



# The Effect of Biodiesel Oxidation Stability on The Removal of Polyunsaturated Fatty Acids

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**Abstract.** Biodiesel has developed as a plant-based fuel alternative over the last 20 years and is now a substitute for fossil diesel oil. Compared to fossil diesel, palm oil biodiesel offers advantages in terms of emissions, toxicity, biodegradability, engine lubrication, and contribution to national energy security. Although palm biodiesel has good quality, its oxidative stability is still lower than that of fossil diesel. This is due to the content of polyunsaturated fatty acids, which ranges from 9-12%, significantly affecting oxidative stability. To improve this stability, methyl esters of polyunsaturated fatty acids need to be removed through a liquid-liquid extraction process using a silver nitrate (AgNO<sub>3</sub>) solution. The extraction process is carried out with various concentrations of AgNO<sub>3</sub> (1 M and 5 M), methanol content in the solution (10%-v, 25%-v, and 50%-v), and the biodiesel to AgNO<sub>3</sub> ratio (1:1 and 1:2) at a temperature of 25- 35°C for 3 hours, followed by the separation of extract and raffinate for 45 minutes. The research results show that the induction period for all variations experienced a decrease compared to biodiesel before extraction. However, GC-MS analysis and iodine number indicated a reduction in polyunsaturated fatty acid methyl esters after the extraction process. The best results in the extraction process were obtained with the variation of 1 M, 10%-v methanol, and a 1:1 ratio, with an induction period of 15.26 hours, polyunsaturated fatty acid methyl ester composition of 0.08%, and iodine number of 49.76 g iodine/100g.

**Keywords:** Biodiesel, Liquid-Liquid Extraction, Polyunsaturated Fatty Acids

## 1 Introduction

As the population grows, the demand for energy sources also increases. Fossil fuels, such as diesel oil, are consumed in large quantities daily. Due to their non-renewable nature, these fuel supplies are dwindling, necessitating alternative sources to replace fossil fuels. Additionally, the use of fossil fuels leads to significant emissions of exhaust gases that cause environmental damage. Therefore, it is essential to develop alternative fuels derived from renewable and environmentally friendly natural resources. However, palm oil biodiesel still has some drawbacks, particularly its oxidative stability, which is much lower than that of fossil diesel. This is due to the presence of unsaturated fatty

acid groups (especially polyunsaturated fatty acids) in palm oil biodiesel. According to Soerawidjaja, the ideal biodiesel should not contain methyl esters of polyunsaturated fatty acids [1, 2]. This study aims to understand the impact of removing methyl esters of polyunsaturated fatty acids from palm oil biodiesel on its oxidative stability and to determine the details of the extraction technology used for removing polyunsaturated fatty acid methyl esters from palm oil biodiesel using an aqueous silver nitrate solution as the solvent.

## 2 Materials and Methods

The core process in efforts to enhance the oxidative stability of biodiesel involves removing polyunsaturated fatty acid content. The method used in this experiment is extraction using a silver nitrate ( $\text{AgNO}_3$ ) solution. The polyunsaturated fatty acids obtained from the first extraction stage are then separated from  $\text{AgNO}_3$  through a second extraction process. The procedures carried out in both the first and second extraction stages are illustrated in the diagram in the following figure.

