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Ende natural zeolite as a catalyst in the biodiesel production from nyamplung oil

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ABSTRACT

Fuel use as a primary energy source is increasing daily, and the reserves of these natural resources are diminishing quickly. Different studies have been performed to see the potential use of the seeds of the Nyamplung plant (*Chalophyllum inophyllum L.*) as biodiesel. To produce biodiesel from Nyamplung oil, a catalyst, such as zeolite, is often required to speed up the reaction, save energy use, and increase the quantity and quality of the biodiesel. There is a high variation in terms of natural zeolite's catalytic activity, depending on the location where the zeolite was formed in the past. The objectives of this study were to characterize and understand the Ende natural zeolite, before and after activation, and to see the catalytic activity of the HCl-activated zeolite in the production of biodiesel from Nyamplung oil. When zeolite was used as a catalyst, optimum effects on the esterification were observed at 700 rpm stirring speed with a reaction time of 15 minutes. These conditions optimally converted 100% of Nyemplung oil into biodiesel.

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1. INTRODUCTION

An increase in the number of human activities requires fuel as the main energy source on a daily basis [1]. However, oil reserves as the main raw material are also depleting very quickly [2]. Different alternatives for energy sources have also been developed lately, such as nuclear and solar energy, but these alternatives often pose high production costs [3, 4]. Biodiesel production has also got its share of attention as an alternative energy source [5]. There have been different research on biodiesel commodities, and one of them is to produce it from the seeds of the Nyamplung/Tamanu plant (*Chalophyllum inophyllum L.*), which often grows in coastal and lowland areas [6]. Indonesia, as an archipelagic country, has its advantage due to its vast coastal region overgrown by Nyamplung plants [7].

The production of biodiesel from the seeds of the Nyamplung plant is considered more economical due to the large number of seeds that can be produced by one tree [8]. In addition, Nyamplung is not consumed, so its utilization can be focused only on biodiesel production [9]. Another advantage of Nyamplung is its relatively fast and fruitful growth throughout the year. It has a high adaptability to tropical climates and does not require any special treatment for its growth

[9]. Ecologically, Nyamplung is also a type of mangrove that protects coastal areas from abrasion [10], adding up the value of planting this tree in the Indonesian coastal region.

Biodiesel from Nyamplung seed oil is made through an esterification or transesterification process [11]. This process requires catalysts to speed up the reaction, save energy, and increase the quantity and quality of the biodiesel yield [12]. The widely used catalyst is often a homogenous catalyst which has a similar phase to the product, making it hard to separate them after the reaction completes [13]. Because of that, the use of heterogeneous catalysts, including zeolite minerals, can be an option [14]. As a mineral, zeolite consists of a silica-alumina component. Its synthetic form, zeolite socony mobile-5 (ZSM-5), has been proven to be one of the best catalysts out there [15]. However, the use of synthetic zeolite comes with a great price that increases the overall production cost, opening up the possibility of employing natural zeolite as a cheaply abundant alternative to ZSM-5 [16].

Indonesia has abundant natural zeolite reserves, including in Ende Regency, East Nusa Tenggara Province [17]. However, a natural zeolite often comes in non-uniform pore sizes filled with different impurities that reduce its catalytic activity and chemical stability under thermal conditions [18]. Therefore, natural zeolite must be activated and modified first before it can be used as a catalyst in biodiesel production [19]. Among all the many variations in the activation procedures, the best results were shown by the natural zeolite activated and modified with hydrochloric acid (HCl) treatment only when compared to the one that was modified with a combination of HCl and metal impregnation [20]. For example, in the esterification of vegetable oil, the most effective percentage of zeolite as a catalyst was shown to be 3% of the total reactant used [21]. The activation of Wonosari natural zeolite with 6 N solution of HCl converted 100% of the feedstock into biodiesel at 60 °C [22]. With the same treatment, natural Bayah zeolite (originated from Sukabumi, West Java) that mostly consists of mordenite crystal could convert up to 70% of glycerol at 60 °C [23].

