

The Utilization of Palm Oil Mill Effluent For Renewable Energy

Rahma Nuryanti¹, Tuty Emilia Agustina^{2*}, Tuti Indah Sari²

¹Graduate Program Student, Chemical Engineering Magister Program, Universitas Sriwijaya, Indonesia

²Chemical Engineering Department, Faculty of Engineering, Universitas Sriwijaya, Indonesia

*Corresponding Author: tuty_agustina@unsri.ac.id

Abstract

The demand of energy in the world today has increased exponentially, therefore, more efforts have been focused on looking for alternative renewable sources, such as biodiesel, which involves fuel produced from oil of plant, or animal fat. The objective of the research, therefore, was to utilize the palm oil mill effluent (POME) as a raw material in the production of biodiesel, by applying varying solvent, extraction time and the effluent to solvent ratio. Furthermore, the best output of oil rendement of (81.07%), in comparison with the total sample taken, was obtained using n-hexane, at an extraction time of 3 days, and ratio of 1:1. Furthermore, the output possessed a high acid number. Hence, it is considered in the process of esterification and transesterification, required in the production of biodiesel. The HCl catalyst ratio of 1.25% (%v) was used in the esterification process, and the lowest acid number of 2.08 mg-KOH/gr was obtained, followed by the transesterification process, using 1.5% (%w) of NaOH catalyst of the oil weight. Hence, the characteristics of biodiesel produced were in accordance with SNI 04-7182-2006.

Keywords: POME, Biodiesel, Esterification and Transesterification, Extraction, n-Hexane

Abstrak

Kebutuhan energi di dunia maupun di Indonesia kini semakin meningkat, sehingga perlu untuk mencari sumber-sumber energi lain yang dikenal dengan energi terbarukan. Biodiesel merupakan bahan bakar yang diproduksi dengan menggunakan minyak nabati atau lemak hewani. Penelitian ini bertujuan untuk memanfaatkan limbah cair pabrik kelapa sawit (PKS) menjadi biodiesel. Bahan baku minyak diekstrak dari limbah cair PKS menggunakan variasi pelarut, waktu ekstraksi, dan rasio volume limbah terhadap pelarut. Rendemen minyak terbaik sebesar 81,07 % minyak terhadap minyak yang terdapat di dalam sampel limbah cair yang diambil, diperoleh dengan menggunakan pelarut n-heksana, waktu ekstraksi 3 hari, rasio volume limbah terhadap pelarut 1:1. Minyak yang diekstrak dari limbah cair PKS memiliki angka asam yang tinggi sehingga dilakukan proses esterifikasi dan transesterifikasi untuk menghasilkan biodiesel. Proses esterifikasi dilakukan menggunakan rasio katalis HCl 1,25% (%v). Didapatkan hasil terbaik dalam menurunkan angka asam di dalam minyak dari limbah yaitu sebesar 2,08 mg-KOH/gr. Proses dilanjutkan dengan reaksi transesterifikasi menggunakan katalis NaOH sebanyak 1,5 % (%w) dari berat minyak. Karakteristik biodiesel yang dihasilkan telah sesuai dengan SNI 04-7182-2006.

Kata Kunci: Limbah Cair PKS, Biodiesel, Esterifikasi dan Transesterifikasi, Ekstraksi, n-Heksana

INTRODUCTION

There is an upsurge in demand for energy in Indonesia and the world, which is caused by economic development and the increasing of energy consumption. Furthermore, in 2008, 153 million of BOE (barrel of oil equivalent) were reported to have been imported [1]. Hence, there is a need for more research and government

intervention, regarding how to prevent the serious lack of energy, by looking into other renewable sources.

Renewable energy is of natural source, which is produced shortly, and also impossible to be out of stock. In Indonesia, the supply and use of new and renewable energy is intensified by the central and regional governments, in accordance with their authority as

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regulated in the law. Furthermore, biodiesel is a type of fuel manufactured, using the plant oil or animal fat, obtained through transesterification and esterification process, with the addition of alcohol and a catalyst [2]. Conversely, they have almost the same characteristics with conventional diesel fuel, although it requires esterification treatment to lower the levels of acidity, and also fat, utilizing an acid catalyst, e.g., HCl or H₂SO₄ [3].