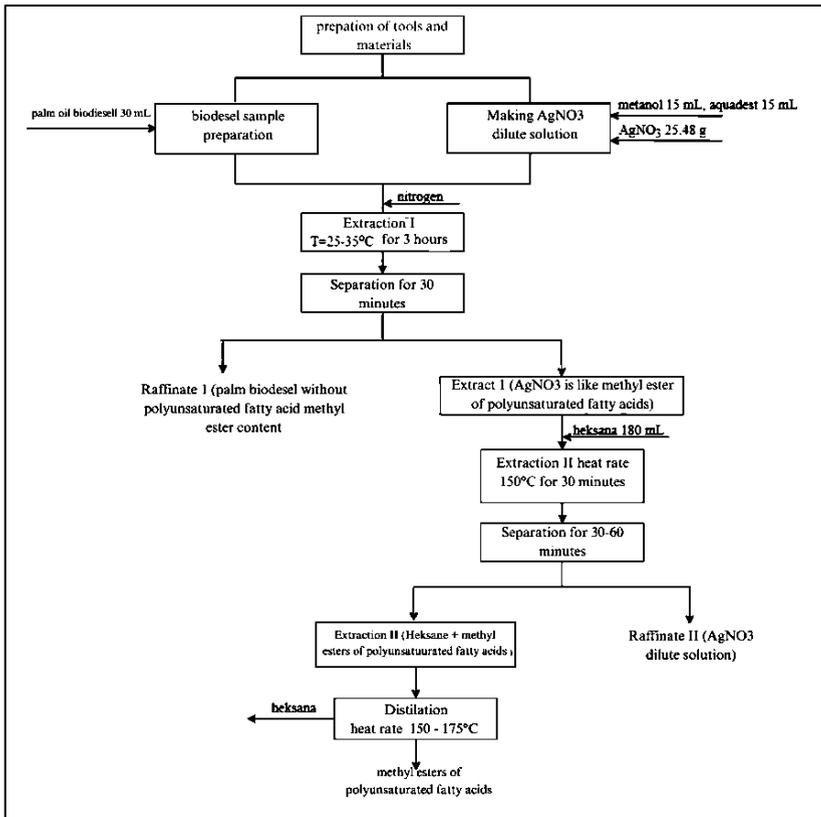


Fig. 1. Flow diagram of polyunsaturated fatty acid extraction process

## 2.1 Preparation of Aqueous Silver Nitrate Solution ( $\text{AgNO}_3$ )

Before proceeding to the core stage of removing polyunsaturated fatty acids from biodiesel, specifically the extraction stage, the initial procedure involves preparing a dilute silver nitrate ( $\text{AgNO}_3$ ) solution, which will later act as an absorbent for the polyunsaturated fatty acids in palm oil biodiesel. The steps involved in this process are as follows:

- A methanol-aquadest mixture of 30 mL is prepared in a beaker, with a methanol volume of 50%-v in the mixture
- Silver nitrate ( $\text{AgNO}_3$ ) of 25.48 grams (for a dilute  $\text{AgNO}_3$  solution with a 5 M concentration) is dissolved in the methanol-aquadest mixture and stirred until the solution becomes homogeneous.
- The same procedure is used to prepare a dilute  $\text{AgNO}_3$  solution with a concentration variation of 1 M and methanol volume variations in the mixture of 10%-v and 25%-v.

## 2.2 Extraction Process I

The procedure sequence for polyunsaturated fatty acid extraction from palm oil biodiesel through the first extraction process is as follows:

- A 30 mL sample of palm oil biodiesel is placed in a 250 mL three-neck Erlenmeyer flask containing a 5 M dilute  $\text{AgNO}_3$  solution.
- A reflux condenser and thermometer are set up on the 250 mL three-neck Erlenmeyer flask, then nitrogen gas is injected into the solution.
- The first extraction process is conducted while stirring the solution with a magnetic stirrer, maintaining the solution temperature at 25-35°C for 3 hours and shielding it from light.
- The solution is transferred into a 100 mL separatory funnel for decantation for 30 minutes, allowing two phases to form: extract I (dilute  $\text{AgNO}_3$  solution containing polyunsaturated fatty acids) and raffinate I (palm oil biodiesel without polyunsaturated fatty acids).
- Extract I is then transferred into a cleaned and dried 250 mL three-neck Erlenmeyer flask for the second extraction stage.
- Raffinate I is washed with aquadest three times to remove any residual  $\text{AgNO}_3$ . The volume of raffinate I is measured, then transferred into a clean sample bottle, ready for analysis

# 3 Results & Discussions

## 3.1 The Effect of Liquid-Liquid Extraction Process with Silver Nitrate ( $\text{AgNO}_3$ ) Solution on the Oxidation Stability of Palm Oil Biodiesel

The removal process of polyunsaturated fatty acid methyl esters begins with the first extraction using a silver nitrate ( $\text{AgNO}_3$ ) solvent, where  $\text{Ag}^+$  ions will bond with the

unsaturated compounds in the biodiesel. The product from the first extraction is separated from  $\text{AgNO}_3$ , while the polyunsaturated fatty acid methyl esters dissolved in  $\text{AgNO}_3$  are further separated by dissolving them in the organic solvent hexane through a second extraction process. Subsequently, another separation between hexane and the polyunsaturated fatty acid methyl esters is performed through distillation, evaporating the hexane and leaving behind the polyunsaturated fatty acid methyl esters, which are then measured and compared to the initial biodiesel volume.

The silver nitrate ( $\text{AgNO}_3$ ) solution used in the liquid-liquid extraction process was varied based on its concentration, specifically 1 M and 5 M, dissolved in different methanol volume percentages (10%-v, 25%-v, and 50%-v), with varying volume ratios of  $\text{AgNO}_3$  solution to palm oil biodiesel (1:1 and 1:2).

