Palm Sludge Oil as Raw Material of Biodiesel Synthesis through Electrolysis Process Used Ag Electrode

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ABSTRACT
Palm Sludge Oil, PSO, is the low quality of palm oil whereas it changes to liquid waste at the factory. It could be synthesis into biodiesel through the electrolysis method with a Pt electrode. PSO will be descending free fatty acid with esterification. Furthermore, PSO transesterification changes to biodiesel of electron transfer way from the electrolysis process. Its electrolysis is used to Supply DC of 15 volts and correlated with two Ag electrodes. The process is having two variables, electrode distance of 1-2 cm and time process of 2.5 – 4 hours. The highest yield of biodiesel proceeded electrode distances of 1.5 cm and took a transesterification time of 3.5 hours. The best yield resulted in 92.51%.

Keywords: Biodiesel, Electrolysis, PSO, Electrode, Ag.

INTRODUCTION
Biodiesel is one of renewable energy and safe for the environment with diesel as fuel. It, one of the biodegradable fuel, is having low CO\textsubscript{2} emission and low sulfuric gas.\(^1\) This circumstance can be to decrease the importing volume of crude oil as diesel fuel. Increasing of biodiesel is also adding Indonesia needed. Increasing biodiesel consumption needs process technology development and diversification. As a result, the raw material was being cheaper. This raw material is palm oil. Diversification of raw material gets low cost with oil-absorbing from wastewater of crude palm oil factory, it called Palm Sludge Oil (PSO). PSO is the low quality of palm oil with free fatty acid more than 20%,\(^2\) Indonesia was one of the highest Crude Palm Oil (CPO) manufacturers in 2015. PSO prediction resulted from manufacturing that is around +/- 30 million tons/year.\(^3\) PSO is having huge potency as a raw material of biodiesel. Biodiesel from PSO is having a good quality resemblance to be resulted by crude palm oil. Biodiesel is conventionally made by homogeneous alkali catalysts, such as NaOH and KOH\(^4\) and acid catalysts of H\textsubscript{2}SO\textsubscript{4}, HCl,\(^5\) and H\textsubscript{3}PO\textsubscript{4}.\(^6\) Other than that, the raw material is having Free Fatty Acid (FFA) > 0.5% and water content > 0.06%. Homogeneous alkali catalyst was several weaknesses such as saponification and catalyst consumption which has been decreasing efficiency for the whole process. Its process doesn't impact by FFA and water content. The electrolysis method of biodiesel synthesis is having several benefits such as reduce energy consumption that process happened at ambient temperature, reduce water consumption until 90% of the biodiesel part, and it resulted in less waste. The key of this method is to make OH- ion at the cathode part and then it will be reacted with an alcohol to create an alkoxide ion. In the end, alkoxide ion reacted triglycerides and resulted in biodiesel.\(^7,9\)

EXPERIMENTAL
Materials
The raw material is PSO were taken from CPO manufacture, Methanol p.a, Aquadest, KOH solid p.a, Alkali water, Phenolphthalein indicator, KOH solution 0,1 N, pH indicator, NaOH solid p.a, NaOH solution 0.1 N, NaCl solution 0.5 N, H\textsubscript{2}SO\textsubscript{4} solution 98%, Ag plate with dimension 3 x 2 x 0.1 cm.
Procedure

Raw Material Preparation
PSO took from CPO manufacture which is filter and heat at a temperature of 105-110°C as long as 2 hours. Furthermore, it was repetitive to filter. PSO will be analyzed acidic value (AV) and saponification value (SV). It was used to analyze methods by Standard Nasional Indonesia (SNI) No. 01-35555-1998. It is supposed to calculate the average molecule weight (MW) from triglyceride.¹⁰

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MW = 56.1 \times 1000 \times \frac{3}{(SV - AV)}
\]

FFA concentration is also based on SNI No. 01-35555-1998.

Esterification
It took PSO sample as many as 100 grams and added methanol of 94.3 mL (molar ratio oil – methanol of 1:20). On the other hand, it also added sulfate acid catalysts of 0.5 mL. Doing reflux at temperature 60-70°C and takes 90 minutes. After that, it separated between alkyl ester and water. To analyze alkyl ester and FFA concentration is less than 5%. It continued transesterification by the electrolysis process.

Electrolysis PSO
It used power supply Direct Current (DC) at 15 volts and related with two Ag's electrodes of space variable 1 – 2 cm. From the esterification process, PSO took 100 grams with measuring glass 250 mL. The added solution of methanol – oil with a ratio of 6 : 1 and added KOH with a variation of 0.4 – 0.7 % weight/weight. To be pipe alkali water as 2% weight/weight and then aquadest is onto a solution of KOH and methanol. Turned electrolysis process as long as 2.5 – 4 hours. After that process, the solution is separated from a funnel. This solution will be settling for around 2 hours which can be made into two layers, top layer, and bottom layer. The top layer is biodiesel crude. Next, it will be into the purification process.

Purification
To wash biodiesel crude used to hot aquadest with a volume ratio of 1:1. This process proceeded until pH achieves at 6.5 -7. Heating biodiesel which to separate methanol and aquadest at 110°C. This way will be finished until not appear vesicle as a result of the heating process. After that yield of biodiesel gets until ambient temperature and measures volume.

Analyze
Biodiesel quality test used to kinematic viscosity at 40°C (SNI 7182:2015), the density of biodiesel at 40°C (SNI 7182:2015), Acidity value at 40°C (SNI 7182:2015), flash point and calculating yield of biodiesel⁹.

