



Enhancing Biodiesel Production from Nyamplung Oil: Kinetic Analysis of Transesterification via Electromagnetic Induction Heating



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Abstract: In the quest for sustainable and environmentally friendly biofuels, Calophyllum inophyllum L., commonly known as Nyamplung, presents a promising feedstock due to its high oil content (75%) and a significant proportion of unsaturated fatty acids (approximately 71%). Notably, the oil extracted from this species exhibits higher viscosity and reduced capillarity compared to conventional kerosene, posing unique challenges for biodiesel conversion. This study explores the efficacy of electromagnetic induction heating as a novel transesterification method to produce biodiesel from Nyamplung oil. The process was optimized across a range of temperatures (45-65°C), reaction times (0.43-1.03 minutes), methanol to oil molar ratios (6:1), and a catalyst concentration of KOH at 2% of the total weight of oil and methanol. The conversion of Nyamplung oil into biodiesel was primarily assessed through the formation of methyl esters, with Gas Chromatography-Mass Spectrometry (GC-MS) employed for analytical verification. A comprehensive kinetic analysis revealed a transesterification reaction rate constant of $rT = 6.46 \times 10^{14} e^{(-1,068.93/RT)}$ [ME], indicating an activation energy requirement of 1,068 kJ/mol at the operational peak temperature of 65° C. This activation energy is notably lower than that observed with microwave heating, suggesting electromagnetic induction as a more efficient heating mechanism for this reaction. The findings underscore the potential of electromagnetic induction heating in enhancing the conversion efficiency of high-viscosity feedstocks like Nyamplung oil into biodiesel, offering a promising avenue for the production of renewable energy sources. The detailed evaluation of reaction kinetics and activation energies within this study not only contributes to the optimization of biodiesel production processes but also reinforces the viability of Calophyllum inophyllum L. as a sustainable biofuel precursor.

Keywords: Activation energy; Biodiesel; Kinetics; Methyl ester; Calophyllum inophyllum L. oil; Electromagnetic induction heating

1 Introduction

The world energy crisis, which occurred in the last century, has encouraged the development of alternative sources by utilizing renewable energy. Biodiesel is an alternative energy being developed as a substitute for diesel fuel with a relatively high level of technological feasibility. In addition, it is an environmentally friendly and renewable fuel solution because it is made from renewable and degradable natural resources, such as plant oils and animal fats. Biodiesel contains simple alkyl esters of fatty acids and is considered to reduce global warming compared to fossil fuels, which produce high CO_2 emissions [1]. Biodiesel is generally produced using a transesterification reaction between triglycerides (such as vegetable oils) and alcohol (usually methanol) with an alkaline catalyst. The reaction produces fatty acid methyl ester (FAME) and glycerol. Carrying out transesterification reactions with alkaline catalysts results in converting triglycerides to biodiesel with a high FAME content, properties similar to diesel fuel, and low operational costs [2]. This reaction is generally carried out at temperatures determined by the boiling point of the type of alcohol used (methanol is usually used), which is 40-100°C [3].

The heating method is commonly used with a hotplate or oil bath [4]. According to Helwani [5], a high biodiesel yield is obtainable by heating. However, it takes longer, i.e., 1 to 2 hours [6–9]. Therefore, conventional heating consumes more energy and requires a longer reaction time [10]. The heating process undergoes three heat transfer

stages: radiation, conduction, and convection. This process causes the loss of a large amount of energy, which leads to a high energy demand from the reaction process.

Along with technological developments, the transesterification reaction time of Nyamplung oil with heating may be shortened by using other methods, such as microwaves, as the energy source. Some studies have carried out this reaction with various types of oil at temperatures of $60-65^{\circ}$ C for a short time. Shakinaz et al., for example, used jatropha oil for 2 minutes [11], cooking oil for 3 minutes [12], yellow horn oil for 10 minutes [13], and palm oil for 4 minutes [14]. However, the newest method by Kurniati [15], electromagnetic induction radiation, has exceeded the time of using microwaves. The result showed that the transesterification heating acceleration was obtained at 65° C in only 0.43 minutes.