Generally, the rising costs of raw materials contribute to the price of the fuel produced because edible oils as a natural source is affected by up to 60%-70% [4]. Furthermore, the utilization of plants and animal oil was considered expensive for the benefits obtained because they are majorly used as food. The cost of production process is a major constraint related to the commercialization of biodiesel production. The use of low cost feedstock is an alternative way of improving the economic value of biodiesel production and its commercial production industry scale [5]. This solution is an effort to supply second generation biofuel and is also expected to produce biodiesel, but not conflict with the provision of food [6]. Therefore, it is necessary to select the variety, not used as ingredients, such as castor, spent, all types of palm oil wastewater, e.g. Palm Oil Mill Effluent (POME), and others.

Indonesia has a great potential to utilize biomass energy from the palm oil industry which has 8% growth per year [7]. POME is one of the by-product of oil palm, derived from the condensates of its sterilization process and water was obtained from the clarification procedure, including hydrocyclone (clay bath), and laundering plant. However, before wastewater can be released into an environment, it must first be processed to set quality standards [8]. Furthermore, to overcome the problem of high acid content in the raw material, biodiesel production involves the use of HCl as a catalyst during esterification process and NaOH in subsequent transesterification processes [9]. However, this procedure can further be catalyzed, using alkaline, with high reaction rates, under the low conditions [10]. Supardan et al. [11] performed a similar research, by using a solvent extraction method with ultrasonic aid to recover oil from the wastewater, This research uses solvent extraction method, because it is easy to remove solvent to get oil [12] while this current study involved solvent variation technique, by applying n-hexane, ethyl acetate, and ethanol to determine the best time. Currently, the investigation of new renewable raw materials for biodiesel synthesis is one of the popular research areas in the biodiesel industry [13].

The process of transesterification involved the use of potassium hydroxide (KOH) catalyst to enhance the yield of biodiesel [14]. Another researcher was examined the

output quality, obtained through this process on palm oil wastewater, by varying the type of catalyst used in the reaction. The highest extract of biodiesel (30.84%) was obtained by using TiO₂:MgO (1:3). However, the assessment of quality results met the new regulation standard of SNI-04-7182-2006, seen from the test of viscosity and specific gravity [15].

The purpose of this research, therefore, is to utilize the POME in the manufacture of biodiesel varying the types of a solvent, time of extraction, and the effluent to solvent volume ratio for oil recovery from wastewater. Conversely, it also involves assessing the reduction of the acid level, through the esterification reaction, followed by the transesterification, using NaOH, and the biodiesel produced was further compared with the standard.

MATERIALS AND METHODS

Materials

The POME was collected from the cooling pond of a palm oil plant, n-hexane, methanol, ethyl acetate, chloroform KOH, ethanol, HCl, potassium hydrogen phthalate, and PP indicators were supplied by Merck.

Methods

The effluent sample and ethanol solvent was mixed at a ratio of 5:1, with a total volume of 300 mL, stirred for 1 hour at 50 rpm. Therefore, the solution was inserted into a separate flask for the extraction process, which was carried out at room temperature. After 24 hours, the parts from dirt and water were separated, and the oil was collected from the top layer. Furthermore, the procedure was repeated, using ethyl acetate and n-hexane solvents with a ratio of 3: 2 and 1: 1, respectively. The time of separation between oil and solvent varied from 1-3 days, and the isolate was inserted into the two neck flask and therefore connected to the condenser. However, the temperature was set on the heater, according to the boiling point of the solvent and distillation was conducted to the point where there was no distillate (solvent) dripping from the condenser. The weight of the oil obtained was computed to estimate its yield and 200 mL was measured into a three-neck flask, to which a magnetic stirrer was inserted. Hence, this set up was connected to a reflux condenser, then heated on a hot plate until it reaches temperatures of 60-65°C. Furthermore, in a separate place, 2.5 mL HCl and 200 mL of oil were mixed with methanol, which was stirred evenly. Moreover, after attaining 60-65°C, the HCl and methanol blend was incorporated slowly into the three neck squash, which was quickly and tightly closed with cork, until a batch reaction condition was obtained. Subsequently after an hour, the reaction results were transferred into a separating flask and let to stand for 1 hour and the water, crude methyl ester and glycerol

produced were separated into different containers, which were weighed on the analytical balance. However, the top layer results, including biodiesel and oil, were put in a glass beaker and further used in the transesterification process, which was carried out using 1.5% (%w) of NaOH as a catalyst.

The crude methyl ester was placed in a separating funnel for the washing process, which was performed using hot water then two layers were formed and the washing water at the bottom layer was removed. However, this process was conducted until the clarity was observed and the final solution, in the form of methyl esters was put into a beaker glass, and heated to 110°C till the entire water evaporated while stirring, then cooled to room temperature after \pm 1 hour. Furthermore, the tance was analyzed to determine the characteristics of density, viscosity, methyl ester level, acid number, free glycerol and total glycerol.