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\text{Biodiesel production yield(%) = } \left( \frac{\text{weight of biodiesel}}{\text{Weight of oil}} \right) \times 100\%
\]

RESULTS AND DISCUSSION
Biodiesel synthesis used PSO but this material should be previously esterification because of the huge FFA content. This esterification does avoid saponification at transesterification with the electrolysis method because it occupied alkali catalysts. Analyzing PSO after esterification in Table-1 is showing FFA content of less than 5%. And then, it will work on transesterification through the electrolysis process.

### Table-1: PSO Test Result after Esterification

| Density (Kg/m³) | Kinematic Viscosity (cSt) | Acid Value (mgKOH/g) | Sapoon Value (mgKOH/g) | FFA (%)  |
|-----------------|---------------------------|----------------------|------------------------|----------|
| 912.6           | 32.4264                   | 7.8293               | 210.9336               | 2.56     |

The Ag electrode to reduce cost on the biodiesel process is having relatively electricity conductivity more than the graphite electrode and platinum electrode. If it compares to the Fe electrode, the Ag electrode has a strong oxidizer and it can be effected hydroxyl ion creating on reduction reaction in electrolysis.⁹
Electrode Distance Effect to Biodiesel Yield

Transesterification of PSO on the electrolysis method gave the amount of electricity amount to triglyceride and methanol solution. Electricity energy flew to the Ag electrode which did oxidizer reaction and reduction reaction on that distance of electrode. A distance of electrode affected to a current of electricity as long as the electrolysis process.\(^{11}\)

![Graph](image)

**Fig.-1: Related of Electrode Distance to Biodiesel Yield**

Electrode distance effect to biodiesel yield shown in graph 1. At electrode distance of 1 – 1.5 cm, it proceeded to increase to biodiesel yield but at a distance of 2 cm was outcome decrease. Both distance electrodes are having an optimum outcome which can be an affected electrode moving. Electrode placement with near position can be the decrease of efficiency because it will proceed short electricity by an electron. That process resulted in a bother of reaction form. Other than that, further electrode distance resulted in electrical resistance more than electrolytes, a decrease of conductivity, and gas vesicle accumulation at the electrode area. This accumulation is the outcome to be inefficient process.\(^{12}\)

Electrolysis Time Effect to Biodiesel Yield

The time of electrolysis is representative of triglyceride transesterification and PSO changes to biodiesel. The increase of electrolysis time will be added electron transfer each electrode. This process proceeded OH\(^-\) an amount that reacted with methanol to create a methoxide ion. This ion will be reacted with triglyceride and then is the outcome of methyl ester or biodiesel. The outcome of time variation of 2.5 – 3.5 hours, it will be adding biodiesel yield such as shown in Fig.-2.

![Graph](image)

**Fig.-2: Graphic of Electrolysis Time to Biodiesel Yield**

Accurately time electrolysis achieves at 4 hours, biodiesel yield will decline. It was the proceeding of equilibrium reaction which this reaction achieved. Furthermore, it is not gaining the result but it will be a
decrease in biodiesel yield. This yield will decline at 4 hours because there is another reaction. That reaction took more than 4 hours, it will be the outcome of glycerol at a product. Another effect, the reaction will be moving to product creation bigger than usual.

Electrode distance and time of electrolysis effect to result of methoxide ion. This circumstance is certainly making electrical resistance to the electrolysis process. If electrical resistance is bigger, it can be less outcome of electron amount which it works electron transfer. Hydroxyl ion (OH\(^{-}\)) will be decline that ion will impact to methanol. This reaction resulted in a methoxide ion. The most factor which will give high concern is electrical resistance on the electrolysis process.

According to the discussion above, transesterification process time and electrode distance related to getting optimum biodiesel yield. In this experiment, the optimum result of electrolysis time at 3.5 hours and electrode distance maximum is 1.5 cm. this condition can get biodiesel yield of 92.51%.

**Biodiesel Quality Standard Analyze**

Biodiesel characterization needed to prove that result was filling the quality standard of fuel. Table-2 shown biodiesel characterization which it took electrolysis time of 3.5 hours and electrode distance is 1.5 hours. All of the research proceed shows all parameters to suit Standard Nasional Indonesia No. 7182 (2015).

Table-2: Biodiesel Characterization of PSO proceeds electrolysis process which time of the process is 2.5 hours and the distance electrode is 1.5 cm.

| Parameter       | SNI 7182 (2015) | Result          |
|-----------------|-----------------|-----------------|
| Density         | 850 kg/m\(^3\)– 890 kg/m\(^3\) | 883.40 kg/m\(^3\) |
| Viscosity       | 2.3 cSt – 6.0 cSt | 4.8869 cSt     |
| Acidic value    | ≤ 0.5 mg-KOH/g  | 0.4405 mg-KOH/g |
| Flash Point     | ≥ Min 100°C     | 170°C          |

**CONCLUSION**

The highest biodiesel yield proceeded at electrode distance is 1.5 cm and the transesterification process is 3.5 hours. This result is 92.51%. Biodiesel characterization resulted was at the density of 883.40 kg/m\(^3\), the kinematic viscosity of 4.8869 cSt, the acidic value of 0.4405 mg KOH/grams and the flashpoint of 170°C. This result filled by SNI No. 7182:2015

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