Silver nitrate ( $\text{AgNO}_3$ ) was selected as the solvent for removing polyunsaturated fatty acid methyl esters because  $\text{AgNO}_3$  is the most effective silver ion for absorbing methyl linoleate and methyl linolenate. The concentration of  $\text{AgNO}_3$  solution was varied at 1 M and 5 M because, at concentrations below 0.1 M,  $\text{AgNO}_3$  does not adequately dissolve polyunsaturated fatty acid methyl esters. The optimal concentration range for  $\text{AgNO}_3$  solution in the extraction process is 1 M to 20 M [3]. Polyunsaturated fatty acid methyl esters in palm oil biodiesel are extracted by  $\text{AgNO}_3$  solvent in a three-neck Erlenmeyer flask connected to a reflux condenser and nitrogen flow, with a thermometer installed to monitor and maintain the reaction temperature during extraction. Nitrogen injection serves to expel oxygen from the air trapped in the Erlenmeyer flask, as the presence of oxygen can affect the oxidative stability of methyl linoleate (polyunsaturated fatty acid methyl ester) in the feed. The use of a reflux condenser helps channel the trapped oxygen out of the Erlenmeyer flask to the external air, ensuring that the palm oil biodiesel and  $\text{AgNO}_3$  mixture in the flask remains oxygen-free throughout the reaction.

The extraction process was conducted for 3 hours at a temperature of 25-35°C with a stirring speed of 150-250 rpm for all experimental variations. Extraction was performed at the low temperature of 25-35°C, and the Erlenmeyer flask was shielded from light using a cloth cover to maintain the stability of polyunsaturated fatty acid methyl esters in palm oil biodiesel, preventing degradation due to heat and light. The 3-hour extraction time was based on Huong, prior research on the removal of polyunsaturated fatty acid methyl esters using tuna oil feed and an  $\text{AgNO}_3$  solvent [4]. According to Huong, a 3-hour period is sufficient to achieve equilibrium in the extraction of polyunsaturated fatty acid methyl esters with an  $\text{AgNO}_3$  solvent [4]. The influence of silver nitrate ( $\text{AgNO}_3$ ) solution concentration on the oxidative stability of palm oil biodiesel was measured through rancimat induction period analysis, iodine number analysis, and Gas Chromatography-Mass Spectroscopy (GC-MS) analysis.

**The Effect of Liquid-Liquid Extraction Process with Silver Nitrate ( $\text{AgNO}_3$ ) Solution on the Oxidation Stability of Palm Oil Biodiesel.** The results of the Rancimat analysis on the liquid-liquid extraction experiment indicate that with the same volume ratio of  $\text{AgNO}_3$  to palm biodiesel and the same percentage of methanol volume in the mixture, the induction period of palm biodiesel decreases as the concentration of  $\text{AgNO}_3$  increases. This finding suggests that a higher concentration of  $\text{AgNO}_3$  solution

leads to a lower purity of the produced biodiesel. This can occur due to dissolved oxygen in the feed, both in the palm biodiesel and in the  $\text{AgNO}_3$  solvent. Additionally, during the extraction process, the presence of agitation increases the concentration of oxygen in the mixture. Although nitrogen was injected during the extraction process, it remains challenging to eliminate the oxygen that was dissolved initially in both the biodiesel and the  $\text{AgNO}_3$  solution. Therefore, from the preparation of equipment and materials, through the extraction and separation processes, to the storage of the product, it is crucial to ensure that everything is free from oxygen, light, and heat, due to the high sensitivity of linoleic acid and linolenic acid to these three factors.

