

Synthesis of Methyl Ester Nitrate from Mahogany Seed Oil (*Swietenia mahagoni* Linn)

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Abstract

Nitration of methyl ester from mahogany oil (*Swietenia mahagoni* Linn) can be produced by Methyl Ester Nitrate (MEN), an additive that is useful for increasing Cetane Numbers in diesel fuel. This study aims to determine the yield of MEN that can be produced from mahogany seed oil after esterification, trans-esterification, and nitration and to identify the MEN compounds produced. Mahogany oil is obtained by pressing mahogany seeds and then degumming to remove the gum. Mahogany oil-free gum is esterified using methanol with the mole ratio of oil: methanol (1: 6), then trans-esterified, also using methanol with mole ratio (1:15) and a methyl ester is obtained. Then the methyl ester was nitrated with HNO<sub>3</sub>, sulfuric acid, and acetic anhydride to obtain a translucent reddish colored MEN product with a yield of 24.99%. The success of the synthesis was shown by the FTIR spectrophotometer in the presence of absorption at 1550 cm<sup>-1</sup> which indicated the presence of the C-ONO<sub>2</sub> group, the absorption at 1365 cm<sup>-1</sup> indicated the presence of the NO<sub>2</sub> group, and at 1118 cm<sup>-1</sup> indicated the presence of the C-N group. The reaction mechanism that occurs during the predicted nitration reaction is an electrophilic substitution reaction and nucleophilic addition.

Keywords: Esterification, Mahoni, methyl ester nitrate, trans-esterification, nitration

INTRODUCTION

The source of energy is one of the most basic needs for human life. Energy needs also continue to increase along with the increase in population and technological advancement. The increase in the population leads to an increase in the use of energy which includes the household, industry, transportation and so on which results in a reduction in the supply of fuel (fuel oil) and a decrease in the quality of fuel, especially diesel fuel (Kholiq, 2015). Low-quality diesel oil is shown by the cetane number which is less than 48. Diesel fuel in Indonesia is particularly low. subsidized has a reduction in methane 47. This requires a transient effort to increase the quality of diesel fuel by an approach to increase the value of the energy value by adding an additive.

One alternative that can be done to increase the amount of methane in waste materials is by using or adding additives such as Ethyl Hexyl Nitrate (EHN), which is a synthesis product of natural oil derivatives and can also be added to the derivative of nutrients synthesized from vegetable oil (Cahyono, 2014). Several types of additives that can be added to diesel fuel are used to improve performance and improve the

quality of fuels such as amyl nitrate, butyl nitrate, ethyl ether, and fatty acids. The additives in diesel can increase the fuel burnt. Additives for diesel fuel have many uses and effects because they can improve engine performance and reduce exhaust emissions (Saputra, Wicaksono, & Irsan, 2018).

The use of EHN as an additive has weaknesses, for example, organic nitrate compounds that are synthesized from natural oil derivatives where the ingredients are not renewable, apart from being relatively expensive because the synthesis process has a fairly long path (Nasikin, Arbianti, & Azis, 2010). Therefore, alternative raw material is needed for the synthesis of additives from vegetable oil with the methyl ester or biodiesel method. One of the other materials that can be used is mahogany oil (*Swietenia mahagoni* Linn) (Cahyono, 2014).

Synthesis of MEN from mahonide oil can be carried out after it has been synthesized as a methyl ester. Synthesis of ethyl esters is carried out through pressing, degumming, esterification, and transesterification step. Degumming is a process of separating mucus or sap in oil and reducing free fatty acids in oil (Meilano, Soetjipto, & Cahyanti, 2017). The esterification reaction is a reaction between carboxylic

acids and alcohols to form esters (Aziz, Nurbayti, & Ulum, 2012). Transesterification is a process that reacts triglycerides in vegetable oil or animal fat with short-chain alcohols such as methanol or ethanol to produce fatty acid methyl esters or biodiesel and glycerol as a by product (Muhammad, Jatranti, & Hakim, 2014).

Nitration is a chemical process that aims to enter the nitro group into compounds. Nitration can be added because there is a mixture of nitric acid ( $\text{HNO}_3$ ) and acetic acid hydride as a catalyst (Junaidi, Ghofur, & Wicakso, 2012). Several studies related to the additives of vegetable oil have been carried out, among others, from wastewater from palm oil (Sundaryono, 2011), from palm oil and the Linn (Mardawati, 2019). In this study was conducted the synthesis of methyl ester nitrate from mahogany seed oil (*Swietenia mahagoni* Linn).

