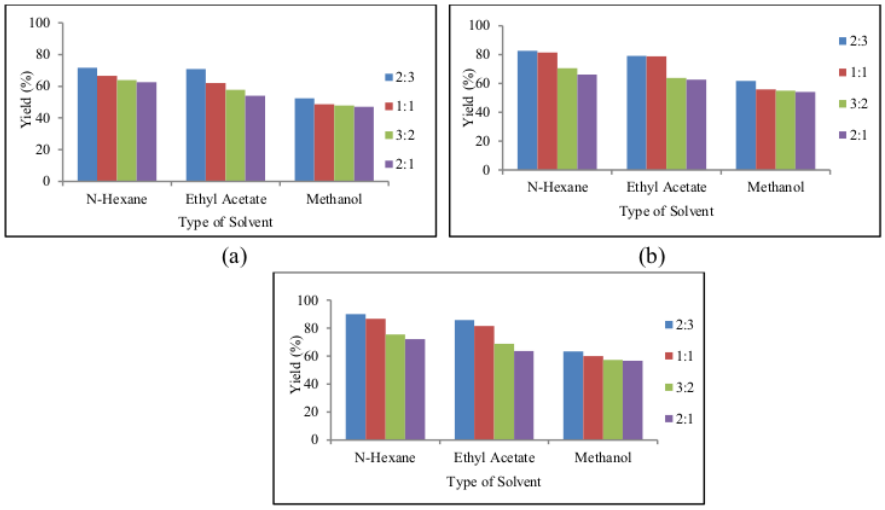

Figure 1. The effect of solvent on yield of oil in extraction process of (a) 24 hours; (b) 48 hours; and (c) 72 hours

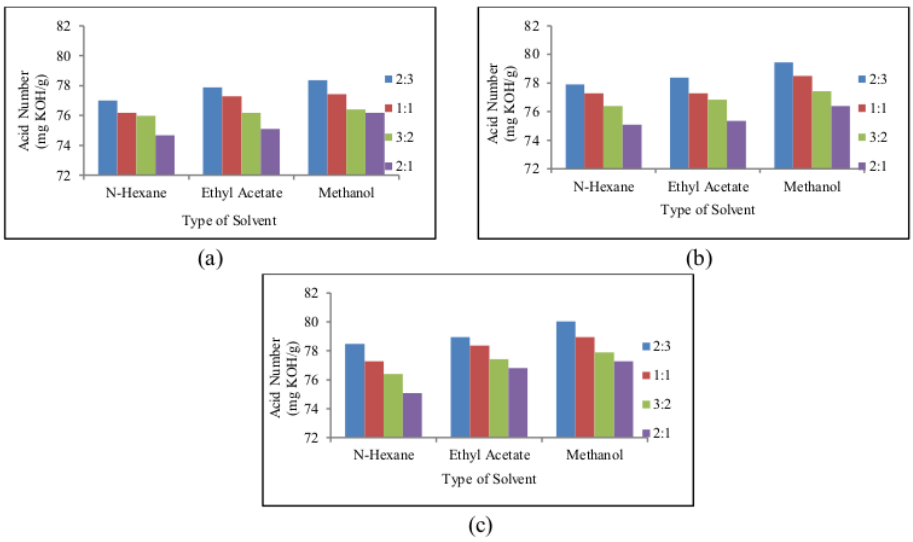

Figure 2. The Effect of solvent on the acid number obtained during (a) 24 hours; (b) 48 hours; and (c) 72 hours of extraction

Depending on the type of solvent, the acid number of the oil recovered during 24 hours of extraction is shown in Figure 2 (a). In the Figure, the highest acid number of 78.36 mg KOH/g, was formed using methanol with the sample to solvent volume ratio of 2:3, while the lowest acid number of 74.69% mg KOH/g was obtained using n-hexane with the sample to solvent volume ratio of 2:1. In this study, the

high acid number during the extraction process was attributed to the fact that methanol was a polar solvent. The water caused triglycerides hydrolyzed into free fatty acid, leading to the increase in the acid number. The acid number of resulted oil from extraction using n-hexane and ethyl acetate lower than using methanol was due to the fact that both n-hexane and ethyl acetate were quite selective in dissolving a non-polar substance, such as triglycerides.

Figure 2 (b) and (c) showed that during extraction for 48 and 72 hours, respectively, the effect of solvent on the acid number showed the same result as the 24 hours of extraction, which meant the more polar the solvent used, the higher the rate of oil acid produced in the extraction process. After 72 hours of extraction, the lowest acid number of 75.10 mg KOH/g was obtained using n-hexane with sample to solvent volume ratio being 2:1. The highest acid number of 80.03 mg KOH/g was found by using methanol with sample to solvent volume ratio being 2:3.