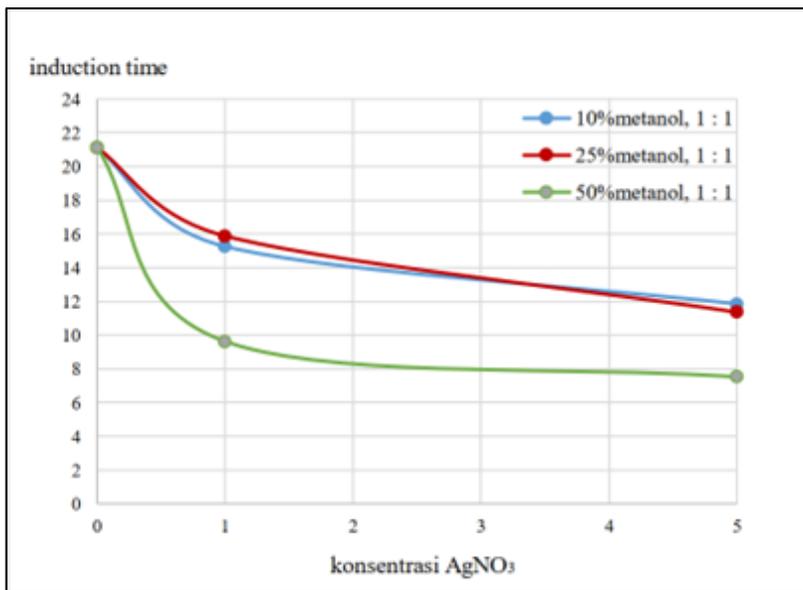


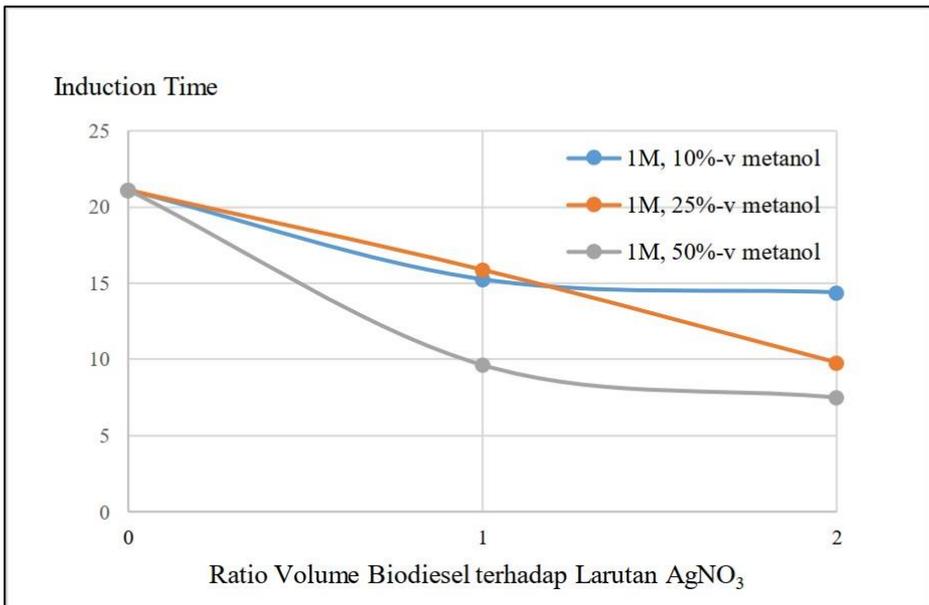
Fig. 2. Effect of  $\text{AgNO}_3$  concentration on the rancimat induction period

The palm biodiesel product obtained from liquid-liquid extraction is also not entirely free from its solvent ( $\text{AgNO}_3$ ). It is possible that residual  $\text{AgNO}_3$  remains in the palm biodiesel during the separation process through decantation. Therefore, it is advisable to wash the biodiesel with distilled water, followed by saturated salt solution. To eliminate any residual water from the washing process, magnesium sulfate can be used. The more frequently the washing process is repeated, the higher the purity level of the resulting palm biodiesel. The presence of water in palm biodiesel can affect the results of the Rancimat induction period analysis, although its impact may not be very significant.

**Effect of Biodiesel Volume Ratio and  $\text{AgNO}_3$  Solution on the Oxidation Stability of Palm Oil Biodiesel.** In addition to varying the concentration of  $\text{AgNO}_3$  solution, this study also examines the effect of the volume ratio of palm biodiesel to the volume of  $\text{AgNO}_3$  solution. This is done to investigate how the amount of solvent in the liquid-

liquid extraction affects the removal of methyl esters of polyunsaturated fatty acids. The experiment varied with volume ratios of palm biodiesel to  $\text{AgNO}_3$  solution of 1:1 and 1:2. As the amount of solvent ( $\text{AgNO}_3$ ) in the mixture increases, more  $\text{Ag}^+$  ions can react with the double bonds in the methyl esters of fatty acids, resulting in a greater composition of polyunsaturated fatty acid methyl esters being removed from the palm biodiesel.

Based on the Rancimat analysis data shown in Fig. 3, the induction period decreases as the volume ratio of palm biodiesel to  $\text{AgNO}_3$  solution increases. This can occur due to the presence of dissolved oxygen in the feed, both in the palm biodiesel and in the  $\text{AgNO}_3$  solvent. Additionally, during the extraction process, the presence of agitation increases the concentration of oxygen in the mixture. Although nitrogen was injected during the extraction process, it remains challenging to remove the oxygen that has been dissolved in both the biodiesel and the  $\text{AgNO}_3$  solution from the beginning. Therefore, from the preparation of equipment and materials, through the extraction and separation processes, to the storage of the product, it is crucial to ensure that everything is completely free from oxygen, light, and heat due to the high sensitivity of linoleic acid and linolenic acid to these three factors.



