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Use of Base Catalysts in Making Biodiesel from Waste Cooking Oil: A Review

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A B S T R A C T

Biodiesel from vegetable oils and animal fats is a more environmentally friendly alternative to conventional fossil fuels. Biodiesel production through esterification and transesterification processes with an emphasis on the role of catalysts in increasing efficiency. The use of homogeneous and heterogeneous catalysts and the advantages and disadvantages of each. Homogeneous catalysts, such as NaOH and KOH, effectively improve the reaction but face product separation and soap formation challenges that can reduce biodiesel yields. In contrast, heterogeneous catalysts such as CaO and zeolites offer reuse and waste reduction advantages, although with slightly lower efficiency. In addition, essential factors such as catalyst concentration, alcohol-to-oil ratio, and reaction temperature are reviewed to maximize biodiesel yields. Optimal catalyst concentration is necessary to increase conversion efficiency, as inappropriate concentrations can slow the reaction. It is important to choose the right catalyst and process conditions for producing biodiesel efficiently while considering the environmental impact of using raw materials, especially palm oil.

Contribution to Sustainable Development Goals (SDGs):
SDG 6: Clean Water and Sanitation
SDG 11: Sustainable Cities and Communities
SDG 13: Climate Action
SDG 15: Life on Land

1. INTRODUCTION

1.1. Research Background

In recent years, fossil fuels have become a global problem due to increasing fuel consumption in line with the increasing population growth in Indonesia [1]. Energy consumption in Indonesia is still dominated by fuel oil (BBM), which reaches 41.7% followed by electricity (19%), natural gas (14.6%), coal (9.1%), LPG (8.1%), and non-energy use (7.5%) [2] . In connection with the increasing population, renewable energy sources have become a serious concern in developing alternative energy sources to replace conventional fuels [3]. Energy has a significant role in the development of a country if its availability and development go hand in hand and support national development. Using coal with biodiesel in developing countries can maintain economic growth and reduce pollution levels that can reduce global warming and prevent climate change [5]. Indonesia is rich in vegetable oil sources, so it has a large potential to develop this alternative energy [6]. Most conventional energy sources are fossil fuels such as coal, oil, and gas. Burning fossil fuels is the primary source of emissions that can cause climate change, especially in cities [7].

Fuel made from vegetable oil or animal fat is usually called biodiesel [8]. As a fuel, biodiesel produces environmentally friendly emission gases compared to conventional fuels [9]. Biodiesel can be processed through esterification reactions and transesterification.

The esterification reaction will produce methyl ester or ethyl ester of fat and glycerol. In contrast, the transesterification reaction is similar to the alcoholization reaction, which produces better-quality biodiesel by undergoing fatty acid exchange and creating new esters [10]. Biodiesel is a renewable fuel derived from natural resources and has characteristics similar to other conventional diesel fuels, so biodiesel can be used as an alternative to fossil fuels [7].

Raw materials in biodiesel production can be soybeans, peanuts, sunflowers, corn, coconuts, palm oil, and other plants. In Indonesia, using palm oil as a raw material for biodiesel is very open, because Indonesia is one of the largest countries producing *crude palm oil* (CPO). However, using palm oil as a raw material is a challenge in itself and can cause conflict where palm oil is also a source of food [11]. Biodiesel production using used cooking oil raw materials can effectively reduce the cost of biodiesel so that it can be sold cheaply [12]. The total cooking oil used by various sectors in Indonesia is 3.88 million tons per year [13]. The free fatty acid content in used cooking oil is higher than the FFA in fresh oil. Usually, the FFA content is greater than 1% by weight [14]. Used cooking oil is waste oil that comes from household waste. Used cooking oil cannot be used continuously because it can harm human health, so used cooking oil can be used as an alternative energy source [15].

1.2. Literature Review

The study used the *literature review method.* This method is a research method used to analyze information from various literature such as scientific journals, books, or research articles to build a theoretical basis or evaluate knowledge in the process of making biodiesel from used cooking oil using a base catalyst.

A catalyst is a substance used in the reaction process between triglycerides (oil or fat) and alcohol (usually methanol or ethanol) in a transesterification process of making biodiesel so that the reaction runs quickly and optimally [18]. The role of the catalyst in the biodiesel-making process is to lower activation energy, increase efficiency, and affect product quality [19]. Several types of catalysts can be used in this reaction, such as homogeneous and heterogeneous base catalysts, homogeneous and heterogeneous acid catalysts, and enzymatic catalysts [20].