3.2. The effect of wastewater sample to solvent volume ratio on the yield of oil and acid number

The variation in sample to solvent volume ratio was meant to determine the effect of sample to solvent volume ratio on the quantity and quality of the oil produced in the extraction process. This variation was also used to establish the most optimum volume ratio of sample to solvent used during the production stage of the biodiesel. The ratio of waste volume and solvent in the process were 1:1, 2:1, 3:2, and 2:3 with a total volume of 300 ml.

The yield of oil in variation of sample to solvent volume ratio using n-hexane, ethyl acetate, and methanol, respectively, were shown in Figure 3 (a), (b), and (c). The result of the study showed the more volume of solvent used, the more oil obtained. Additionally, Figure 3 (a) showed a higher amount of solvent led to a more significant amount of oil being extracted.

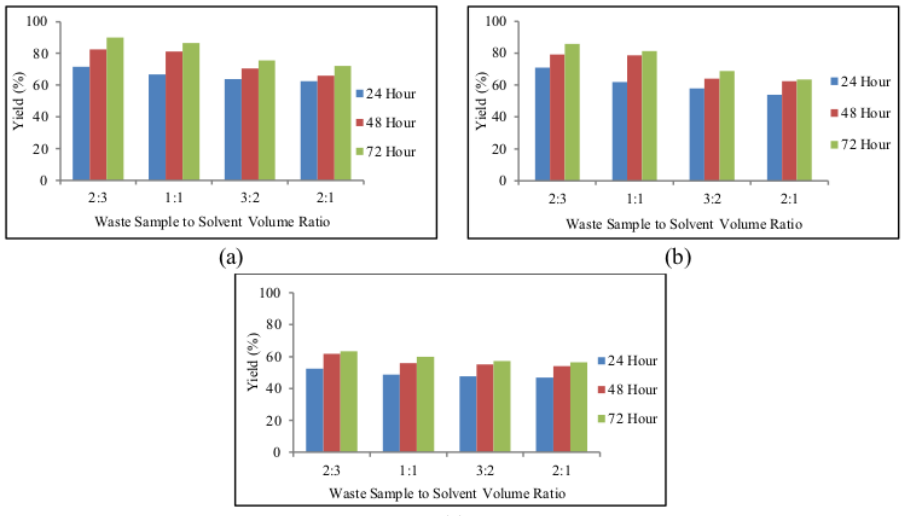

Figure 3. The Effect of sample to solvent volume ratio on the yield of oil produced using (a) n-hexane; (b) ethyl acetate, and (c) methanol solvent

The highest yield of oil of 90%, for the n-hexane solvent was obtained with the sample to solvent volume ratio of 2:3 during 72 hours of extraction as can be seen in Figure 3 (a). This high yield of oil resulted from the adequate amount solvent to penetrate the wastewater, and therefore the oil contained in the waste could be dissolved by the solvent optimally. The lowest yield of oil of 47%, was obtained using methanol solvent within the sample to solvent volume ratio of 2:1 during the 24 hours of extraction, as illustrated in Figure 3 (c). The low yield of oil was attributed to the inadequacy of the

solvent to penetrate the waste and dissolve the oil. According to Ahmad et al., (2008), the yield of oil would increase with the upsurge in a solvent. However, after the solvent increased to a particular level, the increase of yield of oil would decline or even remain constant. If too many solvents are used, the yield of oil will decrease because the solvent not only dissolves the oil but also can dissolve other impurities. The use of too much solvent is also ineffective and inefficient because it can cause more and more other impurities to dissolve. The time used for the separation stage of the solvent and oil will also be longer, so there will be a decomposition of oil and other impurities obtained which can cause changes in the nature and composition of the oil.

The acid number gained using the n-hexane solvent was as shown in Figure 4 (a). A higher of volume of solvent compared to the volume of the waste would lead to a higher acid number. Moreover, the highest acid number of 78.49 mg KOH/g, was in the waste sample to solvent volume ratio of 2:3 during 72 hours of extraction. Contrastingly, the lowest acid number of 74.6 mg KOH/g, was produced in the sample to the solvent volume ratio of 2:1 during 24 hours of extraction. The highest acid number of 80.03 mg KOH/g, was obtained using methanol solvent in the waste to solvent ratio of 2:3 during 72 hours of extraction.