Despite its potency, the properties of natural zeolite vary greatly from one region to another. This is largely due to the environmental factors where the zeolite was formed in the past [24]. The variation in the properties of the natural zeolite provides an opportunity to explore the characteristics of the mineral from different regions in Indonesia, allowing a better understanding of their utilization as a catalyst in different chemical reactions [25]. By doing this, we expect to have a better understanding of the characteristics of the cheaply available natural zeolite from the seashore of Ende District in Flores, East Nusa Tenggara, which has never been researched before. This knowledge will be very useful in the future to develop an alternative to the expensive synthetic zeolite by using what nature has already provided for us. Because of that, the objectives of this study were to characterize and understand the Ende natural zeolite, before and after activation. The catalytic activity of Ende zeolite in biodiesel production from Nyamplung oil through esterification reaction, especially after its activation with hydrochloric acid (HCl), was the highlight of this research. This study mainly focused on the effects of adding an activated natural zeolite as a catalyst towards the stirring speed and the production of methyl ester biodiesel in the esterification of Nyamplung oil.

2. RESEARCH METHODS

2.1. Materials and Tools

The materials used included Ende natural zeolite, Nyamplung oil, ion-free water (aquades), methanol, and 6 M of HCl. The tools used in this study were analytical balance, sieve mesh (size 100), oven, mortar, porcelain dish, triple neck flask (500 ml), thermometer, magnetic stirrer, electric heater, furnace, condenser pipe, stopwatch, X-ray diffractometer (Shimadzu XRD-6000), spectrometer ^{1}H NMR (JEOL JNM-MY60).

2.2. The Activation of Ende Natural Zeolite

Ende natural zeolite rocks were crushed into a fine grain and then placed onto a sieve mesh until they produced 200 mg of powder. After that, the powder of the natural zeolite was soaked in 400 ml of HCl solution (6 M) and then refluxed at 90 °C for 30 minutes while mixing the slurry with a magnetic stirrer. After this process, the zeolite was assumed to be activated, and the sludge was washed with ion-free water (aquades) until the pH of the mixture reached 7.0 [26]. The activated zeolite was then dried

in an oven at 120 °C and then calcinated at 400 °C in a furnace [27]. The resulting activated zeolite would now be called H-Zeolite.

2.3. The Characterization of Ende Natural Zeolite

A characterization of the zeolite before and after activation was conducted with an X-ray diffractometer (XRD) at observation areas between 10 – 90°. This procedure was to determine the changes in the composition and the crystallinity of the mineral after an activation process. The characterization with XRD would generate quantitative and qualitative data related to the crystallinity of the mineral. A follow-up qualitative analysis was carried out by comparing the values of 2θ and *d* (Å) of the samples with the zeolite standard from the International Centre for Diffraction Data. The difference in the *d* value of the sample with the ICDD data was not more than 0.2 [28]. The quantitative analysis was obtained by comparing the diffractogram region of each sample with the standard zeolite diffractogram data, and a calculation was performed using the following equation:

$$\%crystal = \frac{Sample\ intensity\ (\%)}{Standard\ intensity\ (\%)}\ [29] \quad (1)$$

2.4. The Preparation of Nyamplung Oil

Nyamplung oil was filtered to separate any visible impurities, and then heated at 100 – 120 °C for 15 minutes to reduce any moisture content. The resulting products from this procedure were then divided into a separating funnel that separated the agglomerated solid from the oil [11].

2.5. The Esterification of Nyamplung Oil

The obtained Nyamplung oil was then poured into a triple neck flask that acted as a reflux apparatus in which the esterification process for each treatment took place. H-Zeolite catalyst, 3% of the volume of Nyamplung oil (w/v), and methanol (molar ratio of 1: 9) were fed into the reflux apparatus that already contained the oil. The esterification procedure was carried out at 60 °C with differences made in the stirring speed and the reaction time [21]. The treatment variations were performed in two factors with four levels. The stirring speed was performed at four speed levels: 350 rpm, 700 rpm, 1100 rpm, and 1200 rpm. On the other hand, the reaction time was adjusted to 15 minutes, 30 minutes, 45 minutes, 60 minutes, and 120 minutes [30]. The esterified oil was further filtered to get it separated from the heterogeneous catalyst. After that, the filtered oil was centrifuged to separate any impurities. A distillation procedure was then performed to separate the remaining water and methanol from the oil.

