Production of Biodiesel from Microalgae Using Transesterification Batch Reactor with the Assistance of Calcium Oxide Hydrotalcite Catalyst

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Abstract: Research the process of making biodiesel as alternative energy using microalgae *Nannochloropsis s.p* using the In-Situ transesterification method. The manufacturing process is carried out in two stages: in situ transesterification using a batch reactor and distillation process purification. The research was carried out using the fixed variable, namely the molar ratio of oil, algae content: solvent, namely 1:20, and the independent variable stirring speed in batch reactors of 50, 100, 150, 200, and 250 rpm with the catalyst used being a CaO/Hydrotalcite heterogeneous catalyst. This study obtained the highest crude biodiesel yield of 38.36% and the lowest Free Fatty Acid (FFA) content of 2.76 mg NaOH/gram sample at a stirring speed of 250 rpm.

1 INTRODUCTION

The Energy and Mineral Resources (EMR) sector is a sector that plays a vital role in supporting the national economy. The Energy and Mineral Resources sector includes coal, new and renewable energy, oil and gas. Currently, Indonesia still has a high dependence on fossil energy, where dependence on coal is 38%, oil and natural gas is 51%, while on new and renewable energy, it is still relatively low at 11%. Since 2004, Indonesia has become an oil importer country. In 2020, energy consumption increased due to the COVID-19 pandemic, where production is approximately 700 thousand bpd, and consumption is 1.5 million bpd. Biodiesel is a biofuel that is an alternative to petroleum diesel fuel. Biodiesel is an ester hydrocarbon compound derived from long-chain fatty acids. The components of biodiesel depend on the type of material used as raw material because it is related to the chemical structure of oil or lipid compounds produced from raw materials, such as the number of carbon atoms, as well as the number of double bonds in the lipid hydrocarbon bonds. The main raw material for making biodiesel in Indonesia today is Crude Palm Oil (CPO). At the same time, Crude Palm Oil is also the raw material for making cooking oil, so if biodiesel production expands, it can cause a potential scarcity of cooking oil. The cause of biodiesel is currently an alternative fuel that is quite popular because biodiesel is an environmentally friendly fuel, its raw materials are easy to get, and the manufacturing process is not complex. Biodiesel is generally made from vegetable materials, including plant oils and animal fats.

Microalgae can absorb solar energy and bind CO_2 efficiently, producing energy through photosynthesis (Astuti and Sriwuryandari, 2010). Microalgae can be cultivated easily because they use solar energy to

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photosynthesize. The high growth rate allows microalgae to produce more biodiesel feedstock than plant oils or animal fats. Some microalgae have a high lipid content which can be used as an alternative in biodiesel feedstock. The total lipid content of each microalga varies from 20-50%, but some microalgae have a lipid content of more than 40% (Patmawati et al, 2014). The use of microalgae as an alternative raw material for biodiesel production has considerable potential. Indonesia occupies the third position in replacing fossil fuels with microalgae biodiesel in the future (Batten et al, 2011). The reason microalgae is a raw material that has considerable potential is the characteristics of the microalgae itself. Microalgae is biomass with a high growth rate, easy to cultivate, environmentally friendly, easy to dry, and has a high lipid content that is easy to extract.

In a previous study, Edo et al. (2020) researched making biodiesel from the microalgae *Nannochloropsis sp.* using the in-situ transesterification method with the help of a sulfuric acid catalyst. The results showed that the variable molar ratio of microalgae to methanol 1:7 showed the highest crude biodiesel yield of 12% and the lowest FFA content of 0.399 mg NaOH/gr (Mirzayanti et al, 2020). In the same year, Septianto et al. (2020) also researched making biodiesel from the microalgae *Nannochloropsis sp.* using the transesterification method with the help of a CaO/hydrotalcite catalyst. The results showed that at a molar ratio of oil to methanol 1:15 with 10% catalyst weight%, the highest Fatty Acid Methyl Ester (FAME) content was 61.77%, and biodiesel yield was 60.39% (Septianto et al, 2020). In another research conducted by Retya et al. (2022) on the production of biodiesel from the microalgae *Nannochloropsis sp.* using the microwave-assisted in situ transesterification method with the help of a NaOH catalyst, the results showed a molar ratio of oil to methanol of 1:10 with a catalyst concentration of 0.4 M NaOH to obtain a biodiesel yield of 60.39% and an FFA of 0.0088 mg NaOH/gr (Retya et al, 2022).

