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To cite this article: S A Rachman *et al* 2018 *J. Phys.: Conf. Ser.* **1095** 012040

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High Conversion and Yield of Biodiesel using Electrolysis Method

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Abstract. Electrolysis method is one of the newest method recently used for biodiesel production. It is hoped that the use of electrode may minimise energy usage in the process for producing biodiesel. In this research, electrolysis process has been tested using raw materials of crude palm oil (CPO) and waste cooking oil (WCO). Methanol is used as solvent with volumetric ratio of 12:1 to raw material, with catalyst of NaOH and KOH. Stirring is employed to quicken the contact between raw materials and the electrodes. The distance between the two electrodes is 15 mm. Electrolysis is started by stirring the mixture at 500 rpm for 2 hours with electrical voltage varied at 14 V, 16 V, 18 V, 20 V, and 24 V. By the use of this method, biodiesel with best quality has been found from raw material of WCO with maximal conversion of 98.6% and highest yield of 90.26%. This result is achieved at condition of 18 V with catalyst of KOH. According to Faraday laws, current density is proportional to the amount product from anode or cathode. Yet, this also depends on the space between the two electrodes. As conclusion, electrolysis method may make transesterification reaction between triglyceride and methanol to occur which gives yield to biodiesel product with high conversion.

1. INTRODUCTION

Biodiesel is an alternative fuel for diesel machine which is produced from transesterification reaction of vegetable oil or animal oil with short chain alcohol such as methanol. The reaction needs catalyst which normally is of strong bases, that will produce a new chemical called biodiesel. Biodiesel synthesis from waste frying oil using electrolysis method firstly was researched by Guan and Kusabe, et al., 2009 [1]. According to them, the merit of this method is the possibility of using raw materials containing quite high total mixture ($\leq 2\%$ wt) which can be utilised directly at the electrolysis reaction.

At this research, besides WCO, CPO (Crude Palm Oil) is also used as raw material which has not yet been used by other researchers in the catalytic electrolysis reaction, even if this process is considered to be quick, easy, and giving high conversion. The homogeneous catalyst of NaOH and KOH has already generally been used in the synthesis of biodiesel using other method, yet it has never been used in the electrolysis method. By comparing biodiesel product from feedstock of Waste Cooking Oil (WCO) and Crude Palm Oil (CPO) using electrolysis method and catalytic reaction, it is hoped that there will be specific condition giving best conversion and yield.

1.1. Waste Cooking Oil (WCO)

Waste cooking oil (WCO) is waste oil originated from various cooking oil such as corn oil, frying oil, samin oil, etc. This oil comes from domestic use which can be reused for cullinaire, yet from its chemical composition, waste oil consists of substance with the characteristic of being carcinogenic, if it repeatedly heated up at high temperature, that it may cause cancer disease in the long time periode.



1.2. Crude Palm Oil (CPO)

Oil from palm fruit consists of crude palm kernel oil and crude palm oil (CPO) which is found from the kernel of palm fruit and the part of mesocarp of fruit meat *Elaeis guineensis*. *Elaeis guineensis* is an eternal plant which produces high amount of oil and has been become one of the most important vegetable oil for biodiesel feedstock due to its characteristic such as higher cetane number, viscosity and density, productivity, low price, high oxidation stability, good fatty acid content and having plasticity characteristic at room temperature [2]. Palm oil is oil which has saturated fatty acid and unsaturated fatty acid contents of high level, such as palmitic fatty acid, oleic, linoleic, etc. Other raw material used in this research is methanol. At the process of biodiesel production, methanol functions as solvent. Methyl alcohol, or commonly known as methanol, is a substance with molecular formula of CH_3OH . Methanol is the simplest alcohol. The catalyst used is natrium hydroxide (NaOH), which may accelerate reaction rate to quicken the reaction. Kalium hydroxide (KOH) can also be used as catalyst for producing biodiesel. Kalium hydroxide is an inorganic substance with the formula of KOH, and commonly called as potash fire.

1.3. Graphite Electrode

Graphite is a form of carbon allotroph which is grey in colour and has the most stable form under certain condition, where its atomic structure affect its phisycal and chemical characteristics. There are three types of graphite used in the industry, they are in the form of crystalline, lumps and amorphous. Graphite may function as electrical conductor.