2.6. The Analysis of Methyl Ester Biodiesel Levels

The oil was analyzed with a ^{1}H NMR spectrometer after the esterification procedure was completed. It was calculated in the following equation:

$$C_{MAND}{}'\% = 100\ x\ \frac{51_{ME}}{51_{ME}+91_{TG}}\ [31] \quad (2)$$

The following equation was used to determine the percentage of the residual triglycerides (TG) in the product:

$$C_{TG}{}'\% = 100 - C_{ME} \quad (3)$$

The equation below was used to determine the remaining TG in the product where the units were of weight percentage:

$$TG, \frac{b}{b} = \frac{C_{TG}xMW_{TG}xd_{TG}}{(C_{TG}xMW_{TG}xd_{TG})+(C_{ME}xMW_{ME}d_{ME})} \quad (4)$$

Notes:

C_{ME} : conversion into methyl ester biodiesel (%)
I_{ME} : peak integration value of methyl ester biodiesel (%)
I_{TG} : peak integration value of triglycerides (%)
C_{TG} : unconverted triglycerides (%)
MW_{TG} : molecular weight of triglycerides (g.mol^{-1})

MW_{ME} : molecular weight of methyl ester biodiesel ($g.mol^{-1}$)
d_{TG} : triglyceride density ($kg.m^{-3}$)
d_{ME} : density of methyl ester biodiesel ($kg.m^{-3}$).

3. RESULTS AND DISCUSSIONS

3.1. The Characteristics of Ende Natural Zeolite

This research was conducted to better understand the characteristics of the cheaply available natural zeolite from the seashore of Ende District in Flores, East Nusa Tenggara. This kind of research was previously conducted on the natural zeolite from other regions in Indonesia, but not particularly for biodiesel production catalyzed by natural zeolite from the Ende district. The active Ende natural zeolite in this study was mainly utilized as a catalyst in Biodiesel production from Nyamplung oil, by observing its catalytic effects towards the stirring speed and the methyl ester content throughout the entire esterification reaction.

Figure 1 shows the results of XRD analysis for Ende natural zeolite before and after activation with HCl. The identification of the sample was carried out qualitatively and quantitatively. This process was conducted to determine the types of minerals that make up the natural zeolite and the degree of crystallinity by identifying the three highest peaks in the diffractogram of Ende natural zeolite. The peaks in Figure 1 showed that the natural zeolite consisted of 36.63% of mordenite crystal (2θ: 26.70°/d (Å): 3.33), 6.18% of clinoptilolite crystal (2θ: 25.80°/d (Å): 3.45), and 5.39% of quartz crystal (2θ: 27.80°/d (Å): 4.23).

After activation from its natural form into H-Zeolite, the main composition appeared to have the following changes: 55.27% of mordenite crystals (2θ: 26.78°/d (Å): 3.31), 5.21% of clinoptilolite crystal (2θ: 25.76°/d (Å): 3.43), and 5.69% of quartz crystal (2θ: 21.05°/d (A): 4.21). The environmental conditions where zeolite was formed in the past really affect its composition. Flores Island lies in the ring of fire that has an effect on the alteration process of the magma that flows towards the sea, forming the currently observed mineral composition within Ende natural zeolite [17]. The activation procedure with HCl only increased the phase crystallinity of mordenite due to the structural rearrangement of these crystals that are more prone to attack from HCl. On the other hand, the phase crystallinity of quartz did not appear to be affected due to its more stable structure, whereas the decrease in clinoptilolite crystal may be related to the structural destruction caused by HCl.

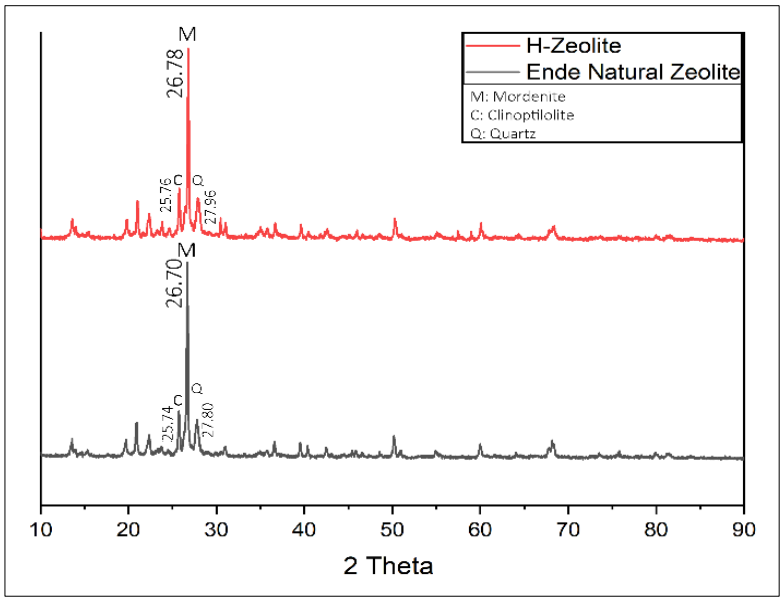

Figure 1. The results of XRD analysis before and after the activation with HCl.