In this research, the *Nannochloropsis sp.* microalgae type is used as a raw material for biodiesel using the In-Situ transesterification method. The catalyst used was a CaO/hydrotalcite heterogeneous catalyst with methanol as a solvent as well as a reactant in the in-situ transesterification process and n-hexane as a co-solvent which was carried out using a batch reactor that had been designed. The research used a fixed variable, the molar ratio of oil algae content and solvent 1:20, and the independent variable is stirrer speed in a batch reactor.

2 LITERATURE REVIEW

Microalgae are classified as autotrophic organisms that reproduce through the process of photosynthesis. The unicellular structure found in microalgae allows them to convert solar energy into chemical energy easily (Liu et al, 2016). It is estimated that microalgae can produce 200 times more oil content than other oil-producing plants (Sharma et al, 2012). Microalgae are also known as marine plants with advantages over other fuel sources. They do not require large areas, produce biomass quickly, and use CO_2 gas in the growth process to reduce air pollution (Gultom, 2018). Generally, there are three different microalgae growth conditions: phototrophic, heterotrophic, and mixed. Under phototrophic conditions, microalgae are highly dependent on sunlight as energy and CO_2 as carbon sources. Phototrophic conditions are often referred to as autotrophic photosynthesis. The second condition, namely the growth of heterotrophic microalgae, requires organic carbon as an energy source. Some commonly used organic nutrient sources include glucose, acetate, and glycerol. Microalgae growth is also influenced by its physiological properties (Hindarso et al, 2015). The physiology of this microalgae species can affect nutrient uptake and its culture media. Naturally, microalgae plants that live in open ponds will quickly grow to cover the pond's surface. If the microalgae physiology is very good, these conditions can stimulate biomass production with high oil and starch content. However, certain physiological responses do not allow microalgae to survive in these ponds. Of the several microalgae studied, the type of microalgae *Nannochloropsis sp.* can produce lipid products.

Lipid content in microalgae *Nannochloropsis sp.* is quite high, namely 31% to 68% of its dry weight (Chisti, 2013). *Nannochloropsis sp.* is microalgae that are yellow-green, round, small in size, and 2-4 μm in diameter (Salam et al, 2016). There are membrane-enclosed cell walls, mitochondria, chloroplasts, and nuclei in the morphology of *Nannochloropsis sp.* The chloroplast is bell-shaped, located at the edge of the cell, and has a light-sensitive stigma. *Nannochloropsis sp.* has six species: *Nannochloropsis graditana*, *Nannochloropsis granulata*, *Nannochloropsis limnetic*, *Nannochloropsis oceanica*, *Nannochloropsis salina*, *Nannochloropsis oculate*. Microalgae also have an essential function in marine ecosystems. Acts as a natural food for zooplankton and fish larvae because it is rich in carbohydrates, proteins, fats, minerals, and amino acids. *Nannochloropsis sp.* is a widely cultivated microalga and is rich in benefits, especially regarding health. It is perfect for consumption by zooplankton, such as rotifers, because it has a high content of Eicosapentaenoic Acid (EPA) and Docosahexaenoic Acid (DHA) (Meria et al, 2021).

The transesterification reaction is a chemical reaction between triglycerides and alcohol that uses a catalyst to produce monomers known as biodiesel products. Common solvents in the method other than methanol are NaOH, carbonates, and alkoxides such as sodium methoxide, CO_2, sodium propoxide, and sodium butoxide. Several kinds of catalysts can be used in the transesterification method, such as an acid, alkaline, or heterogeneous catalyst. In the transesterification method, a reaction occurs to form triglycerides contained in the raw material with methanol as a solvent using a catalyst. During the reaction process, triglycerides create methyl esters, fatty acids, and glycerol; the glycerol layer will decrease in the existing biodiesel. In addition, there is an in-situ transesterification method, a direct transesterification process of biomass rich in lipids or oil without knowing the extract and the purification process separately. During the process, the raw material will directly react with alcohol using a catalyst. This transesterification process can coincide with the response or first reactant process followed by an extraction process (Panjaitan et al, 2018).

3 EXPERIMENTAL METHODS

3.1 Preparation of Catalyst

Catalyst CaO/hydrotalcite was prepared by the method of incipient wetness impregnation. Hydrotalcite as much as 10 grams in the oven for 12 hours at a temperature of 100ºC. $CaCO_3$ is calcined to CaO in a furnace for 3 hours at 900°C then weighed with a loading ratio of 1:1 to hydrotalcite. After the CaO is calcined, the CaO is cooled and dissolved in distilled water. The incipient wetness impregnation method was used for hydrotalcite by spraying it with CaO solution in stages. The CaO-Hydrotalcite mixture dried in an oven for 12 hours at 100°C. The dry CaO-Hydrotalcite mix was then calcined in a furnace for 3 hours at 900°C (Heraldy et al, 2017).