1.4. Electrolysis Cell

Electrolysis cell is the main equipment used in the electrolysis process, consisting of dc current source and positive and negative electrodes. The substance to be electrolysed is an electrolyte, in the form of solution or liquid (melt) of pure substance. If a liquid or solution electrolyte is charged with electrical dc current via the electrode rod, the ions in the said liquid or solution will move to the electrode with different/opposite charge. Chemical reaction will occur when electric current is flown via electrolyte solution, when electrical energy is converted into chemical energy (redox reaction). There are 3 characteristics in the electrolysis process, which are:

- There is electrolyte solution consisting of free ions.
- These ions may give or take/accept electron so that the electron may flow via the solution.
- There is a source of electricity from outside, such as battery, which supply direct current electricity (dc).

2. RESEARCH METHODOLOGY

This research is carried out in the Laboratorium of New Energy and Renewable Energy in Sriwijaya University, Palembang.

2.1. Equipment Used

A dc Stavolt potentiostat equipped with anode and cathode connectors, two graphite electrodes (P=15 cm), a beaker glass (capacity of 250 mL), and a magnetic stirrer are employed in this research.

Equipment Arrangement

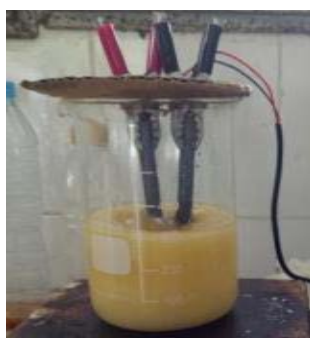


Figure 1. Apparatus for Electrolysis with its arrangement

2.2. Experimental Procedure

Biodiesel Synthesis

- Electrolytic apparatus is set up precisely. The distance between electrodes was set at 15 mm, and it is confirmed that the Stavolt cable connectors to cathode and anode have been placed properly.
- The electrolyte cell is filled with mixtures of oil and methanol with volumetric ratio of 1:12.
- Stavolt is switched on, so does the magnetic stirrer which is adjusted to medium rate. Reaction time is set for 2 hours. The voltage is varied and controlled with dc Stavolt potentiostat at 14 V to 24 V.
- Reaction product is examined visually and the data are recorded and reported for every hour.
- After reaction time of 2 hours, the product mixture is filled into separation column to separate biodiesel from glycerol.
- Product of biodiesel is washed with hot water to eliminate the rest of glycerol and triglyceride.
- To completely free the product from water and methanol, evaporation was carried out at temperature of 120 C for 2 hours.
- The purified biodiesel was analysed using gas chromatography to get its composition and its water content. Picnometer is used to measure water content, whilst a viscometer is employed to measure the density of the product.

3) RESULTS AND DISCUSSION

The result and discussion of this research is presented as follows. Results from the analysis of the two raw materials of waste oil and crude palm oil using gas chromatography show different composition between the two materials. The composition of fatty acid in crude palm oil is depicted in Table 1, whilst the composition of fatty acid in waste cooking oil can be seen in Table 2.

The characteristics of the two raw materials are: the percentage of FFA is 1,33% wt in WCO, and 1,24% wt in CPO, whilst the water content is 0,1318% wt in WCO and 0,1209% wt in CPO. The reaction is carried out for 2 hours at STP condition. In this method, NaCl has also been added, which makes the solution became an electrolyte, so as the transfer of ion between anode and cathode may occur well.

Table 1 The composition of fatty acid in crude palm oil

Fatty acid	Result (%)
Lauric Acid (C12)	0,14
Myristic Acid (C14)	1,64
Palmitic Acid (C16)	32,45
Stearic Acid (C18)	3,97
Oleic Acid (C18:1)	40,45
Linoleic Acid (C18:2)	21,18
Arachidic Acid (C20)	0,17

Table 2 The composition of fatty acid in waste cooking oil

Fatty acid	Result (%)
Lauric Acid (C12)	0,07
Myristic Acid (C14)	1,35
Palmitic Acid (C16)	38,48
Stearic Acid (C18)	16,29
Oleic Acid (C18:1)	27,98
Linoleic Acid (C18:2)	15,72
Arachidic Acid (C20)	0,11