The crystal arrangement of clinoptilolite, a 4-ring structure, will collapse in HCl solution, leading to a detachment and dissolvement of the Aluminum (Al) atoms from within the zeolite's skeleton into the solution [32]. In this process, the elemental Al will eventually come out as aluminum chloride ($AlCl_3$), whereas the ones that remain within the skeleton will appear in the form of aluminum hydroxylate ($Al(OH)_3$) [19]. Under hydrothermal conditions, tectosilicates ($Si(OH)_4$) will then form a new crystalline phase within the zeolite's skeleton, leading to an increase in the mordenite crystal [19]. Figure 2 presents the overall mechanism of a dealumination reaction that may have occurred within the zeolite's skeleton during activation with an acid solution.

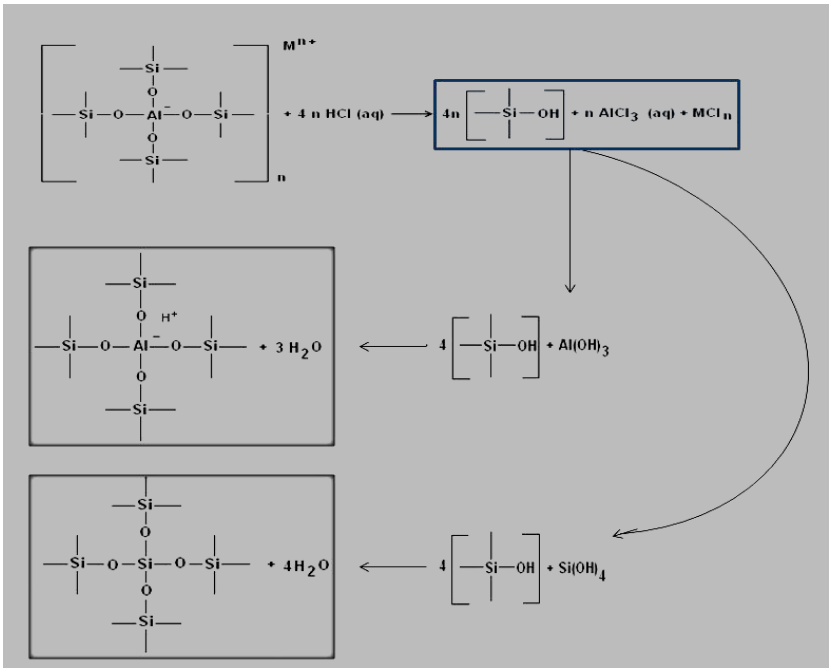

Figure 2. The dealumination process within the zeolite's skeleton (adapted from [19]).

Acid-mediated activation of zeolite often releases Al atoms and other cations from within the zeolite's skeleton. The empty molecular space within the zeolite's structure will then be filled with Silica (Si) atoms, thus increasing the Si/Al ratio in the zeolite [19]. The use of HCl also allows the hydrogen protons (H^+) from HCl to penetrate the skeleton and form additional active sites within the skeleton, producing a more reactive zeolite [20].

Evidently, a decrease in the *d* value and a shift in the 2θ towards a larger value after acid treatment of natural zeolite are also an indication of a decrease in the mineral's volume [28]. A shrinking volume of zeolite is positively correlated to an increase in the outer surface of the mineral, allowing more substrates to react with the zeolite during catalysis. An increase in the acidity and the surface area of zeolite allows easier penetration and diffusion of the reactants into its pore channel, reducing the reaction time for the conversion of Nyamplung oil into biodiesel [33].

The calcination of zeolite at 400 °C widens the pore channel [27]. The pore channels are microreactors that help break the long hydrocarbon chain of triglycerides and perform a molecular rearrangement of the reactants into methyl ester biodiesel [20]. Furthermore, the heat-stable modernite crystal found as the major component of Ende natural zeolite is well suited for a high-temperature reaction. This structural stability and integrity will not be easily destroyed by the high temperature in the reaction.