## METHODOLOGY

### Materials and Instrumentals

The tools used in this research are a set of reflux tools, hot plate, gel (Pyrex), chemical beaker (Pyrex), Erlenmeyer (Pyrex), funnel (Pyrex), separating funnel (Pyrex), spatula, dropper, vial, dark bottle, stirring rod, thermometer, oven, static, clamp, analytical gauge, magnetic stirrer, hot plate, and hydraulic press. The FTIR (Fourier Transform Infrared) brand IR Buck M500 Scientific is also used. The materials used are seed oil, n-hexane, acetic acid hydride p.a, diethyl ether ( $(\text{C}_2\text{H}_5)_2\text{O}$ ), sodium sulfate ( $\text{Na}_2\text{SO}_4$ ), potassium chloride (KOH) pa, citric acid ( $\text{HNO}_3$ ) pa, acetate anhydride ( $\text{CH}_3\text{CO}$ ) $_2\text{O}$ , acid sulfate ( $\text{H}_2\text{SO}_4$ ) pa, Whatman filter paper, phenolphthalein indicator, aluminum foil, tissue, and distilled water.

### Methods

#### Mahogany Fruit Sampling

The mahogany samples used in this study were obtained from Anduonohu Village, Poasia District, Kendari City, Southeast Sulawesi.

#### Mahogany Seed Oil Preparation

The seeds obtained after separating the seeds and fruit shells are aerated at temperature for two to three days. Furthermore, the seeds are refined using a refining machine (blender) so that the seeds are obtained. The dried seeds are refined in a blender and then the powder is pressed using a hydraulic press and dirty oil is produced. Impurity is separated.

The pressed oil is degumming with the addition of 0.4 mL of 20%  $\text{H}_3\text{PO}_4$  solution and then put in a 150 mL chemical beaker that contains 100 mL of

mahogany oil. Then the solution is heated at 80 °C for 15 minutes, then stirred using a magnetic stirrer, then it is put in a separate push, cooled, left to stand until it is in two-phase form, with a lower phase (sediment or sap) and upper phase (mahogany oil). Subsequently, the filtrate (upper phase) obtained was washed with 30 mL very high strength at a temperature of 60 °C while stirring using a magnetic stirrer for 15 minutes then put in a separate wheel and left to stand in two-phase form, the lower phase is water and the upper phase is oil. Washing is repeated until the pH of the oil is neutral. Furthermore, it is heated at a temperature of 105-110 °C to remove the remaining water which is indicated by the absence of water bubbles (Damayanti & Bariroh, 2012).

### Esterification-Transesterification Reaction

Esterification is carried out by reacting the oil with methanol at the mol ratio (1:15) using a 1% sulfuric acid catalyst ( $\text{H}_2\text{SO}_4$ ). The first step begins by inserting the degumming result oil in a second laboratory that has been equipped with a condenser and a heater. The sample was then heated to a temperature of 65°C while slowly adding methanol and sulfuric acid ( $\text{H}_2\text{SO}_4$ ) was stirred using a magnetic stirrer for one hour. The resulting reaction mixture is then put in a separate tube and left to stand for 24 hours until it forms two phases. The bottom phase was taken and then washed with warm water until the pH was neutral (Mohan, Jala, Kaki, Prasad, & Rao, 2016).

Transesterification is carried out by reacting the oil esterification results with methanol at a molar ratio (methanol: oil) which is (6: 1) with 1% (w / v) KOH catalyst of robot oil (Damayanti & Bariroh, 2012). Initially, the esterification result is inserted into the second laboratory which has been equipped with a condenser and ambient heat stirred then heated to 60°C, methanol, and KOH are added slowly by stirring using a magnetic stirrer for one hour. The reaction is then stopped then the sample is put in a separate tube and allowed to stand for 24 hours until it forms two phases. The upper phase is taken and washed with me very to the point of neutral. The remaining water during washing is removed by heating at a temperature of 105-110 °C (Santos, Malveira, Cruz, & Fernandes, 2010).