3.1. The Effect of Catalyst Variation, Electrical Voltage, and Raw Material to Conversion and Yield of Biodiesel Product

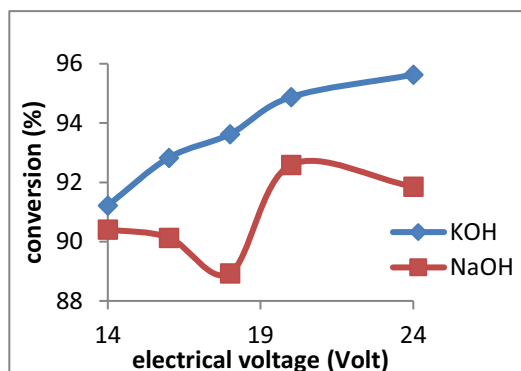


Figure 2a. The Value of Conversion from Raw Material of CPO

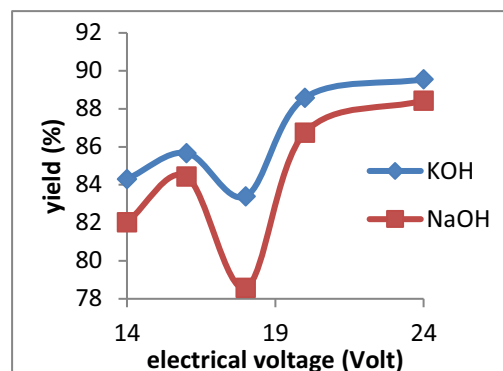


Figure 2b. The value of yield from raw material of CPO

From Figure 2a and 2b, the value of conversion is fluctuative and the yield of biodiesel from raw material of CPO increases with the increase of electrical voltage. The best conversion is 95.6% at voltage of 24 Volt, using catalyst of KOH, whilst the best yield is 89.55% at voltage of 24 Volt, with catalyst of KOH. According to Guan and Kusakabe, 2009 [1] in the electrolysis process, the higher the voltage causes the production of hydroxide ion become more and more. This ion is produced continuously at cathode and can react immediately with methanol and oil at transesterification reaction. But, there is decrease of conversion and yield at several points in Figure 2a and 2b. These were caused by saponification reaction accompanying transesterification process. The saponification reaction may occur due to the availability of hydroxyl group at the structure of the catalyst used, that can decrease the yield of biodiesel product. Even if NaOH and KOH are both have the characteristic of being catalyst, yet NaOH has higher effect in its catalyst performance caused by its higher base characteristic than KOH, so as it is easier to form soap as the side product of the reaction [3].

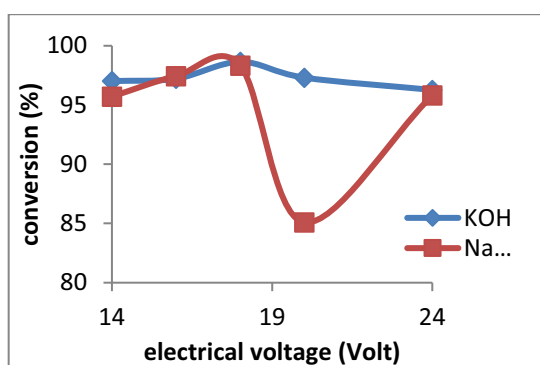


Figure 3a The value of conversion from raw material of WCO

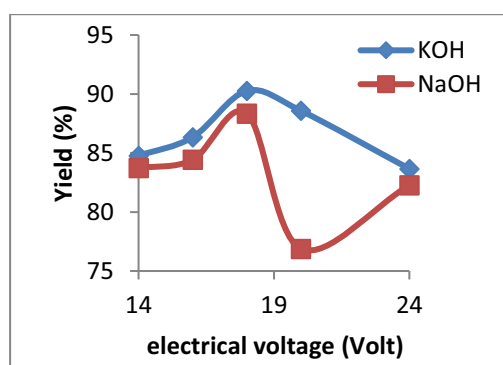


Figure 3b The value of yield from raw material of WCO

From Figure 3a and 3b, the value of conversion is quite fluctuative. The yield from raw material of WCO increases at potential up to 18 V, and decreases at voltage up to 24 V for reaction with KOH as catalyst. Product yield increases at potential up to 18 V, decreases at voltage up to 20 V and increases again at potential up to 24 Volt for catalyst of NaOH. The value of best conversion from raw material of waste cooking oil is 98.6%, and the value of best yield is 90.2% at voltage of 18 V, with catalyst of KOH. The decreases of conversion and yield may occur due to the formation of saponification reaction.