**Fig. 3.** Effect of the volume ratio of biodiesel and  $\text{AgNO}_3$  solution on the Rancimat induction period

The amount of  $\text{AgNO}_3$  solution in the 1:2 variation (with 15 ml of palm biodiesel) is obviously greater than the amount of  $\text{AgNO}_3$  solution in the 1:1 variation (with 30 ml of palm biodiesel). This can result in the purity of the biodiesel obtained from the 1:2 variation being lower than that from the 1:1 variation, as the decantation process will

be more difficult and take longer to separate. Additionally, due to the higher concentration of  $\text{AgNO}_3$  in the 1:2 variation, the washing process to remove residual  $\text{AgNO}_3$  during decantation must be performed more frequently to achieve a purer palm biodiesel product.

**Effect of Methanol Composition in  $\text{AgNO}_3$  Solution on the Oxidation Stability of Palm Oil Biodiesel.** The addition of methanol aims to enhance the solubility of methyl esters of polyunsaturated fatty acids in the  $\text{AgNO}_3$  solution due to its high selectivity. The choice of methanol over other alcohol solvents is based on its polarity, as it has the shortest hydrocarbon chain, resulting in higher solubility in water. The variations in methanol composition in this experiment are 10%-v, 25%-v, and 50%-v. This is based on Huong's, research, which explains that the solubility of  $\text{AgNO}_3$  is greater in water than in methanol [4], so at a methanol composition of 60%-v in the solution, the optimum point is reached.

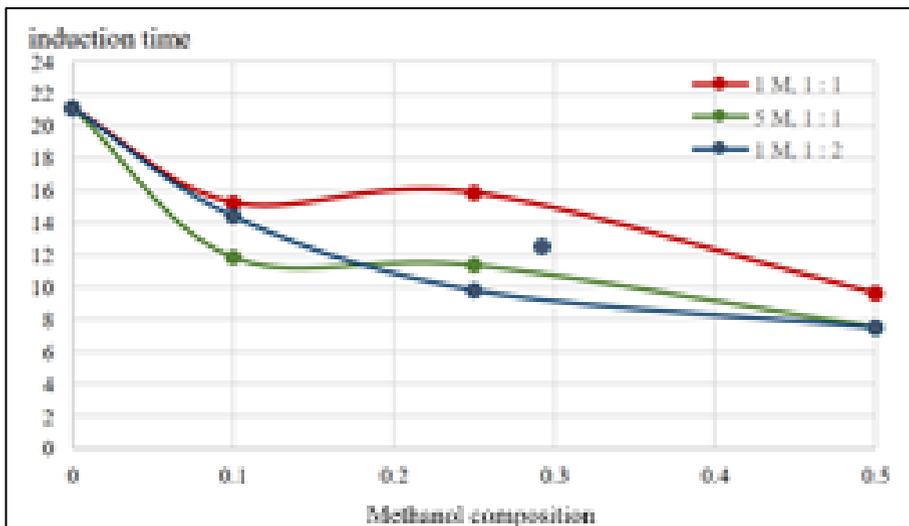


Fig. 4. Effect of methanol composition in  $\text{AgNO}_3$  solution on the rancimat induction period

Based on the Rancimat analysis results shown in Fig. 4, the induction period decreases as the composition of methanol in the mixture increases. This can occur due to the presence of dissolved oxygen in the feed, both in the palm biodiesel and in the  $\text{AgNO}_3$  solvent. Additionally, during the extraction process, the presence of agitation increases the concentration of oxygen in the mixture. Although nitrogen was injected during the extraction process, it remains challenging to remove the oxygen that has been dissolved from the beginning in both the biodiesel and the  $\text{AgNO}_3$  solution. Therefore, from the preparation of equipment and materials, through the extraction and separation processes, to the storage of the product, it is crucial to ensure that everything is completely free from oxygen, light, and heat due to the high sensitivity of linoleic acid and linolenic

acid to these three factors. Furthermore, during the extraction process using a reflux condenser and nitrogen injection, the top of the condenser is left open as an outlet for the oxygen displaced during the extraction process. As a result, a small amount of methanol in the mixture is also carried out, and the agitation influences the amount of methanol vapor formed during the extraction process. Additionally, considering that the solubility of  $\text{AgNO}_3$  is greater in water than in methanol, when dissolving solid  $\text{AgNO}_3$ , it is advisable to have a much higher composition of water compared to methanol in the mixture so that the dilute  $\text{AgNO}_3$  solution can blend perfectly with the oil phase during the liquid-liquid extraction process.

### 3.2 Effect of Liquid-Liquid Extraction Process with Silver Nitrate Solution ( $\text{AgNO}_3$ ) on Post- Extraction Polyunsaturated Fatty Acid Methyl Ester Composition

The effect of the  $\text{AgNO}_3$  solvent in absorbing the content of methyl esters of polyunsaturated fatty acids from palm biodiesel was analyzed using Gas Chromatography-Mass Spectrometry (GC-MS). The GC-MS analysis can determine the comparison between the composition of methyl esters of polyunsaturated fatty acids before and after the liquid-liquid extraction.