3.2 In Situ Transesterification

Microalgae *Nannochloropsis sp.* was weighed and then put into a batch reactor along with methanol and CaO/hydrotalcite catalyst according to the variables set. The top nozzle of the reactor is closed, and the stirrer and reactor heater are turned on with the stirring speed according to the variable set until the reaction time has been determined. After the reaction time has been reached, the product mixture is removed from the reactor through the bottom nozzle and then cooled to room temperature. The residue in the product mixture is separated from the filtrate using a filtrate vacuum. The filtered residue was washed using 30 mL of a combination of methanol-n-hexane 1:1 (v/v) to recover the remaining biofuel. The filtrate was put into a separatory funnel, n-hexane was added with a ratio of 1:1 (v/v), then shaken and allowed to stand until two layers were formed for 30 minutes. The bottom layer was removed from the separatory funnel and added n-hexane with a ratio of 1:1 (v/v), then shaken and allowed to stand until two layers were formed for 8 hours. The top layer is washed using distilled water to bind the remaining catalyst and glycerol, which is still left in the mixture. The top layer is considered a transesterification product and then refined to separate the biofuel and solvent.

3.3 Refining

The product from the transesterification reaction is put into a boiling flask, then placed on a hotplate, and a solvent container is placed at the end of the condenser. The heater is turned on until the temperature in the boiling flask reaches 70 °C. Heating can be stopped if all the n-hexane solvent has evaporated with no more steam dripping at the end of the condenser. The distillation product is cooled down to room temperature. The distillate product was put into the oven at 70 °C for 4 hours to evaporate the solvent and water contained in the product. The product is cooled and then analyzed for its yield and acid number (SNI 7182:2015). The formula for yield calculation is as follows:

$$\text{Yield} = \frac{weight\ of\ crude\ biodiesel}{weight\ of\ dry\ microalgae} \times 100\% \quad (1)$$

The formula for Free Fatty Acid (FFA) calculation is as follows:

$$\text{FFA} = \frac{MW \times N \times V}{W} \quad (2)$$

MW = Molecular mass
N = Concentration of NaOH
V = Consumption of NaOH
W = Weight of crude biodiesel

4 RESULTS AND DISCUSSION

Research on making biodiesel from microalgae *Nannochloropsis sp.* using the in-situ transesterification batch reactor with the help of a CaO/hydrotalcite catalyst was carried out in 3 stages, namely the catalyst synthesis stage, the transesterification stage, and the distillation stage. The catalyst synthesis stage is carried out to manufacture CaO/hydrotalcite catalyst using the incipient wetness impregnation method, where Hydrotalcite is impregnated by spraying it with CaO solution according to the specified variables. CaO is obtained from the compound $CaCO_3$, calcined at 900 °C. In a study by Royani et al. (2016), when $CaCO_3$ is calcined to a temperature of 900 °C, it will decompose into CaO and CO_2 (Royani et al, 2016). In the In-Situ transesterification stage, a series of processes run simultaneously. The first is extracting oil from the base material, which is carried out by methanol and co-solvent n-hexane. Then the triglycerides react with methanol to form methyl esters in the transesterification reaction. Methanol is a reactant in the transesterification reaction and a lipid-extracting solution contained in microalgae. N-hexane acts as a co-solvent in the extraction process. Adding n-hexane as a co-solvent can increase the lipid extracted from microalgae (Panjaitan et al, 2018). CaO/Hydrotalcite catalyst can speed up the transesterification reaction at the in-situ transesterification stage (Januar, 2014).

Figure 1 shows the effect of stirring speed on biodiesel yield based on variations in reactor stirring speed. Figure 1 shows that the stirring speed affects the yield of crude products formed. The faster the stirring speed is given, the more yield of crude products is formed. It happens because the stirring speed can increase the material particles' movement. Collision activity and contact between one particle and another material particle are becoming more frequent, causing chemical reactions to occur more rapidly (Miskah et al, 2017). Adding n-hexane to transesterification can optimize the yield result because n-hexane as a co-solvent can contact first with the lipid in microalgae and then reacts with methanol (Dianursanti, 2015). The highest yield of crude product is found at the variable stirring speed of 250 rpm, producing a crude yield of 38.36%. The results obtained were lower when compared to the previous study by Retya (2022), which was 71.7%. This is because the method used is in situ microwave-assisted transesterifications. Microwave radiation is more effective in breaking down microalgae cells (Barqi, 2015; Khan, 2021). Therefore, the lipid extraction process runs faster. Methanol, as a solvent, is also very good at absorbing microwave radiation to support the transesterification reaction (Retya et al, 2022).