Base catalysts are the most commonly used because the transesterification reaction will react faster than acid catalysts. Base catalysts are divided into two types, namely homogeneous and heterogeneous bases examples of homogeneous base catalysts such as Sodium hydroxide (NaOH) and Potassium hydroxide (KOH). Homogeneous base catalysts have the property of being readily soluble in the reaction but difficult to separate at the end of the reaction, while the disadvantage is that they are not suitable for oils with high FFA levels because they will result in soap (saponification). Heterogeneous base catalysts include calcium oxide (CaO) and Magnesium oxide (MgO). Heterogeneous base catalysts have insoluble properties in the reaction, so they are easily separated and can be reused and the advantage of this catalyst is that it is environmentally friendly and suitable for cleaner processes.

Acid catalysts are catalysts used when the oil raw material has a high free fatty acid content (>2%). Acid catalysts are also divided into two types, namely homogeneous and heterogeneous acids [22]. Homogeneous acid catalysts include sulfuric acid (H_2SO_4) and hydrochloric acid (HCl), while heterogeneous acids include zirconium oxide acid (ZrO_2) and solid sulfonic acid. Acid catalysts have slower properties than base catalysts and require higher temperatures and reaction times [23].

Enzymatic catalysts are catalysts that use lipase enzymes to convert triglycerides into biodiesel. The advantages of this catalyst are that it does not produce soap and is suitable for oils with high FFA levels, but its disadvantages are that it has high costs and long reaction times [24].

Calcium Oxide (CaO) is a heterogeneous catalyst in solid form that can be easily separated at the end of the reaction. However, the weakness of the CaO catalyst is that it easily reacts with air-containing water to form $Ca(OH)_2$ which causes a decrease in its catalyst activation, so it is necessary to add another metal to the catalyst using the wet impregnation method [25].

The biodiesel manufacturing process can be done with two reactions: esterification and transesterification. First, the initial stage is carried out by preparing raw materials, catalysts, and methanol. The oil raw materials used usually have a high FFA content of >2%, the methanol used is usually 200-300% mol of FFA, and the catalyst used in this reaction is sulfuric acid (H_2SO_4). Then the oil raw materials are heated until the temperature reaches around 55-60℃. Then the esterification process is carried out, where methanol is mixed with oil and sulfuric acid catalyst. In this reaction, FFA will be converted into methyl ester (FAME/ *fatty acid methyl ester*) and water, this process lasts for 1-2 hours [27]. After the reaction takes place, the purification stage is carried out, where the results of the reaction are separated from the remaining methanol and water, the water produced must be separated because it can interfere with the following process. Chemical reactions that occur in the esterification reaction:

$$\text{R-COOH} + \text{CH}_3\text{OH} \xrightarrow{\text{H}_2\text{SO}_4} \text{R-COOCH}_3 + \text{H}_2\text{O}$$

A transesterification reaction will then be carried out based on the results of the esterification reaction. Transesterification is a chemical reaction between triglycerides and alcohol using a base catalyst (such as NaOH or KOH), at the end of the process it will produce biodiesel (FAME) and glycerol as products [28]. In the initial stage, the catalyst and methanol will be mixed. The purpose of mixing the base catalyst with methanol is to form a methoxide solution. The function of the methoxide solution is to help accelerate the reaction between triglycerides (oil or fat) and methanol to produce biodiesel. Furthermore, the transesterification reaction is carried out, at this stage the esterified oil is heated to a temperature of around 55-60℃, and then the methoxide solution is added and stirred, which lasts for around 1-2 hours. At this stage, 2 layers of solution will be produced, where the top is methyl ester (biodiesel) and the bottom layer is glycerol [10]. These layers occur due to the difference in density between biodiesel and glycerol, where glycerol density has a higher value than the density of biodiesel. Chemical reactions that occur in the transesterification reaction:

$$C_3H_5(OOCR)_3 + 3\ CH_3OH \longrightarrow 3RCOOCH_3 + C_3H_8O_3$$

After the transesterification reaction, biodiesel purification will be carried out. At this stage, biodiesel is washed using warm water (±70℃) 3 times, removing residual catalyst, alcohol, and other impurities. In the last stage, biodiesel is dried at around 110-120℃ to remove water [29].