**Table 1.** Composition of polyunsaturated fatty acid methyl esters before and after extraction

| Chemical Formula                       | Types of fatty acids   | Fatty acid methyl ester composition |  |                                       |   |  |   |   |  |  |
|--|------------------------|-------------------------------------|--|---------------------------------------|---|--|---|---|--|--|
|  |                        | Before extraction                   | 1 M, 10%-v metanol, 1 : 1 without nitrogen | 1 M, 25%-v metanol, 1 nitrogen inject | 1 M, 50%-v metanol, 1 : 1 nitrogen inject | 5 M, 10%-v Metanol, 1 : 1 without nitrogen | 5 M, 25%-v Metanol, 1 : 1 nitrogen inject | 5 M, 50%-v metanol, 1 : 1 nitrogen inject | 1 M, 25%-v Metanol, 1 : 2 without nitrogen | 1 M, 50%-v metanol, 1 : 2 without nitrogen |
|  |                        |                                     |  |                                       |   |  |   |   |  |  |
| $\text{C}_{13}\text{H}_{22}\text{O}_2$ | Unsaturated duplicate  | 0.01                                | 0.00                                       | 0.00                                  | 0.00                                      | 0.00                                       | 0.00                                      | 0.00                                      | 0.00                                       | 0.00                                       |
| $\text{C}_{19}\text{H}_{36}\text{O}_2$ | Unsaturated duplicate  | 0.01                                | 0.00                                       | 0.00                                  | 0.00                                      | 0.00                                       | 0.00                                      | 0.00                                      | 0.00                                       | 0.00                                       |
| $\text{C}_{19}\text{H}_{32}\text{O}_2$ | Unsaturated triplicate | 0.03                                | 0.03                                       | 0.06                                  | 0.54                                      | 0.01                                       | 0.05                                      | 0.02                                      | 0.00                                       | 0.00                                       |
| $\text{C}_{23}\text{H}_{38}\text{O}_2$ | Unsaturated triplicate | 0.07                                | 0.05                                       | 0.09                                  | 0.00                                      | 0.04                                       | 0.08                                      | 0.07                                      | 0.00                                       | 0.00                                       |
| $\text{C}_{17}\text{H}_{30}\text{O}_2$ | Unsaturated duplicate  | 0.00                                | 0.00                                       | 0.06                                  | 0.00                                      | 0.00                                       | 0.05                                      | 0.00                                      | 0.00                                       | 0.00                                       |
| $\text{C}_{20}\text{H}_{34}\text{O}_2$ | Unsaturated triplicate | 0.00                                | 0.00                                       | 0.00                                  | 0.04                                      | 0.00                                       | 0.00                                      | 0.00                                      | 0.00                                       | 0.00                                       |
| $\text{C}_{19}\text{H}_{34}\text{O}_2$ | Unsaturated duplicate  | 0.00                                | 0.00                                       | 0.00                                  | 0.02                                      | 0.00                                       | 0.00                                      | 0.00                                      | 24.60                                      | 0.00                                       |
| Total                                  | 0,12                   | 0.08                                | 0.21                                       | 0.60                                  | 0.05                                      | 0.18                                       | 0.09                                      | 24.60                                     | 0.00                                       |  |

The data in Table 1 show that the overall composition of methyl esters of polyunsaturated fatty acids in palm biodiesel is 0.12%, indicating that the quality of the palm biodiesel itself is already quite good to meet fuel criteria, especially considering the high

Rancimat induction period of 21.11 hours. With the implementation of liquid-liquid extraction using  $\text{AgNO}_3$  solvent, the composition of methyl esters of polyunsaturated fatty acids decreased from 0.12% to 0.05%. The injection of nitrogen during the extraction process had no effect on the GC-MS analysis results. This is because the reaction took place over only 3 hours in a tightly sealed Erlenmeyer flask, with low light intensity and moderate stirring speed (150-250 rpm), so the amount of dissolved oxygen in the mixture was likely minimal. Additionally, Table 1 shows that the composition of methanol in the mixture significantly affects the removal of methyl esters of polyunsaturated fatty acids. The best results were obtained from the sample with 5 M, 10%-v methanol, 1:1 (without nitrogen), followed by the sample with 1 M, 10%-v methanol, 1:1 (without nitrogen), and 5 M, 50%-v methanol, 1:1 (with nitrogen injection). As the concentration of  $\text{AgNO}_3$  increases and the percentage volume of methanol in the mixture decreases, the percentage of methyl esters of polyunsaturated fatty acids that can be removed from the palm biodiesel increases. This occurs because the solubility of  $\text{AgNO}_3$  in water is greater than its solubility in methanol, allowing solid  $\text{AgNO}_3$  to mix well in the solution when a much higher amount of water is present, resulting in optimal complex bond formation with the methyl esters of polyunsaturated fatty acids. Even with a small composition, the addition of methanol in the mixture significantly influences the selectivity of the silver nitrate solution for extracting methyl esters of polyunsaturated fatty acids, possibly because the solubility of alpha-linolenic acid methyl ester is much greater than that of oleic acid methyl ester in methanol [5].

