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Trans-esterification of *pangansius hypolatamus* tallow waste with ethanol by electrolysis process and KOH as catalyst

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ABSTRACT

The consumption of fuel energy continues to increase every year, while most of the fuel used today still comes from fossil sources that are harmful to the environment and non-renewable. One promising alternative is ethyl ester derived from catfish (*Pangasius hypothalamus*) tallow waste. In this study, ethyl ester was produced through a transesterification process using a KOH catalyst. The results showed that a raw material to ethanol molar ratio of 1:6 and 1.5% catalyst concentration yielded the best quality ethyl ester, with a yield of 92.4058%. The biodiesel produced met the SNI 7182:2015 standard in terms of density, viscosity, flash point, and calorific value. This research demonstrates that catfish tallow waste can serve as an environmentally friendly raw material for biodiesel production and supports the development of renewable and sustainable energy alternatives.

1. Introduction

The world population is increasing rapidly over time as long as energy consumption and the portion of conventional energy keep decreasing, mostly fossil-derived. Fossil fuel's reduction in future availability is caused by the primary extraction of fossil fuels associated with fuel use, energy utilization, and the production of other products such as mineral fertilizer. The extraction of fossil fuels has a social impact on the future because the reserve of these fuels is reduced for future generations. Several negative environmental impacts caused by fossil fuel usage, such as global climate changes, ozone depletion issues, air pollution, and many more, also concern interrelated energy issues [1]. Depletion of fossil-derived fuel and its environmental problem has raised awareness to look for alternative renewable resources and environmentally friendly fuels. Biodiesel, one of the bioenergy options, appears to be the most suitable alternative to reduce the usage of fossil-derived energy by substituting conventional fossil fuels.

Biodiesel is an alternative fuel produced by renewable sources such as vegetable oil and animal fat-based oil by reaction process with some alcohol compound in the presence of a catalyst. The term biodiesel refers to the ester products produced in the transesterification of lipids that involve the reaction of triacylglycerol and free fatty acids (FFA) with short chains of alcohol compounds such as methanol and ethanol. Alcohol in transesterification acts as a reactant that produces the ethoxide group, which is firmly nucleophile and tends to attack the carbonyl moiety in glyceride molecules to produce alkyl-ester and glycerol [2]. The addition of catalysts can make biodiesel production more efficient by increasing the reaction rate and decreasing the energy of the activation reaction. Biodiesel production utilizes a homogeneous alkaline catalyst, such as NaOH and KOH. Still, for low-quality waste oils containing a high content of Free Fatty Acids (FFA) and water, acid catalysts are needed to avoid undesirable side reactions, such as saponification reaction, which could affect the low conversion of biodiesel and product separation problems [3].

Feedstock availability is one of the most influential factors in the production and commercialization of biodiesel. Oil feedstocks and catalysts influence about 60–85% of the total production cost of biodiesel fuels [4], which makes the biodiesel production cost expensive. However, the deployment of low-cost and sustainable waste biomass materials is necessary to solve this production affordability problem. Animal oils, otherwise referred to as conventional feedstock, have been studied by several researchers as an abundant and cheap feedstock source for its manufacture. Utilization of beef tallow-based oil rendered from discarded wastes of leather tanneries and animal slaughterhouses has been used as the raw material for biodiesel production [5]. Biodiesel production using chicken oil derived from waste chicken skin as the feedstock has been studied [6]. Research about biodiesel production is carried out using tilapia fish oil provided by the Fish Unit [7]. Among several animal oils, fish oil is observed as an abundant and cheap material with the potential for biodiesel production feedstock.

Recently, the catfish (Pangasius hypothalamus) also known as patin fish demand in fish processing industries has been growing remarkably to adequate consumer demand. Patin fish are mainly produced in Indonesia, Vietnam, Thailand, Cambodia, Bangladesh, and China. In Indonesia, the amount of patin fish production reached 373.257,53 tons in 2018, and the world demand for this fish is 752.222 tons, which has increased

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yearly [8]. The whole body of patin fish contains approximately 40% more oil than other freshwater fish and produces 25% waste fraction such as head, tail, belly fat, eyes, and viscera that can be rendered to produce fish oil [9]. The generation of the waste fraction of catfish, especially the waste belly fat presents a potential opportunity for biodiesel production [10]. A previous study investigated biodiesel production by patin fish oil as the feedstock and showed the viscosity of biodiesel meets the standard for biodiesel characteristics by 2 hours reaction time. The physiochemical properties of catfish oil-based biodiesel produced met the biodiesel standard of ASTM D6751 by reacting catfish oil with methanol in a 1:12 molar ratio [11].