Data Analysis

The oil rendement was calculated by equation 1:

$$RM = \frac{MM}{ML} \times 100\% \quad (1)$$

where RM is oil rendement (%), MM is oil weight (g), and ML is effluent weight (g). And the characteristic of biodiesel was analyzed based on SNI 04-7182-2006.

RESULTS AND DISCUSSION

The Effect of Effluent to Solvent Volume Ratio on Oil Rendement

Figure 1, 2, and 3 describe the effect of effluent to solvent volume ratio on oil rendement, with the variation of extraction time.

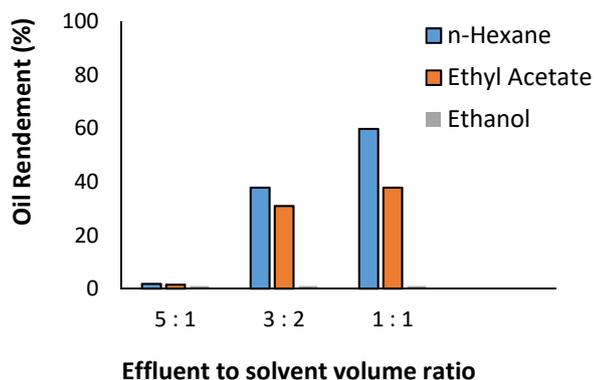


Figure 1. The Effect of effluent to solvent volume ratio on oil rendement by one-day extraction.

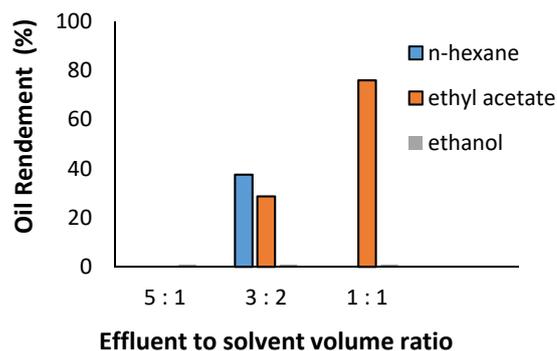


Figure 2. The Effect of effluent to solvent volume ratio on oil rendement within two days of extraction.

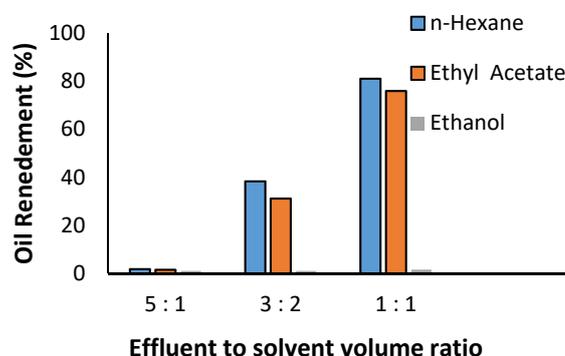


Figure 3. The effect of effluent to solvent volume ratio on oil rendement within three days of extraction

Figure 1 shows that the highest oil rendement was obtained using n-hexane, at a ratio of 1 :1 (150 mL each), although the quantity of solvent is maximum. Furthermore, a similar case was observed on the methyl acetate solvent, the oil rendement increased by the elevation of effluent amount, till the enhanced oil rendement was small relatively or tends to be constant [9]. However, this research indicated the highest yield of 81.07 %, was obtained using n-hexane, at the solvent effluent to volume ratio of 1:1, and extraction time of three days.

The Effect of Solvent Type on the Oil Rendement

The comparison of oil rendement based on the solvent type can be seen in Figure 4. It shows that a polar solvent such as ethanol was not effective in the oil extraction process from POME because it dissolves into the water (in this case, wastewater), which is also hard to recover for reuse. Hence, non-polar and semi-polar solvents like n-hexane and ethyl acetate are more suitable for the procedure, as they are capable of dissolving into oil and further easier to recover for recycle.