According to research by Guan and Kusakabe 2009 [1] with WCO as raw material, using electrolysis method without catalyst, the process is able to give yield of 97%. Even if this WCO has high water content of 0.5% wt and acid number of 7.7 mg KOH/gr, which was afraid may cause saponification. Other raw material used in their research was corn oil which gives yield of 98.5%. Equipments and other chemicals used in that research had have high quality, such as platinum electrode (Pt), which has very

much helped the reaction to achieve highest yield. Compare with this recent work which uses graphite electrode and gives highest yield of 90.33%.

3.2. The Effect of Variation of Catalyst, Voltage, and Raw Material to the Viscosity of Biodiesel Product

Kinematic viscosity is one of the characteristic should be paid in attention for biodiesel fuel and petrodiesel. Viscosity must be lowered from its initial value in the raw material by conducting transesterification process to the raw material substance[4] (Knothe G and Steidley K.R., 2005). Tesfa B., et al., 2010 [5] said that high viscosity may increase the risk of machinery problem such as carbon deposit at the filter, bad atomisation of fuel at spraying, increase the need of energy for fuel pumping, and wearing of fuel pump and injector.

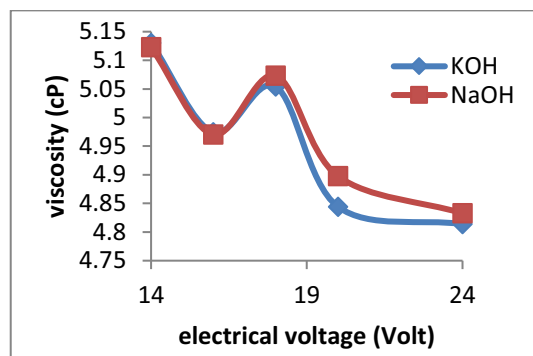


Figure 4 The value of viscosity of biodiesel from CPO

Figure 4 shows that initially the viscosity has decreased with the increase of electrical voltage up to potential of 16 V, but the viscosity increases at voltage up to 18 V before it decreases again at voltage up to 24 V. This is may be due to the increase of tension which makes evaporation process in the solution mixture for reaction becomes more and thus increases the viscosity of the product. The presence of impurities in the product is due to the imperfect separation process of biodiesel from glycerol, or it may also be due to the unclean process during washing stage of the biodiesel. The lowest viscosity is 4.77 cSt for biodiesel product using voltage of 18 V and catalyst of NaOH. For all biodiesel products with raw material of CPO, the viscosity has meet the requirement in SNI standard 7182:2015 no 2 with kinematic viscosity range of 2.3-6.0 cSt.

In Figure 5, the value of viscosity decreases with the increase of electrical voltage up to potential of 18 V. But, when the potential is increased to 24 V, the viscosity of biodiesel tends to increase. The viscosity of the samples of biodiesel product from raw material of WCO are all in the range of the standard kinematic viscosity for biodiesel which is 3 – 6.0 cSt.

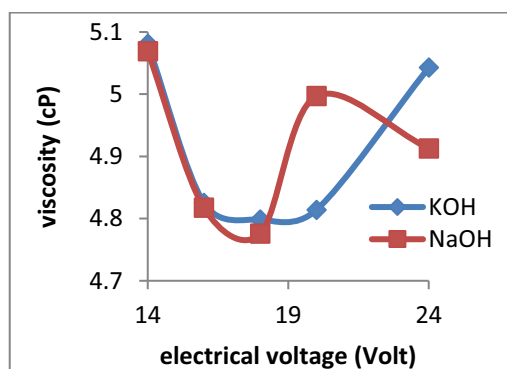


Figure 5 The value of viscosity of biodiesel from WCO

3.3. The Effect of Variation of Catalyst, Voltage and Raw Material to the Density of Biodiesel Product

Density is one of the most important parameters in the physical properties of biodiesel because it can affect the performance of machinery and the characteristics of its emission. According to Figure 6, the value of biodiesel density from CPO in this work tends to be stable with electrical voltage, except at voltage of 18 V with catalyst of KOH, which has lowest value of 0.873 gr/mL.