### Nitration Reaction

Nitration is treated by adding 2.9 mL of nitric acid to 0.07 ml of  $\text{H}_2\text{SO}_4$  and with 2.1 mL of acetic anhydride catalyst in the triple tablet. Next, add 2.3 mL of methyl ester which is done by adding dropwise then the solution is refluxed for 30 minutes at 28-300 °C

with stirring using a magnetic stirrer at 200 rpm. The resulting product is then put into a separator that has been filled with 200 mL of water and 25 mL of diethyl ethers while stirring, then it is allowed to stand for several times until it forms two phases where the upper phase is a methyl ester nitrate and the lower phase is water and the residual acid is separated using algae.

#### **Identification with a Spectrophotometer Fourier Transform Infrared (FTIR)**

The composition of the methyl ester (ME) and the synthesized ethyl ester nitrate (MEN) from mahogany seed oil were identified by using the FTIR spectrophotometer with the IR Buck M500 Scientific brand at a wavelength of 4000-400  $\text{cm}^{-1}$  with 32 seconds of the scan, 4 resolution, and 80 Torr pressure.

### **RESULTS AND DISCUSSION**

#### **Mahogany Oil Preparation (*Swietenia mahagoni* L.)**

The oil of mahonide is obtained from the seeds of mahogany which have been separated from the outer shell and then dried in the sun for two to three days to reduce the water level. Reducing the water content of the seeds is also intended to make it easier to press the seeds of seeds to obtain more optimal oil (Musta, Haetami, & Salmawati, 2017). The pressing process is carried out using a 20-tonne hydraulic press.

The mahogany oil obtained is colored yellowish black with bouquets. The obtained mahogany oil still contains impurities that cannot be dissolved in the oil as shown in Figure 1a, then it is filtered before further purification by degumming.

#### **Degumming**

Mahoni oil obtained through the pressing process, after being filtered, still contains a lot of impurities, for that reason, it will be grumbling to separate the resin or mucus which consists of phosphatide, protein, residue, carbohydrates, water, and resin. The substance that is usually used to attract gum (sap) is phosphoric acid ( $\text{H}_3\text{PO}_4$ ) (Hasibuan, Sahirman, & Yudawati, 2013). The precipitate formed from the degumming results indicates that the phosphorus acid has bound the impurities in the oil. The phosphatide deposits formed were separated using filter paper (Prihanto & Rahayu, 2015). After degumming, the mahogany oil which was previously dark in color, thick and smelled clearer and colored reddish as shown in Figure 1b, this is also by (Musta et al., 2017; Rezki, Musta, & Haetami, 2017; Sutapa, Rosmawaty, & Samual, 2013).

#### **Esterification-Transesterification Reaction**

Esterification is used as a preliminary process to convert Free Fatty Acid to methyl ester to reduce FFA levels in vegetable oils before being transesterified with base catalysts to convert triglycerides into methyl esters (Hasahatan, Sunaryo, & Komariah, 2012).

Transesterification is the process of cutting long chains of glycerides into short-chain esters. Alkyl esters can be obtained from the reaction result of vegetable oils with an amount of alcohol through the help of catalysts. The reaction results in addition to producing alkyl esters also produce byproducts in the form of glycerols. Transesterification reactions run slowly, so base catalysts are needed to reduce the activation energy and accelerate the reaction (Muhammad et al., 2014). Damayanti & Bariroh (2012) state that transesterification is a step in breaking down triglycerides (vegetable oils) into alkyl esters, which are reacted with alcohol and produce a side product of sugar.

The effectiveness of the transesterified reaction is influenced by a variety of factors. But the most influential are the mole factor (oil: methanol), temperature, stirring, and catalyst. The more the amount of methanol used, the more methyl ester produced also increases. The increase in resistance shifts the equilibrium towards the product so that it is expected that the maximum number of products is formed. Meanwhile, the transesterification process can be carried out with either NaOH homogeneous catalysts (Fransina, Sutapa, & Hehanussa, 2013) and heterogeneous catalysts such as CaO (Bandjar, Sutapa, Rosmawaty, & Mahulau, 2014).