Biodiesel production generally goes through a transesterification process with a catalyst with the addition of heat at a specific temperature. This method has some weaknesses because it needs relatively high energy due to high-temperature operation and saponification usually significantly interferes with the transesterification process [12]. Diversification of biodiesel production needs to be done to produce a more efficient process. The manufacture of biodiesel using the electrolysis method is one of the innovations in the biodiesel manufacturing process that can be used on feedstock that has a water content of more than 2% and high free fatty acids such as those used in cooking oil and animal oils with higher converted products [13]. Therefore, in this study, the production of biodiesel using catfish oil based on the waste fraction of catfish was investigated by using Potassium Hydroxide (KOH) as the catalyst. The effect of oil to ethyl-alcohol molar ratio and the catalyst loading was studied to obtain the maximum yield and perhaps it can achieve the best biodiesel characteristics of ethyl ester through the electrolysis method by formulating some variables.

2. Materials and Methods

2.1. Tools

Analytical balance, beaker glass, burette, cathode and anode Copper (Cu), container, dropper, erlenmeyer flask, hotplate, glass rod, measuring flask, viscometer, oven, picnometer, knife, power supply, measuring flask, magnetic stirrer, separating funnel, spatula, thermometer and waterbath.

2.2. Materials

Patin fish (Pangasius hypothalamus) waste, potassium hydroxide (≥99.95%), natrium chloride (≥99.95%), ethyl-Alcohol (96%), aquadest and phenolphtalein.

2.3. Methods

The methodology for biodiesel production in this research is divided into some steps. Waste patin fish being sorted and cleaned before being processed to obtain the fish oil. The fish oil then being used for biodiesel production with several variations on the molar ratio with the ethyl alcohol by molar ratio (1:5; 1:6; 1:7) and potassium hydroxide (1%; 1,5%; 2%) by weight.

2.3.1. Preparation of raw material

Waste patin fish is washed then dried and the fat weighed with an analytical balance. The fat is steamed for 2 hours to produce fish oil. The fish oil was collected in a glass bottle.

2.3.2. Raw material analysis process

10 grams of catfish oil was poured into an Erlenmeyer. Then the sample is solved in 25 mL of ethanol in 50ºC after that, added 2 drops of phenolphthalein indicator. The sample is titrated using KOH 0,1 N until the color is changed into pink for 30 seconds. Free Fatty Acid (FFA) that formed by fat of patin fish is calculated.

2.3.3. Electrolysis process

KOH is mixed with Ethanol with variation of mole ratio (1:5, 1:6, 1:7) until all the KOH is dissolved. Then, NaCl at ratio 0,56 wt% of oil and aquadest at ratio 2wt% of oil is mixed too. Ethanol and KOH as well as the salt solution (NaCl and distilled water) were mixed to 100 mL of catfish oil in a glass container. The solution was electrolysed with the help of copper electrodes, then voltage of 20V and 30V with an electrode distance of 3 cm for 2 hours and stirring was done. within 2 hours and constant stirring with a magnetic stirrer at a rotation speed of 500 rpm. After that, the electrolysed solution was covered with plastic and given a hole for electrode injection then electrolysis run for 2 hours.

The results were allowed to stand for 24 hours and the converted biodiesel was separated. the converted biodiesel was separated using a separating funnel. The biodiesel obtained was then washed with distilled water that had been heated to 50ºC. The biodiesel was allowed to stand until two layers formed again and then separated by a separating funnel. separated by a separating funnel. This was done several times until the the last wash result looks clean.

3. Results and Discussion

3.1. The effect of feed and catalyst ratios on the yield

Figure 1 shows the effect of catalyst and feed ratio on the yield of produced biodiesel. The variation of the catalyst that produces the most significant yield is in the 1:6 molar ratio with a 1.5% catalyst, which is 92.4058%, and the lowest percentage is obtained in the 1:5 variation with a 2% catalyst. The ratio of the average raw material to produce the highest yield was 1:6 [14]. The decrease in yield at variations of 1:5 and 1:7 with a 2% catalyst was caused by excessive ethanol, which could shift the reaction back to the reactants and cause the yield to decrease. This is also influenced by the percentage of catalyst, where an excessive percentage of catalyst will trigger side reactions with triglycerides in the form of glycerol [15].