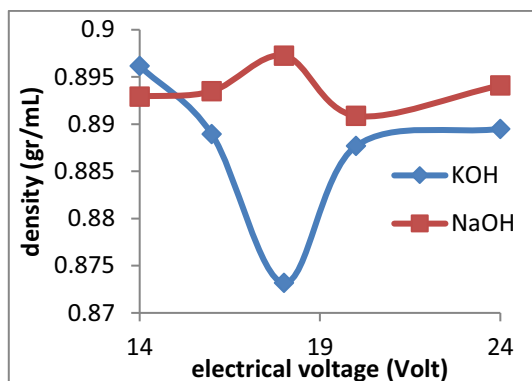


Figure 6 The Value of Biodiesel Density from CPO

According to the work by Nezihe A, et al., 2007 [6], biodiesel produced using catalyst of 1.5% KOH has density of 0.879 gr/cm^3 . With catalyst concentration which are not far different between the two works (at 1% wt KOH for the present work), the density resulted from the two works are almost of the same, even if the previous work does not use electrolysis method. The standard quality for biodiesel density based on SNI (Indonesian National standart) 7182:2015, [7] is $0.85\text{-}0.89 \text{ gr/cm}^3$.

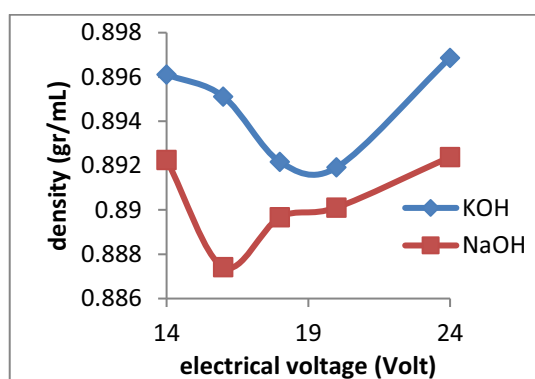


Figure 7 The Value of Biodiesel Density from WCO

Figure 7 shows that the density of biodiesel from raw material of WCO using catalyst of NaOH and potential between 16 V and 20 V, has been the best value, which fulfill the SNI requirement. When the voltage is increased to 24 V, the value of density is proportional to the value of kinematic viscosity, which is over 0.89 gr/cm^3 , and does not meet the requirement of SNI 7182:2015, [7].

3.4. The Effect of Variation of Catalyst, Voltage, and Raw Material to the Acid Number of Biodiesel Product

Figure 8 shows the acid number of biodiesel product from raw material of CPO. All samples of biodiesel product from CPO have low acid number. The value of acid number produced at electrical potential of 16 V to 24 V is about $0.024684 \text{ mg KOH/gr}$. The standard of acid number in SNI 7182:2015 is maximum of 0.5 mg KOH/gr . The lower the acid number, the better the quality of the product. Based on this, all biodiesel products from CPO have fulfill the requirement of acid number in the SNI 7182:2015, [7].

Acid number is connected with the pH of biodiesel produced. The degree of acidity will affect corrosion characteristic of the biodiesel. The small value of this acid number indicates that the biodiesel produced has good quality, with degree of corrosivity which is low. The acid number of biodiesel produced in Figure 9 has the value which is not far different with the acid number of biodiesel in Figure 8. The acid numbers in those two figures are far lower than the acid number of the raw material, WCO, which is at 0.029 mg KOH/gr . That makes the biodiesel product has fulfill SNI 7182:2015, [7].

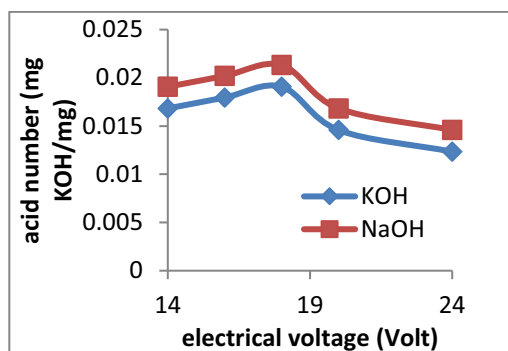


Figure 8 The Value of Acid Number of Biodiesel from CPO

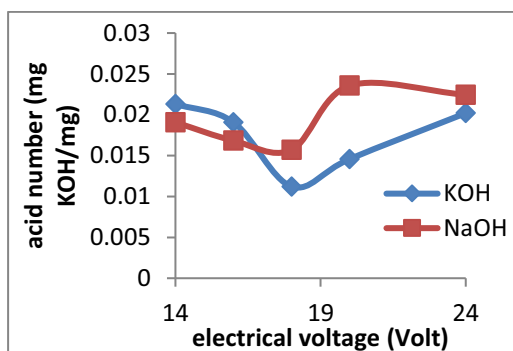


Figure 9 The Value of Acid Number of Biodiesel from WCO

High value of acid number, may cause problem in the combustion system of diesel machine, in the form of precipitate (carbon residue). Other than being precipitate, the value of acid number which is high also may affect the quality of biodiesel product of FFA Biodiesel. The content of FFA (free fatty acid) in the raw material will affect the type of reaction (chosen) which will be carried out. The CPO used has FFA content of 1.24 %.