#### **Nitration Reaction**

Nitration is the process of entering the nitro group into organic compounds or other minerals using a mixture of nitric acid and sulfuric acid. The nitrate process can be divided into 2 types, namely the manufacture of nitro compounds and the manufacture of nitrate esters. The nitro ion can be generated from the interaction of nitric acid with sulfuric acid as a catalyst. Through the titration of the methyl ester, the amount of oxygen-molecular components of the methyl ester increases so that the methyl ester has more oxygen, which is very necessary for the perfection of the combustion process so that it increases diesel fuel additives. Nitracymethyl ester of mahonide oil with acetic hydride and sulfuric acid produced a translucent red color product as shown in Figure 1c.

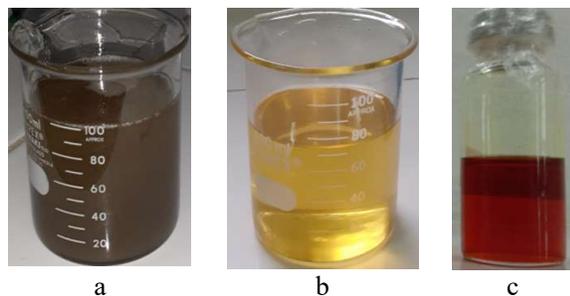


Figure 1. a) Mahogany pressed oil; b) Mahogany degummed oil; c) MEN

The absorption of group C=C on the wavenumber of  $1658.78\text{ cm}^{-1}$ , the absorption of the group CH<sub>2</sub> in the shown in  $1435.04\text{ cm}^{-1}$ , the C-OH bond shown in  $1033.85\text{ cm}^{-1}$  and the absorption of the OH group at the wavenumber  $3471.87\text{ cm}^{-1}$ . The results of the interpretation obtained show that there is an agreement with (Mursiti, Fitriani Rahayu, Maylia Rosanti, & Nurjaya, 2019) and (Sumartono, Wahyono, Latifah, Pratiwi, & Siswani, 2018).

As for the uptake of methyl ester nitrate, it showed that there were several different peaks with the FTIR spectrum of mahogany oil, among others, at the wavenumber of  $1550\text{ cm}^{-1}$  which was predicted as the

Table 1. Comparison of infrared absorption peaks

Vibration	Wavenumber ( $\text{cm}^{-1}$ )			
	Sampel Mahogany Oil	Mahogany Oil (Mursiti et al., 2019)	MEN Sample	Menthyl Esther Nitrate (Abdullah et al., 2012)
O-H	3471.87	3550-3200	-	-
C-CH <sub>3</sub>	2924.04 and 2854.65	3000-2800	-	-
C=O	1743.65	1740-1720	-	-
C=C	1658.78	1620-1680	-	-
C-ONO <sub>2</sub>	-	-	1550	1545-1660
NO <sub>2</sub>	-	-	1365	1300-1500
C-N	-	-	1118	1180-1360
CH <sub>2</sub>	1435.04	1470-1450	-	-
O-CO	1373.32	1320-1210	-	-
C-OH	1033.85	-	-	-

### The FTIR Spechtrophotometer Characterization

Identification using FTIR instrument aims to determine its functions, thus the FTIR spectrum of mahogany oil shows that water can absorb the functions, including the absorption of the C-CH<sub>3</sub> group at wavenumber  $2924.09\text{ cm}^{-1}$  and  $2854.65\text{ cm}^{-1}$ .

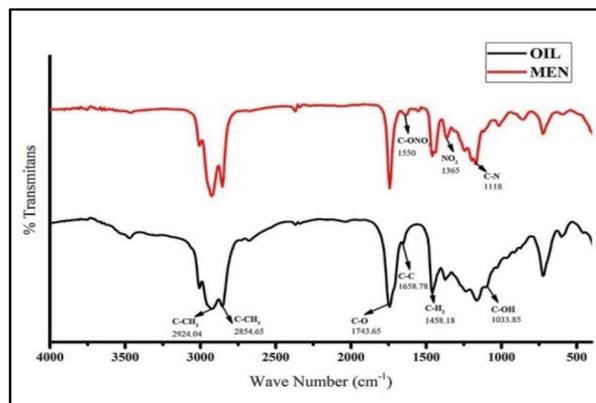


Figure 2. The IR Spectrum Comparison of Oil and Mahogany MEN

presence of C-ONO<sub>2</sub> and C=C bonds in the methyl ester molecule, as well as at the wavenumber of  $1365\text{ cm}^{-1}$  which was predicted as NO<sub>2</sub> bonding with C-N at the wavenumber of  $1118\text{ cm}^{-1}$ . The words of these waves correspond to the numbers of O-NO<sub>2</sub> waves formed in the research conducted by (Junaidi et al., 2012).