1.3. Research Objective

This study aims to analyze factors that can affect yield value such as reaction temperature, reaction time, and catalyst.

2. MATERIALS AND METHODS

Biodiesel production is usually done using an esterification reaction and a transesterification reaction. In transesterification reaction, biodiesel can be processed from animal oil or fat (triglycerides), which will be reacted with short-chain alcohol such as methanol and ethanol, which can produce a mixture of alkyl ester and glycerol in the presence of homogeneous or heterogeneous catalyst. Several factors can affect the transesterification process of vegetable oil, such as catalyst selection, molar ratio of alcohol/vegetable oil, purity of reactants, and temperature [7].

Catalysts are compounds used in a chemical reaction process that accelerate the reaction. In biodiesel manufacturing, the catalysts used are generally homogeneous and heterogeneous [16]. Homogeneous catalysts can be acids and bases, such as CH_3NaO, H_2SO_4, HCl, NaOH, and KOH. Heterogeneous catalysts include CaO, zeolite, titanium, and activated carbon [3]. The weakness of homogeneous catalysts is that they are difficult to separate from the resulting solution; in the transesterification reaction, this catalyst can react with ALB, which can form soap, making it challenging to separate glycerol and can reduce biodiesel yield, cannot be reused and will become a hazardous waste if disposed of directly. The advantages of heterogeneous catalysts are that they can reduce wasted water and the catalyst can also be reused for the next process.

Biodiesel can be produced from fatty acids by esterification or transesterification processes [26]. Oil used as raw material for biodiesel which has high free fatty acid (FFA) content (0.5-3%), if using a homogeneous base catalyst, must go through 2 process stages, namely, esterification and transesterification process [26].

3. RESULT AND DISCUSSION

3.1. *The effect of catalyst on biodiesel yield value*

The relationship between the effect of catalyst concentration on biodiesel yield is that the catalyst itself produces highly reactive methoxide ions, which can accelerate the transesterification reaction between triglycerides and methanol. If the catalyst concentration is higher, it can affect the reaction rate, and the reaction will be faster. However, if the excess catalyst at a certain point will not provide additional benefits and can cause soap formation if the water content in the reactor is high, especially in oils containing high free fatty acids (FFA), suppose the catalyst concentration is too low. In that case, it can cause the reaction to run slowly. The resulting biodiesel yield is lower because the amount of methoxide ions formed is insufficient to break down triglycerides effectively.

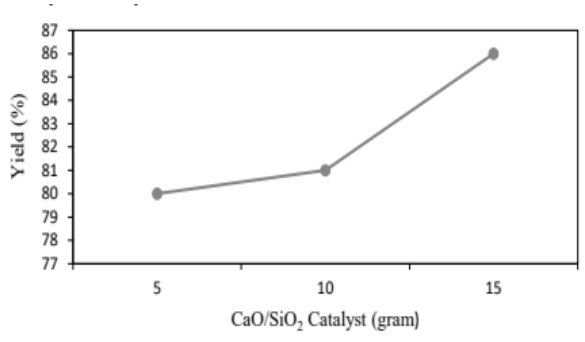

Fig. 1. Effect of biodiesel yield value on variations in CaO/SiO_2 catalyst [31].

The image above shows that when the catalyst is 5 grams, it produces a yield of 80%. Then, the catalyst value should be increased to 10 grams so that the yield value rises slightly to 81%. When the catalyst value is increased again, the yield value will increase to 86%. However, the increase is insignificant, meaning that the catalyst likely only acts as an accelerator of the reaction without increasing the product produced.

3.2 Effect of reaction temperature on biodiesel yield value

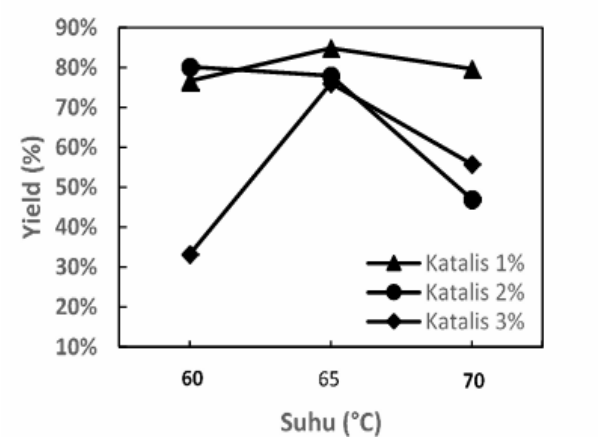

Fig. 2. Effect of reaction temperature and percentage of CaO-NaOH catalyst on biodiesel yield [11].