3.2. The Effect of Stirring Speed on the Biodiesel Conversion from Nyamplung Oil

Figure 3 shows the effect of stirring speed in the reaction catalyzed by H-Zeolite to produce biodiesel from Nyamplung oil. Stirring is usually performed to increase the reaction speed because this

process will allow the oil particles to move freely and collide with each other, splitting them into methyl ester [33]. As a heterogeneous catalyst, H-Zeolite used in the production of biodiesel from Nyamplung oil forms solid and liquid phases [22]. The liquid phase consists of oil and methanol which have different polar properties [16]. The reaction rate at this initial step is low due to a relatively low mass transfer in a heterogeneous chemical system. The reaction rate then increases over time, after more methyl ester has reacted with methanol [20].

The stirring speed has a major effect during the initial step of the reaction, producing more methyl ester inside the chemical system. As the reversible reaction keeps progressing, the increasing concentration of the products will push the reaction back into the reactants' side, negating the production of biodiesel from Nyamplung oil. In general, the stirring speed in the esterification for biodiesel production ranges from 350 - 1200 rpm. The bigger the stirring speed, the bigger the conversion of triglyceride into methyl ester, but it also increases the energy demand for that particularly high stirring speed.

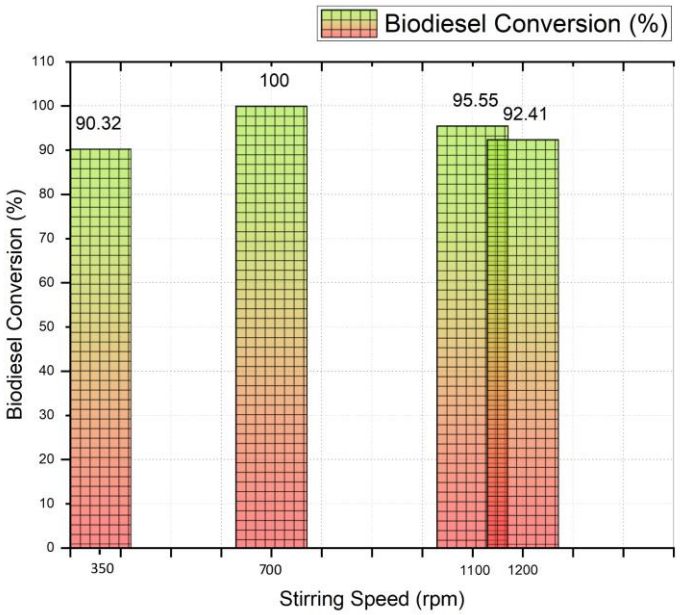

Figure 3. The effect of stirring speed with active H-zeolite as a catalyst on the production of biodiesel from Nyamplung oil.

Figure 3 shows that 700 rpm stirring speed converted 100% of the reactants into biodiesel. As previously mentioned, the bigger the stirring speed, the more methyl ester biodiesel can be produced. However, when zeolite was added as a catalyst, an increase in the stirring speed did not have any significant effect anymore into the conversion's yield. The optimum stirring speed in this experiment (700 rpm) increased the likelihood of collisions between the chemicals in the solution, allowing 100% conversion into biodiesel.

As seen in Figure 3, in the presence of the catalyst, a further increase in the stirring speed above 700 rpm did not have any better effect on the biodiesel yield. These data pointed out that the rate of esterification reaction was affected by the interaction of the catalyst and the reaction temperature. If the stirring speed was increased even more, the collision between the chemicals in the solution would only negatively affect the conversion of the Nyamplung oil into methyl ester biodiesel, decreasing the biodiesel yield [34]. An increase in the stirring speed was also suspected to have an effect on higher water by-products (data not available). Nyamplung oil always has some water content in its liquid, and the water content is directly proportional to the availability of triglyceride. An increase in the water content in the zeolite-catalyzed esterification reaction was a clue that the stirring speed had shifted the reaction back into the reactants' side, producing triglycerides from methyl ester. The mechanism of the esterification reaction of triglycerides to methyl ester can be seen in Figure 4.