The interpretation of the IR spectrum showed the production of synthetic methyl ester nitrate (MEN) from methyl ester, sulfuric acid, and nitric acid and predicted as Figure 2 (Diop, Ben Talouba, Balland, & Mouhab, 2019) reported that methyl ester nitrate is formed from the nitro group and nitrate groups on methyl ester double bonds. The results of the nitration which showed the inclusion of nitro and nitrate groups in the methyl ester of mahonide oil can be clarified by the predicted reaction mechanism based on the presence of groups formed and identified through IR absorption at  $1550\text{ cm}^{-1}$  (C-ONO<sub>2</sub>) and,  $1365\text{ cm}^{-1}$  (NO<sub>2</sub>) and  $1118\text{ cm}^{-1}$  (C-wave-N) angels. The reaction mechanisms that take place are predicted to be a sub-site electrophilic (SE) and addition nucleophilic (AN) as shown in Figure 3.

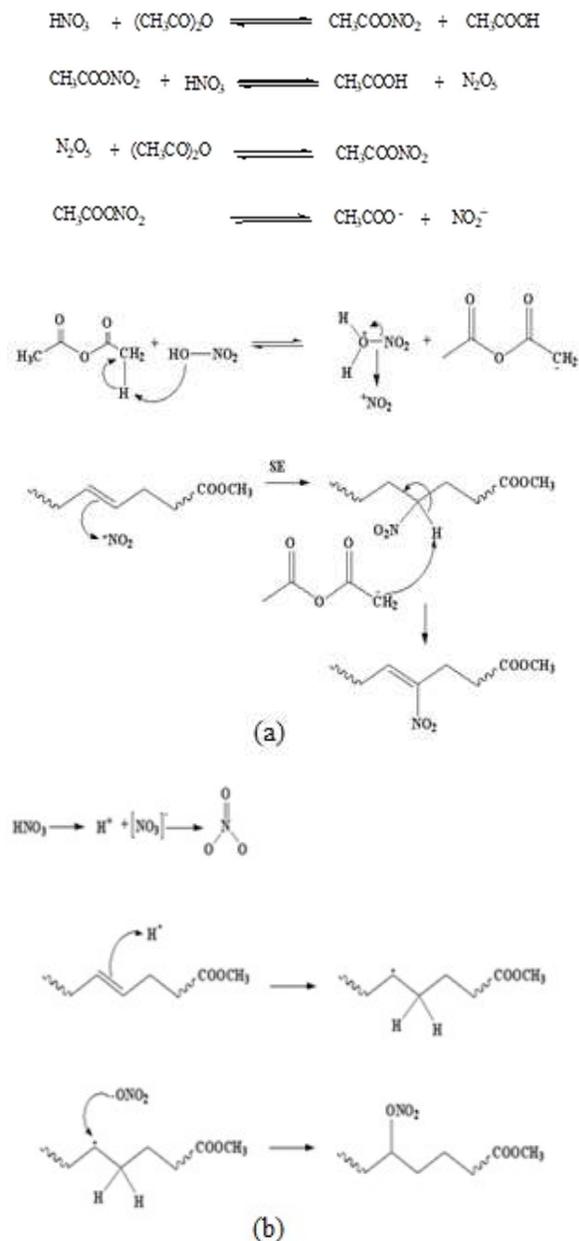


Figure 3. Mechanism Reaction Prediction of MEN by (a) electrophilic reaction and (b) nucleophilic reaction.

## CONCLUSION

Nitration of methyl ester oil produced a translucent reddish product with a yield of 24.99%. Characterization of methyl ester nitrate (MEN) by FTIR spectrophotometer showed absorption at  $1550\text{ cm}^{-1}$  which indicated the presence of C-ONO<sub>2</sub> groups, absorption at  $1365\text{ cm}^{-1}$  indicated the presence of NO<sub>2</sub> groups as well as at  $1118\text{ cm}^{-1}$  indicated the presence of C-N groups.

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