### 3.3 Effect of Liquid-Liquid Extraction Process with Silver Nitrate Solution ( $\text{AgNO}_3$ ) on Iodine Number

The iodine number is one of the parameters that can be used to determine the amount of methyl esters of polyunsaturated fatty acids in biodiesel. The iodine number indicates the number of double bonds that can be absorbed by iodine. A lower iodine number signifies a smaller content of methyl esters of polyunsaturated fatty acids in a given biodiesel.

**Table 2.** Iodine number before and after extraction

| Operating conditions | Experimental variation |  |                      | Iodine number (g iod/100g) |                    |
|----------------------|------------------------|--|----------------------|----------------------------|--------------------|
|                      | Concentration          | Comparison of Palm Oil Biodiesel Volume to $\text{AgNO}_3$ | Methanol composition |                            | Nitrogen injection |
| Before extraction    |                        | -  |                      | 51.011                     |                    |
|                      | 1 M                    | 1 : 2  | 10%-v                | No                         | 50.257             |
|                      |                        |  | 25%-v                | No                         | 50.760             |
|                      |                        |  | 50%-v                | No                         | 50.659             |

| Operating conditions | Experimental variation |  |                      | Iodine number (g iod/100g) |                    |
|----------------------|------------------------|--|----------------------|----------------------------|--------------------|
|                      | Concentration          | Comparison of Palm Oil Biodiesel Volume to AgNO <sub>3</sub> | Methanol composition |                            | Nitrogen injection |
| After extraction     | 1 M                    | 1 : 1  | 10%-v                | No                         | 49.755             |
|                      |                        |  | 25%-v                | Yes                        | 40.206             |
|                      |                        |  | 50%-v                | Yes                        | 48.498             |
|                      | 5 M                    | 1 : 1  | 10%-v                | No                         | 47.745             |
|                      |                        |  | 25%-v                | Yes                        | 40.206             |
|                      |                        |  | 50%-v                | Yes                        | 39.045             |

Based on Table 2, it can be seen that the iodine number before extraction is 51.011 g of iodine/100 g. After extraction, the iodine number decreases as the concentration of AgNO<sub>3</sub> and the composition of methanol increase. The difference in the volume of methanol in the mixture does not significantly affect the iodine number; while there is a decrease as the volume of methanol increases, it is not substantial. Table 2 also shows that in the experimental variation of 1 M, 1:1, and 50%-v methanol, the iodine number increases from the previous variation of 1 M, 1:1, and 25%-v methanol. This analysis can be related to the previous discussion on the effect of palm biodiesel extraction on the GC-MS analysis. In the experimental variation of 1 M, 1:1, and 25%-v methanol, the composition of methyl esters of polyunsaturated fatty acids also shows a significant increase. As explained earlier, the percentage volume of methanol should be adjusted according to the concentration of the AgNO<sub>3</sub> solution to ensure that the solid AgNO<sub>3</sub> dissolves well in the mixture. As the concentration of the AgNO<sub>3</sub> solution increases, the volume of methanol in the mixture also needs to increase, and vice versa. This way, the AgNO<sub>3</sub> solution can effectively absorb the methyl esters of polyunsaturated fatty acids, as supported by the results of the GC-MS analysis and the iodine number. Additionally, the purity and shelf life of the samples for analysis must also be considered. Storing samples for an extended period before analysis can affect the results of the Rancimat, GC-MS, and iodine number analyses. Even if stored in tightly sealed containers in a low-light environment at room temperature, the presence of oxygen cannot be avoided when transferring palm biodiesel samples into sample bottles. Although in very small amounts, the presence of oxygen can still lead to oxidation. Therefore, the shelf life of post-extraction samples should be monitored to minimize oxidation. Furthermore, if the biodiesel resulting from extraction is not purified, residual solid AgNO<sub>3</sub> may accumulate at the bottom if the sample is stored for too long. This also underscores the importance of washing biodiesel to remove residual AgNO<sub>3</sub> after extraction.