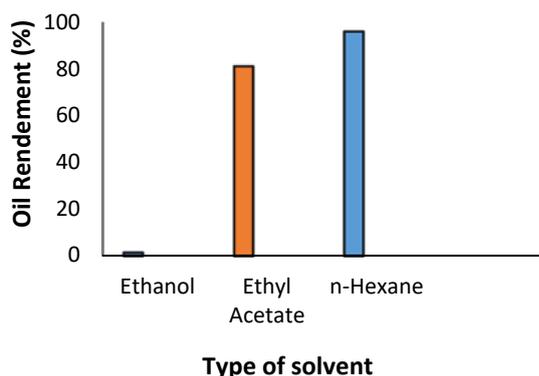


Figure 4. The effect of solvent type on the oil rendement within three days of extraction

The influence of applying n-hexane and ethyl acetate on the oil rendement can be seen in Figure 4, where the previous gave a yield than the latter. N-hexane as a non polar solvent is capable of dissolving much more oil in the POME, compared to a semi-polar solvent, because the isolate also possesses a non-polar characteristic [16].

The Effect of Extraction Time on the Oil Rendement of n-Hexane Solvent

In general, extract obtained increased due to the elevated contact time, which give a chance for more extraction. Furthermore, the result showed that the best yield involved the use of n-hexane within 3 days, after which, there was no significant increase, as demonstrated in Figure 5. However, this effect was similar when using ethyl acetate, and the highest oil rendement occurred after 3 days of extraction, with the effluent to solvent volume ratio of 1:1.

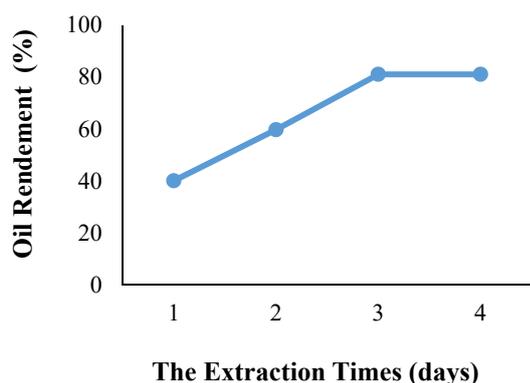


Figure 5. The influence of the extraction time extraction on oil rendement by using effluent to n-hexane volume ratio of 1:1

The Esterification and Transesterification Process

The extraction obtained from POME was then used as a raw material for biodiesel, through esterification process, which was carried out, using 1.25% (%v) of

HCl catalyst, and the acid number of 2.08 mg-KOH/g was obtained. Moreover, during this phase, the catalyst converts the free fatty acids to methyl ester and water [17]. Raw materials with a high FFA content are not easily converted by transesterification reaction because there will be a reaction between the base catalyst and FFA to form soaps [18]. The process was therefore continued by transesterification reaction, using methanol and NaOH catalyst of 1.5% (%w) to produce methyl ester [19].

The rate of transesterification reaction is strongly influenced by the reaction temperature. Generally the reaction is carried out at temperatures close to the boiling point of methanol (60-70°C) at atmospheric pressure. By increasing the temperature up from that temperature, more methanol will be lost or evaporated [20]. So in this research, the reaction temperature was keep constant at 60-65°C.

The Characteristic of Biodiesel Based on SNI 04-7182-2006

In a study conducted by Leela et al. [21], POME has been also used as a raw material for making biodiesel. The samples from four different sources of POME treatment ponds have been extracted using hexane solvents to separate oil from wastewater. The oil obtained is then esterified and transesterified to obtain biodiesel which has fulfilled the characteristics standard of biodiesel [21]. In this study, the biodiesel produced has a density of 0.84 g/mL, the viscosity of 3.83 cSt, methyl ester number of 99.4%, free and total glycerol of 0.11% and 0.13%, respectively. Furthermore, all produced final outcomes met the SNI 04-7182-2006 specifications, except the density, as can be shown in Table 1. though it was very close to the standard. Therefore, it can be concluded that POME can be processed into biodiesel through the esterification and transesterification processes.

Table 1. The characteristic of biodiesel from POME compare to SNI 04-7182-2006

Parameter	Characteristics of Biodiesel	
	POME	Quality Standard
Density (g/mL)	0.84	0.85 – 0.89
Kinematic viscosity (cSt)	3.8	2.3 – 6.0
Acid number (mg-KOH/g)	0.55	Max. 0.8
Methyl ester (wt%)	99.4	Min. 96.5
Free of glycerol (wt%)	0.01	Max. 0.02
Total of glycerol (wt%)	0.13	Max. 0.24

CONCLUSION

Based on the results and the discussion, the following conclusions were made:

1. The extraction process from POME produces the best of oil rendement of 81.07% of the sample taken, using n-hexane as the solvent, an effluent to solvent volume ratio of 1:1, and extraction time of three days.
2. The esterification process followed by the transesterification process of oil from POME is capable of producing biodiesel with characteristic in accordance with SNI 04-07182-2006, except density, though the value obtained was very close to the standard.

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