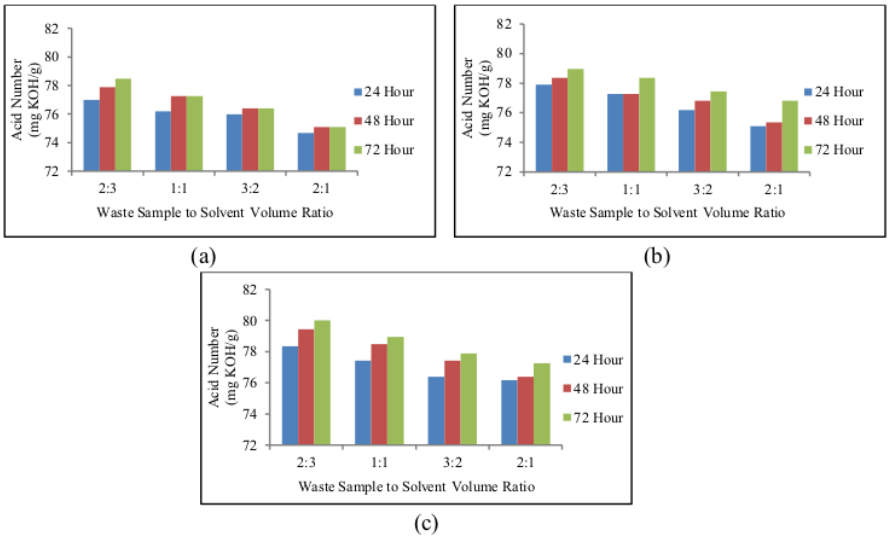

Figure 4. The Effect of Sample to Solvent Volume Ratio on the Acid Number Obtained using (a) n-hexane; (b) ethyl acetate; and (c) methanol Solvent

3.3. The effect of extraction time on the yield of oil and acid number

The variation in extraction time was meant to determine the effect of extraction time between 24-72 hours on the quantity and quality of the oil obtained. Additionally, it was also purposed to establish the most optimum time, which was later used in the biodiesel production stage. The yield of oil produced in the variation of extraction time using the n-hexane solvent was as shown in Figure 5 (a).

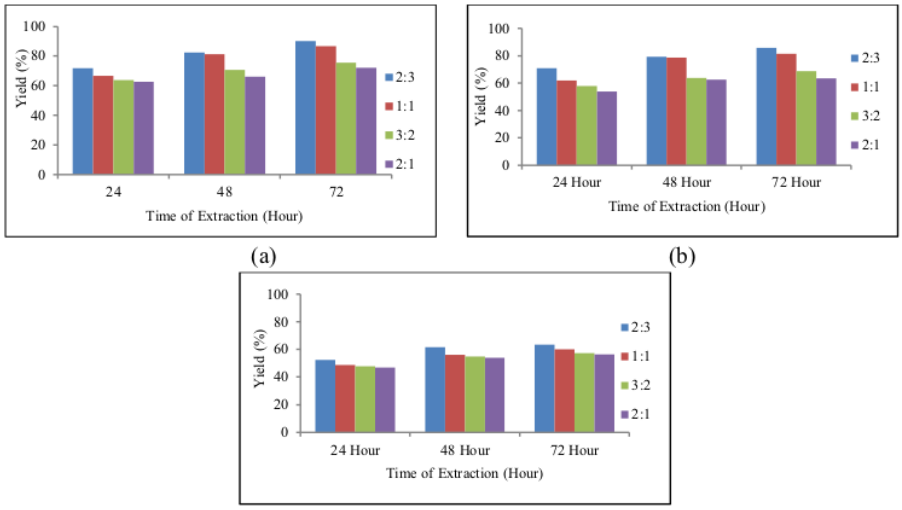

Figure 5. The Effect of Extraction Time on the Yield of Oil using (a) n-hexane; (b) ethyl acetate; and (c) methanol Solvent

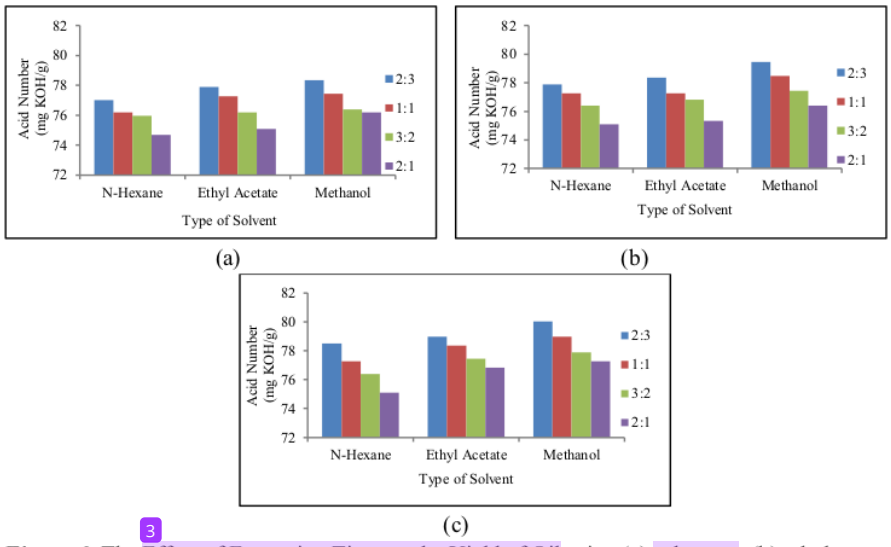

Figure 6. The Effect of Extraction Time on the Yield of Oil using (a) n-hexane; (b) ethyl acetate; and (c) methanol Solvent