### 3.4 Effect of Liquid-Liquid Extraction Process with Silver Nitrate ( $\text{AgNO}_3$ ) Solution on the Obtaining of Polyunsaturated Fatty Acid Methyl Esters

In addition to Rancimat analysis, iodine number, and GC-MS, another method to assess the performance of  $\text{AgNO}_3$  in removing methyl esters of polyunsaturated fatty acids is by separating these methyl esters from  $\text{AgNO}_3$ . The separation is conducted through extraction by dissolving the methyl esters of polyunsaturated fatty acids in the organic solvent hexane, followed by distillation. The choice of hexane as a solvent for recovering the methyl esters is based on its low boiling point, allowing for an easy separation process that does not require high temperatures.

This second extraction process was conducted for 60 minutes at a temperature of 50-70°C. A study by Misawa noted that to dissolve oil in hexane, the ratio of hexane volume to methyl ester volume is 3.3:1 [3]. Additionally, Misawa conducted the same experiment with a different ratio of 17.5:1 [3]. Based on Misawa's research, the hexane-to-methyl ester ratio chosen in this experiment is 6:1 for the variation with 30 ml of palm biodiesel and 12:1 for the variation with 15 ml of biodiesel [3]. The stirring speed in the second extraction was set at 200-250 rpm, higher than in the first extraction, to ensure thorough mixing due to the greater volume of solution in the second extraction compared to the first. The methyl esters of polyunsaturated fatty acids dissolved in hexane are then separated from  $\text{AgNO}_3$  by decantation, conducted over 30-60 minutes. The final stage is distillation to further separate hexane from the methyl esters of polyunsaturated fatty acids. Distillation is carried out at 60-80°C, considering hexane's boiling point of 62°C. The volume of methyl esters of polyunsaturated fatty acids remaining after distillation is measured and compared with the initial volume of palm biodiesel

**Table 3.** Obtaining methyl esters of polyunsaturated fatty acids after distillation

| Experiment Variations     | Initial biodiesel volume | Initial PUFA volume based on GC-MS analysis | Final PUFA volume from distillation |
|---------------------------|--------------------------|---|-------------------------------------|
| 1 M, 10%-v metanol, 1 : 1 | 30 ml                    | 3.60 ml                                     | 3 ml                                |
| 1 M, 25%-v metanol, 1 : 1 | 30 ml                    | 3.60 ml                                     | 3.7 ml                              |
| 1 M, 50%-v metanol, 1 : 1 | 30 ml                    | 3.60 ml                                     | 3.9 ml                              |
| 1 M, 10%-v metanol, 1 : 2 | 15 ml                    | 1.80 ml                                     | < 0.5 ml                            |
| 1 M, 25%-v metanol, 1 : 2 | 15 ml                    | 1.80 ml                                     | 1 ml                                |
| 1 M, 50%-v metanol, 1 : 2 | 15 ml                    | 1.80 ml                                     | 1.3 ml                              |
| 5 M, 10%-v metanol, 1 : 1 | 30 ml                    | 3.60 ml                                     | 0.5 ml                              |
| 5 M, 25%-v metanol, 1 : 1 | 30 ml                    | 3.60 ml                                     | 2.5 ml                              |
| 5 M, 50%-v metanol, 1 : 1 | 30 ml                    | 3.60 ml                                     | 4.5 ml                              |

Based on the data in Table 3, it can be seen that in some experimental variations, such as 1 M, 25%-v methanol; 1:1, 1 M, 50%-v methanol, 1:1; and 5 M, 50%-v methanol, 1:1, the final volume of methyl esters of polyunsaturated fatty acids obtained is actually greater than the calculated volume of methyl esters of polyunsaturated fatty acids GC-MS analysis. This may be due to the distillation process, where the hexane did not completely separate and remained in the oil, thereby being measured together with the methyl esters of polyunsaturated fatty acids. Therefore, the ratio between the volume of methyl esters of polyunsaturated fatty acids and the initial volume of palm biodiesel cannot yet be used as an indicator of  $\text{AgNO}_3$ 's effectiveness, unless GC-MS analysis is performed to confirm the percentage of methyl esters of polyunsaturated fatty acids present in the oil after distillation.

## 4 Conclusions

Based on the research conducted, it can be concluded that methyl esters of polyunsaturated fatty acids were successfully removed from palm biodiesel through extraction with silver nitrate and adsorption with silver acetate, although this did not improve the oxidative stability of the biodiesel. Liquid-liquid extraction with silver nitrate as a solvent to remove methyl esters of polyunsaturated fatty acids from palm biodiesel was performed at a temperature of 25-35°C for 3 hours with a stirring speed of 150-250 rpm and nitrogen injection, followed by separation of the mixture for 30 minutes. The best extraction results were obtained with a sample using a silver nitrate solution concentration of 1 M, 50%-v methanol in the solution, and a biodiesel-to-silver nitrate solution volume ratio of 1:2, resulting in a post-extraction composition of 0% polyunsaturated methyl esters and an iodine value of 50.659 g iodine/100 g.

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