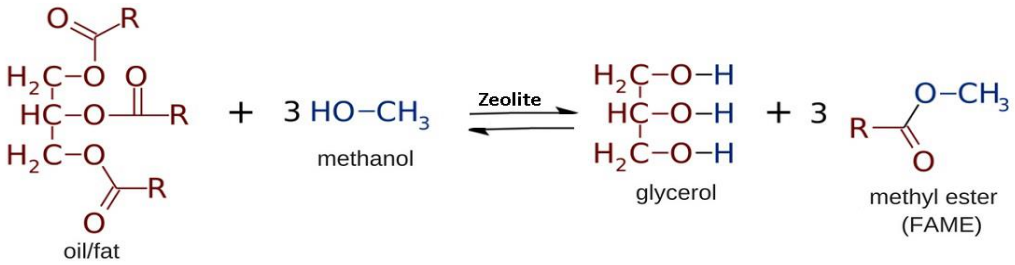

Figure 4. The general mechanism of H-zeolite catalyzed esterification reaction (adapted from ..)

3.3. The Effect of Reaction Time on the Production of Biodiesel

The effect of the H-Zeolite catalyst on the reaction time is shown in Figure 5. In an esterification reaction, the long hydrocarbon chains of crude Nyamplung oil are broken down into glycerol and methyl ester. In the progression of the chemical reaction, the time needed for the reaction is directly proportional to the conversion of the long hydrocarbon molecules into biodiesel, allowing more molecules to react over time [35]. However, due to its reversibility, a longer reaction time will eventually form the by-products, reducing the biodiesel yield [36].

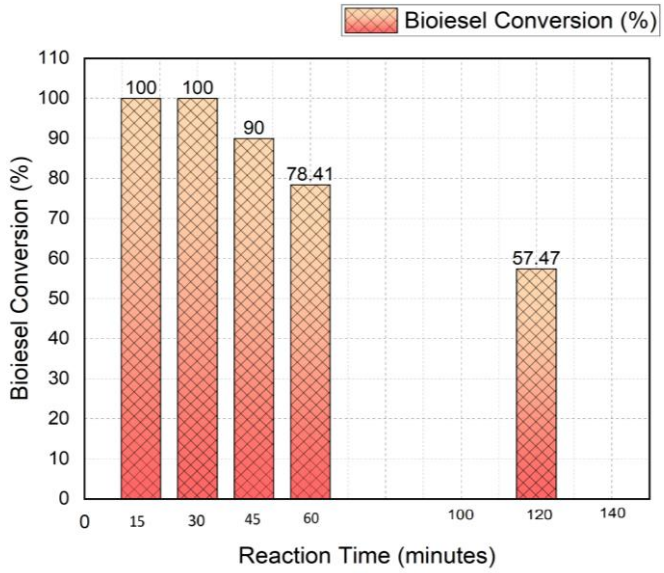

Figure 5. The effect of the reaction time with H-zeolite catalyst in the conversion of Nyamplung oil into biodiesel.

If the reaction time has exceeded the optimum limit, the methyl ester product will reproduce triglycerides and decrease the percentage of the conversion. As shown in Figure 5, the optimum reaction time was 15 minutes. This reaction time got the most optimum conversion when compared to 30, 45, and 60 minutes. The use of H-zeolite as a catalyst allowed a faster reaction time. A faster reaction time may reduce the risk of a shift from the methyl ester product side back into the triglyceride reactant side in this chemical system.

4. CONCLUSION

The study results revealed that active H-zeolite from the natural zeolite has great potential in catalyzing the esterification and the production of biodiesel from Nyamplung oil. Optimal conditions were achieved at a stirring speed of 700 rpm and a reaction time of 15 minutes. These conditions allowed 100% conversion of Nyamplung oil into biodiesel. However, this research was mainly focused on the

effects of H-zeolite as a catalyst on biodiesel yield based on the observation of the stirring speed and the reaction time. The exciting results generated by this study may provide a better direction in biodiesel production from Nyamplung oil. To do so, biodiesel characterization and a test on an engine can further enrich the diversity of research in this field. Furthermore this study revealed that Ende natural zeolite needed to support this claim so that the industry can benefit from sufficient information regarding a cheaper and more abundant alternative for synthetic zeolite that has been employed nowadays as a catalyst. Has a great crystallinity that leads to a good capability in catalyzing the esterification reaction of Nyamplung oil. The trait of great crystallinity alone allows natural zeolite to withstand different temperature treatments, generating a possibility of a longer utilization of natural zeolite at an industrial scale.

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