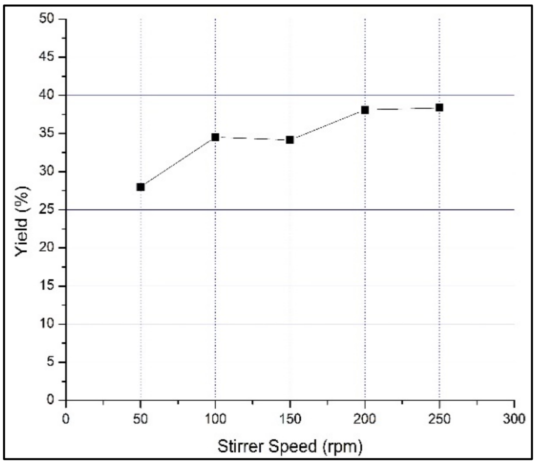

Figure 1: Effect of Stirrer Speed on Yield Biodiesel

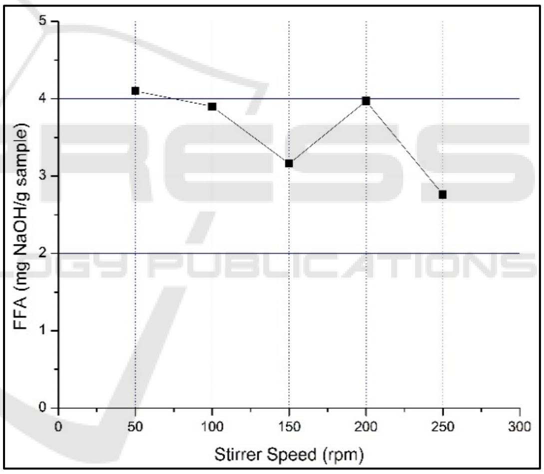

Figure 2: Effect of Stirrer Speed on Free Fatty Acid Content of Biodiesel

Figure 2 shows the effect of stirring speed on FFA crude levels based on stirrer speed variations. Figure 2 shows that the stirring rate affects the formed FFA crude product. The FFA crude product that is formed is related to the yield of the produced crude product. The greater the yield of crude product, the smaller the FFA crude product formed. It happens because the conversion of biodiesel becomes larger and suppresses the conversion of FFA formation. FFA levels in crude biodiesel products must be minimized because FFA can react with metals at high temperatures inside the engine when biodiesel is used (Adhani et al, 2016). In the FFA test results, the lowest FFA content was obtained at the variable stirring speed of 250 rpm with an acid number content of 2.76 mg NaOH/gram sample. The acid value in biodiesel is still above the Standar Nasional Indonesia (SNI) 7182: 2015 quality standard, which is 0.5 mg NaOH/gram sample. The FFA level in the biodiesel product formed is still higher when compared to research conducted by Baqi (2022), and Julrohiniar (2022), where the FFA levels produced were 0.52 mg NaOH/gram sample and 0.321 mg NaOH/gram sample. It is due to the biodiesel manufactured by Baqi (2022) using a base catalyst KOH and Julrohiniar (2022) using an SO_4^{2-}/TiO_2 base catalyst in which the contained fatty acids are transformed into dimethyl ether (Baqi et al, 2022; Julrohiniar et al, 2022). The crude biodiesel product is shown in Figure 3.

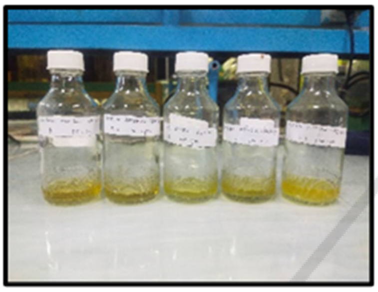

Figure 3: The Crude Biodiesel Product

5 CONCLUSION

Based on this research, it can be concluded that biodiesel production from microalgae *Nannochloropsis sp* with CaO/hydrotalcite catalyst using the in-situ transesterification batch reactor produced the highest yield is 38.36% at a reactor stirring speed of 250 rpm, and the lowest Free Fatty Acid content is 2.76 mg NaOH/gram of sample at a reactor stirring speed of 250 rpm.

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