3.5. The Effect of Variation of Catalyst, Voltage, and Raw Material to the Free Fatty Acid of Biodiesel Product

The performance of catalyst of NaOH and KOH to catalyse transesterification reaction may decrease the percentage of FFA in the biodiesel product. When connected with yield (in Figure 2 and 3) it can be seen that the product from raw material of CPO with catalyst of KOH in Figure 10 has % FFA lower producing yield biodiesel and higher conversion.

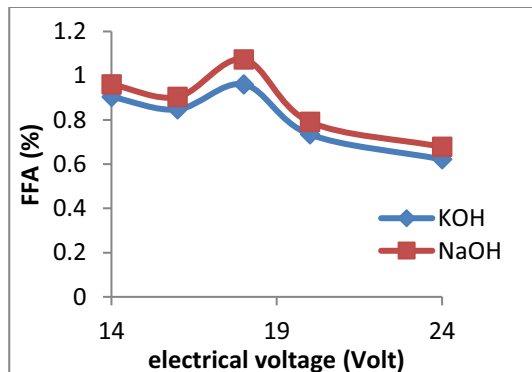


Figure 10 The Percentage of FFA in Biodiesel from CPO

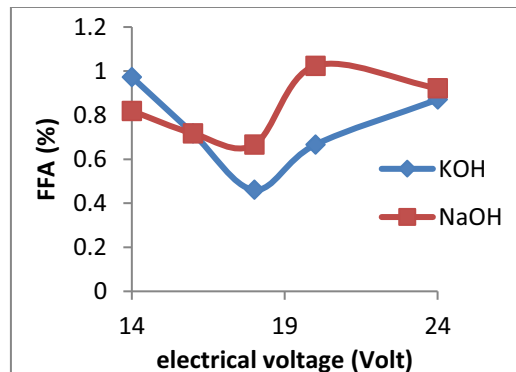


Figure 11 The Percentage of FFA in Biodiesel from WCO

From Figure 11, the percentage of FFA is not far different from the results from Figure 9 where the biodiesel product from KOH has lower percent of FFA. As a whole, the percentage of FFA content in the biodiesel product is lower compared with biodiesel from WCO which has FFA content of 1.3312 %. Based on SNI 7182:2015, part of the biodiesel from WCO has fulfill the requirement of standard quality.

3.6. The Effect of Catalyst Variation, Voltage, and Raw Material to Water Content of Biodiesel Product

Water content in the two raw materials for producing biodiesel in this research are quite high, they are 1.33 % and 0.98 % . After going through electrolysis reaction, some samples of the biodiesel product as in Figure 12, have water content which are quite fluctuatives. With catalyst of KOH and potential of 16 V, the water content in the biodiesel product has still been quite high. This is because the heating process of biodiesel has not yet been completed, or less long time. Heating has been done to decrease water content in the biodiesel product. Other source of water content in the product is from the water used for electrolysis process (at the amount of 2 % wt to the oil), which contributes in the residual water content. According to Guan and Kusakabe 2009 [1], the most active area where transesterification takes place in

the electrolysis is in the cathode where the water is electrolysed. The presence of water content of 2 % affect the movement electrical charge between cathode and anode.