3.2. The effect of feed and catalyst ratios on the density

The measurement of biodiesel density aims to determine the relationship between the density value and the calorific value produced per unit of fuel. Furthermore, Density is important to measure so the delay between the injection and combustion chamber of the fuel is known [16]. The density of all biodiesel samples obtained was 851-880 kg/m3, where this

value qualified by SNI 7182-2015 standard, which was in the range of 850-890 kg/m3. The density of biodiesel tends to decrease along with the increase in the percentage of catalyst used in each variation of the ethanol ratio, this result shows through Figure 2, where the lowest density of biodiesel is in catalyst 2%. The more catalysts used in the transesterification reaction, the density of biodiesel produced tends to decrease because excess catalyst causes a saponification reaction that forms glycerol whose density is greater than the density of biodiesel [17]. The imperfection of the washing and purification process will cause a greater density, affecting fuel consumption [18].

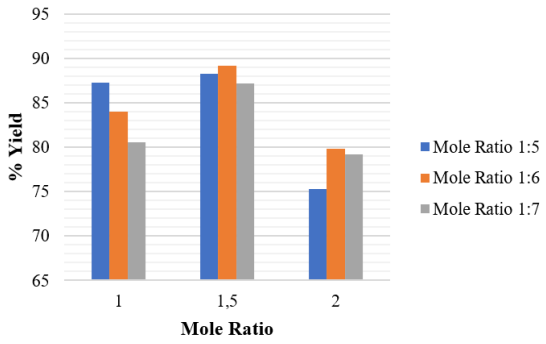

Fig. 1. Yield of biodiesel product

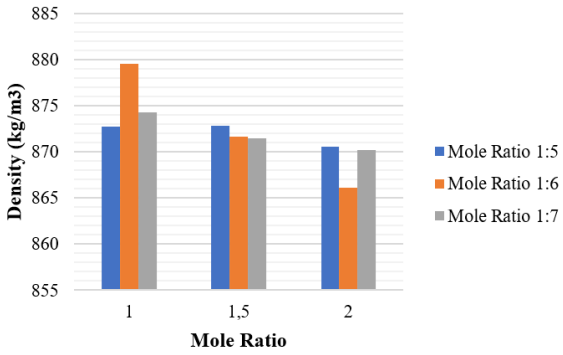

Fig. 2. Density of biodiesel product

3.3. The effect of feed and catalyst ratios on the viscosity

The viscosity value of this electrolysis method is shown from Figure 3. The highest viscosity and qualified SNI biodiesel standard is in the ratio of 1:6 feedstock with a 2% catalyst which is 5.3331 cSt, and overall biodiesel with a 2% catalyst also qualified SNI. The effect of variations in the mole ratio of raw materials and ethanol in this study shown the best viscosity when using the mole ratio of raw materials of oil and ethanol 1:6 with a 2% catalyst. This is in accordance with the previous study that each decrease in the density value will result in a smaller viscosity value [19]. The yield of biodiesel at a 1.5% and 2% catalyst had the best viscosity value of the entire sample because it was related to the higher the catalyst concentration, the higher the reaction rate, so that the triglyceride chain could split into fatty acid esters and lower the molecular weight. The viscosity of biodiesel also decreases at a catalyst concentration of 2% because it is caused by the use of the optimum catalyst concentration, where optimum catalyst concentration will increase the conversion of triglycerides, but if the catalyst concentration is too high, it will cause the formation of an emulsion [20].

Some samples of biodiesel not qualified by SNI biodiesel viscosity quality standard can be caused by several things, such as the raw material used and, the high viscosity of patin fish fat. Alcohol type can also cause a reasonably high viscosity value because ethanol has a long enough carbon chain, so it is more challenging to transesterify. The double bond in ethanol will also affect the increase in the viscosity value [21].

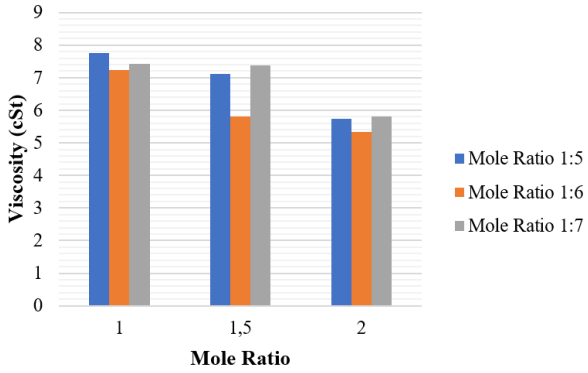

Fig. 3. Viscosity of biodiesel product

3.4. The effect of feed and catalyst ratios on calorific value

The range of calorific values for this electrolysis method can be seen in Figure 4. All samples from this study have qualified standards for biodiesel calorific value according to SNI, which is a maximum of 9938.76 cal/gr. The whole sample has a calorific value in the range of 9,200-9,400 cal/gr. The highest calorific value is in this process on the ratio of 1:6 raw material with a 1.5% catalyst.