The highest yield of oil of 90%, was found during 72 hours of extraction with the sample to solvent volume ratio of 2:1. Contrastingly, the lowest yield of oil of 62.50%, was obtained in the 24 hours of extraction with the sample to solvent volume ratio of 2:1, as can be seen in Figure 5 (a). Similar results were found when using ethyl acetate and methanol, the highest yield of oil was attained after 72 hours of extraction while the lowest yield of oil was reached after 24 hours of extraction, as demonstrated in

Figure 5 (b) and (c). Moreover, the longer the extraction time, the more the yield of oil produced. The long duration of extraction allowed the contact process between solvent and the wastewater sample. The dissolving rate of waste also increased with the increase in the extraction time, leading to solvent saturation. This caused the decrease of yield of oil that marked the optimum time of extraction since the amount of oil component was limited, and the solvent used had the ability to dissolve the waste.

The effect of extraction time on the acid number using n-hexane solvent was as shown in Figure 6 (a). It could be concluded that a longer extraction time would increase the acid number. Also, the lowest acid number of 74.69 mg KOH/g, was obtained during 24 hours of extraction with the sample to solvent volume ratio of 2:1. In contrast, the highest acid number of 78.49 mg KOH/g, was produced during 72 hours of extraction with the sample to solvent volume ratio of 2:3.

The effect of extraction time on the acid number produced using ethyl acetate and methanol were shown in Figure 6 (b) and (c), respectively. The finding was similar to the use of n-hexane solvent, showing the longer the extraction time would increase the acid number. Around of 5% increase in acid number was obtained during 72 hours of extraction

3.4. The study of cooling pond wastewater as the raw material of biodiesel

The oil produced from the extraction of the cooling pond had the potential to be used as the raw material of biodiesel. The oil that will be processed into biodiesel is the oil that produces the highest yield of oil by utilizing n-hexane solvent with the sample to solvent volume ratio of 2:3 during 72 hours of extraction time. The oil obtained from the extraction of cooling pond wastewater still contained various fats, such as free fatty acid and triglycerides. The free fatty acid contained in the oil was one of the determining factors in making the biodiesel. The free fatty acid content in the cooling pond wastewater before esterification was 35.82%.

The oil still contained a higher acid number to be used as the material of biodiesel. It would produce soap through soaping reaction suppose it was used as the primary material during the transesterification process using a base catalyst. To decrease the free fatty acid content, esterification using acid catalyst HCI was needed. Later, the transesterification process was conducted using a base catalyst of NaOH to obtain the biodiesel product with characteristics which met the standard of SNI 04-7182-2006.

The esterification reaction was carried out at the temperature of 65^{o}C using acid catalyst of HCI of about 1.25% (%v) for 1 hour. The acid number gained in this process was 2.09 mg KOH/g with the free fatty acid of 0.96 %. The oil from esterification process was taken to the transesterification process. According to Gafar et al., (2012), the raw material used in the esterification process should have a free fatty acid less of than 2% to prevent the soaping formation [12].

In this study, the transesterification process was carried out at the temperature of 65^{o}C using NaOH catalyst about 1.5 % of the oil volume. The acid number produced was 0.54 mg KOH/g, viscosity of 3.83 cSt, density of 0.84 g/ml, methyl ester 99.40%, free glycerol of 0.01%, and total glycerol of 0.13% and therefore the biodiesel met the standard of SNI 04-7182-2006. Nevertheless, the density did not meet the standard but the result is very close. From the study, it could be concluded that cooling pond wastewater had the potential to be used as raw material for biodiesel production.

4. Conclusion

Based on the results, it was concluded that with the more polar solvent used, the yield of oil kept decreasing while the acid number increased. Moreover, the greater the ratio of cooling pond wastewater sample to the solvent, the yield of oil and acid number obtained will increase. Also, the yield of oil and acid number were increasing with the longer of extraction time. The oil obtained can be used as a raw material for making biodiesel through the esterification and transesterification processes. The biodiesel produced has been met the standard of SNI 0471822006 for density, kinematic viscosity, acid number, saponification number, methyl ester, free glycerol, total glycerol, and oxidation stability.

ACKNOWLEDGEMENT

The authors are very thankful to the Ministry of Research, Technology and Higher Education of the Republic of Indonesia for financial support through the Consortium Research Grant of 2018 and to Waste Treatment Technology Laboratory Chemical Engineering Department of Universitas Sriwijaya.

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