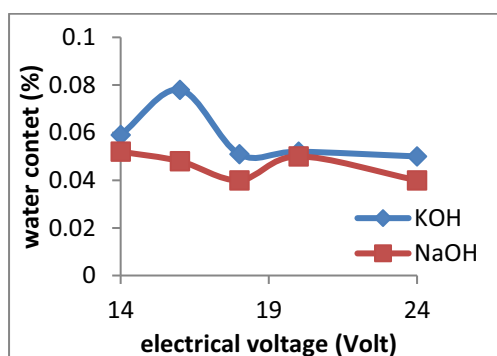


Figure 12 Water Content in Biodiesel from CPO

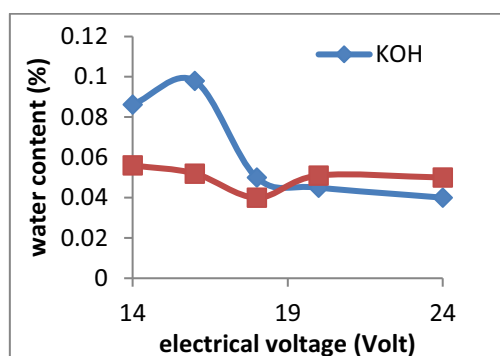


Figure 13 Water Content in Biodiesel from WCO

In Figure 13 the product of biodiesel from raw material of WCO is also not far different from raw material of CPO, only for product at 20 V and 24 V, KOH has lower water content than catalyst NaOH. According to Fregolente et al., 2012 [8] the existence of water in the biodiesel or in the diesel may cause water accumulation and the development of microbes in the water canal of fuel. Moreover, according to I.M Atadshi, et al., 2012 [9], the problem caused by water content in the biodiesel makes difficulty in the reaction for synthesis of biodiesel during alkali catalysation process in the transesterification, the decrease of biodiesel quality, the decrease of combustion heat, corrosion in the combustion system, and acceleration of hydrolysis reaction. This is why, for standard of biodiesel fuel, its water content is controlled by SNI 7182:2015 no 8 with maximum volume of 0.05 % vol. So, some biodiesel products from CPO and WCO in this work have fulfill the said standard.

3.7. The Effect of the Variation of Catalyst, Voltage, and Raw Material to the Total Glycerol in the Biodiesel Product

According to Bondioli P and Bella LD 2005 [10] some amount of glycerol contained in the biodiesel which is used as diesel blending is one of the cause failure in the machinery and combustion system in the automotives. That is why, in SNI 7182:2015 is fixed maximum glycerol total for biodiesel of 0.24 %. For raw material samples, total glycerol measured, that is 10.4% raw material of CPO and 10.8% for raw material of WCO. Based on Figure 14 almost all product has decrease in glycerol which is very drastic, which is below the number of one. From all biodiesel based on Figure 14 there is none fulfill SNI from its total glycerol.

In Figure 15, even if has total glycerol which is decrease far from initial raw material, only one sample which has fulfill SNI 7182:2015, that is the biodiesel using catalyst KOH with potential of 18 V. To the other product which has not fulfill SNI, the cause of this happening is has not been maximum of the transesterification process, so that needs time longer so that the reaction may occur maximal.

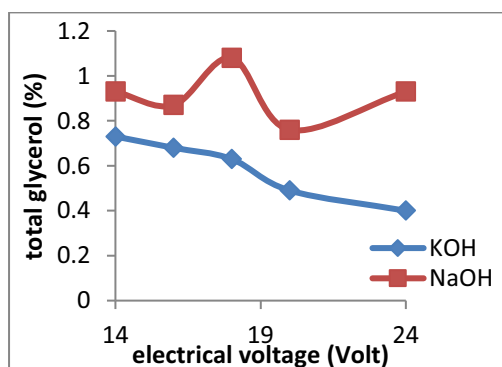


Figure 14 Total Glycerol in Biodiesel from CPO

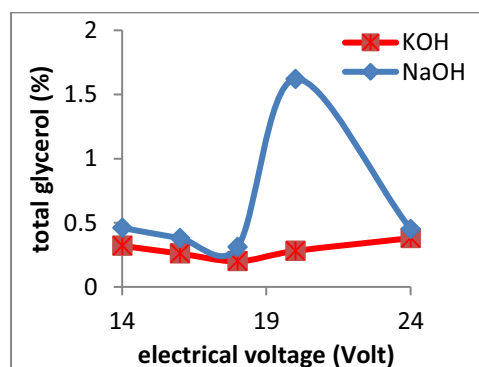


Figure 15 Total Glycerol in Biodiesel from WCO

CONCLUSION

The production of biodiesel with electrolysis method if it uses raw material of waste cooking oil gives highest conversion of 98.6%, with best catalyst of KOH at 18 V, whilst if it uses raw material of crude palm oil gives the conversion of maximal 98.3% with best catalyst of NaOH.

The product of biodiesel made from raw material of waste cooking oil shows better quality than that made from raw material of crude palm oil. This can be seen from the total biodiesel glycerol from raw material of waste cooking oil which is at the amount of 0.2, which has meet the requirement of biodiesel quality standard of SNI 7182:2015 which is at 0.24, whilst biodiesel from raw material of crude plam oil has total glycerol of 0.4.

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