Based on Figure 2, it can be seen that with an increase in temperature up to 70℃ and above, the yield value of biodiesel obtained is relatively low. This is because, in the transesterification process, the temperature has reached optimum conditions, namely at a temperature of 65℃. The picture above shows the transesterification reaction between used cooking oil using a KOH catalyst of 1.5%, and the optimum reaction temperature is obtained at 65℃. In the manufacture of biodiesel, the higher the reaction temperature, the higher the yield value of the biodiesel. This is because at high temperatures, the reactant molecules will move and collide, so they will quickly react to form fatty acid esters [36]. The higher the reaction temperature, the greater the reaction rate constant and the faster the reaction rate. However, increasing the temperature will reduce the resulting product if the reaction has reached the optimum temperature. The picture above shows that the best biodiesel yield value is produced at 85% by adding a catalyst of 1% and a reaction temperature of 65℃. Meanwhile, the lowest yield value produced was 30% with a reaction temperature ratio of 60℃ and the addition of a catalyst of 1%.

3.3 Effect of reaction time on biodiesel yield value

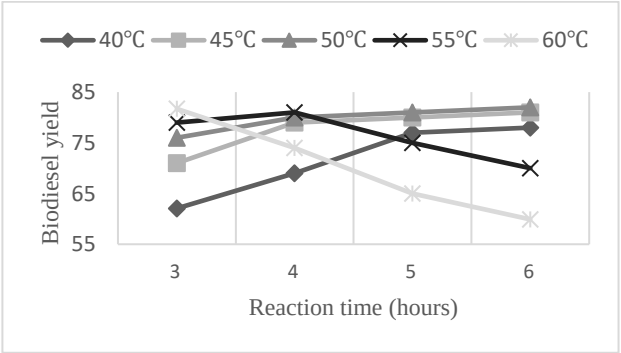

Fig. 3. Effect of reaction time and temperature on yield value [33].

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In the image above, you can see that the highest yield value was produced when the reaction time lasted for 3 hours. at a temperature of 60 °C, while the lowest was at a temperature of 40 °C. When using a longer reaction time, a significant change occurs at a reaction temperature of 60 °C, namely, the initial yield value of the reaction produced 81.7% to 59.9%. While at the lowest temperature of 40 °C, there was a significant increase in the yield value, which was initially 62.07% to 77.77%. The image above illustrates that if the reaction temperature used is lower than the optimum temperature, the time required to achieve a high or optimum yield value takes quite a long time. Meanwhile, suppose the reaction temperature used is higher than the optimum temperature. In that case, it will require a fast time in biodiesel production, but if the reaction time is extended, the yield value will decrease. In the image above, the highest yield value is produced at a temperature of 50 °C with a reaction time of 6 hours, while the lowest yield value is produced at a temperature of 60°C with a reaction time of 6 hours.

4. CONCLUSION

Several factors can affect the reaction rate when making biodiesel, such as using catalyst mixtures, reaction time, and reaction temperature. The addition of catalysts greatly affects the yield value of biodiesel. The addition of the amount of catalyst must also be adjusted because if the amount of catalyst added is too much it can cause a saponification reaction which can reduce the yield value to be produced. However, if the amount of catalyst added is too little, the reaction will run slowly and take a long time. The more the ratio of oil-methanol moles used, the yield value that will be produced will also increase. Reaction time affects the reaction process if the time used can reduce the yield value of biodiesel produced. The reaction temperature also has an effect because if the reaction temperature is higher, the biodiesel yield value will also increase. However, if the reaction temperature has reached the optimum temperature, then increasing the temperature can reduce the product to be produced. From the discussion above, it can be concluded that the optimum use of catalyst is 15 grams, while the optimum temperature is 65 °C, and the effect of time and reaction temperature is 50 °C and 6 hours.

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