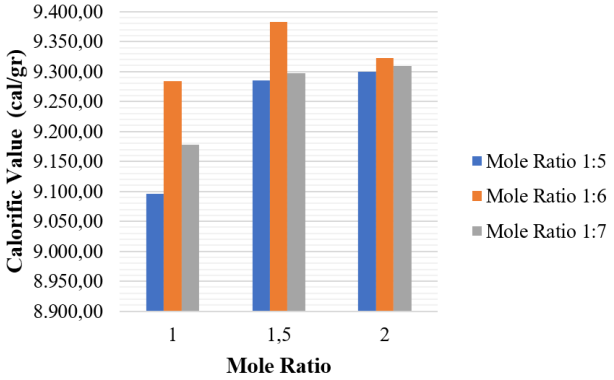

Fig. 4. Calorific value of biodiesel product

The calorific value tends to increase with the addition of each percent catalyst because it is in line with the higher fish oil that was converted into biodiesel. It is known that biodiesel, which has a low calorific value, will reduce heat release in the engine, increasing fuel consumption. The calorific value will also influence the mileage of the fuel because this value indicates engine performance and combustion characteristics [22]. The use of biodiesel with a low calorific value also has

harmful effects on the performance and exhaust emissions of diesel engines.

3.5. The effect of feed and catalyst ratios on flash point

All biodiesel samples analyzed by flash point in this study have qualified by SNI 7182-2015 that at least biodiesel has a minimum flash point of 100 °C. The flash point value of biodiesel with 1% catalyst variation shows a value that tends to increase, while at a 2% catalyst variation, it tends to decrease as shown in Figure 5. The increase in flash points can be caused by the presence of water in the mixture or residual glycerol and catalyst used in biodiesel products [23]. The difference in the flash point between the products can also be caused by impurities and residual reactants that increase the flash point, namely unreacted patin oil. Flash point is in the ratio of 1:6 raw material with 1.5% catalyst has a value at 186.4°C. This flash point test is vital to be tested in order to determine the endurance capacity of biodiesel against the heating process that occurs in the engine. The higher the flash point of biodiesel, the better and safer to use because it minimizes the possibility of an explosion and is easier to store, but a flash point that is too high also indicates low volatility [24]. Several factors, such as reversible transesterification reactions can cause fluctuating flash point values in biodiesel. Flash point also depends on the type of alcohol used, and ethanol has a higher flash point than methanol because ethanol has a double bond to oxygen, where this double bond also has an effect and reaction [25].

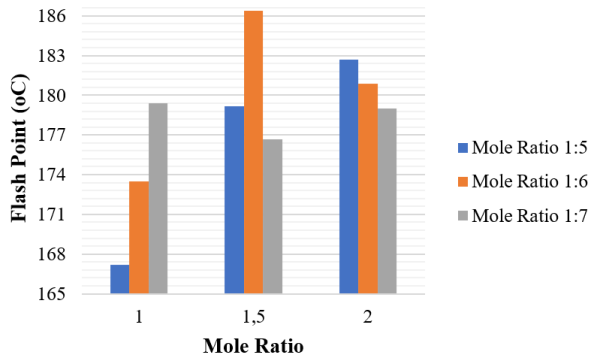

Fig. 5. Flash point of biodiesel product

4. Conclusion

This study concluded waste patin fish were one alternative that can used as raw material for making biodiesel, as proven by the results of density, viscosity, flash point, and calorific value analysis in this research that meet SNI 7182:2015 standards. The higher the amount of catalyst used, the better the quality of the resulting biodiesel and following SNI 7182:2015. The mole ratio of raw material and ethanol at 1:6 produces ethyl ester with quality that tends to be better in accordance with SNI 7182:2015. Biodiesel production on copper electrodes produces the best quality and the highest yield value at a voltage of 20V with a raw material ratio of 1:6 and a catalyst amount of 1.5% and the resulting yield is 92.4058%. Thus, further studies need to examine other catalyst variations, voltage, and electrodes related to biodiesel production.

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