In connection with the effect of heating on the transesterification reaction, it is necessary to study the reaction kinetics using electromagnetic induction. In this case, the most critical parameter was calculating the reaction rate speed and the activation energy. When you study reaction kinetics and activation energy to improve the transesterification process, you can find out what factors affect the rate of transesterification, like temperature, reactant concentration, and catalyst type. Knowing activation energy helps determine optimal operating conditions to achieve a desired reaction rate. By understanding reaction kinetics, optimal reaction times can be chosen to maximize conversion and minimize energy waste. Using activation energy can help select a suitable catalyst with high activity and energy efficiency. On the other hand, reaction kinetics and activation energy can help control the reaction and prevent the formation of undesirable side products. Thus, it is possible to produce high-quality and high-purity transesterification products. Optimizing the transesterification process through understanding reaction kinetics and activation energy can help reduce production costs. That can be achieved by increasing process efficiency, reducing reaction times, and increasing conversion. To do this, the goal of this paper is to look into the reaction rate constant and activation energy of turning Nyamplung oil into biodiesel using electromagnetic induction as the energy source. The transesterification reaction experiments with the help of electromagnetic induction were carried out based on previous research [15]. As a comparison, analysis was also carried out using a hot plate and microwave with the same methanol:oil molar ratio, namely a ratio of 6:1, with a 2% KOH catalyst.

2 Materials and Methods

2.1 Materials

The primary raw material used was Nyamplung oil, obtained from Kebumen Regency, Central Java, Indonesia [16]. Supporting materials include technical 99.8% methanol, 95% p.a. ethanol, technical KOH, p.a. NaOH, polytetrafluoroethylene film, p.a. oxalic acid, and distilled water.

2.2 Research Procedure

2.2.1 Transesterification process

The transesterification process is a chemical reaction involving triglycerides and alcohol in the presence of a catalyst to form esters and glycerol. The Nyamplung oil transesterification process was obtained with a KOH catalyst ratio of 6:1, 1% at a temperature of 65°C. In the first stage, a KOH catalyst of 2% by oil weight is dissolved in methanol until the KOH crystals dissolve properly. The resulting mixture of KOH catalyst and methanol is called potassium methoxide. After that, the container was closed at the top to prevent oxidation with the surrounding air while measuring the volume and mass of esterified oil at 70 ml (61.6 grams). The amount of methanol needed follows the molar ratio to Nyamplung oil, namely 6:1, where the molecular weight of the oil is 704.2 g/mol and the density of methanol is 0.944 g/cm^3 . In the second stage, potassium methoxide was added to the Erlenmeyer flask containing oil and stirred for 5 minutes. Finally, it is heated to a temperature of 65°C using electromagnetic induction radiation with a schematic diagram as shown in Figure 1.

The length of the transesterification process can be seen in the change in oil color and glycerol formation. Finally, the glycerol formed must be separated from the biodiesel, washed, and dried. In this paper, electromagnetic induction heating is used. This process originates from vibrations in the molecules caused by induced heat radiation, which produces uniform heat in the molecules. The resulting generated heat will penetrate and stimulate the molecules evenly, not just the surface. Heating due to radiation can speed up reactions by rapidly vibrating reactant molecules. The longer the radiation time given to the transesterification reaction, the greater the heat produced by the vibration of the reactant molecules until it reaches an optimum state. The transesterification time at a temperature of 65 has been controlled automatically by a microcontroller. Laptops display and store output data such as temperature, current, power, and voltage.

2.2.2 Biodiesel product separation

The results of the transesterification reaction are meticulously separated from raw biodiesel, and the by-product is glycerol; therefore, the crude biodiesel product is purer. This separation is performed precisely using a separating

funnel, leveraging the principles of gravity, compound polarity, and the density difference between biodiesel and glycerol. The process is then followed by a thorough washing with warm water at a temperature of 70° C.

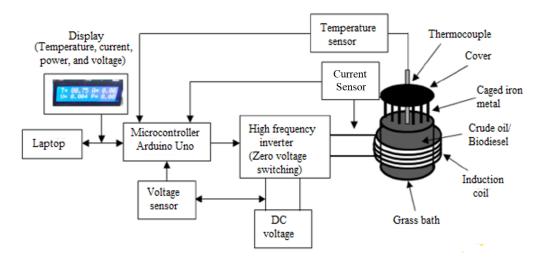


Figure 1. Schematic diagram of a transesterification device using electromagnetic induction

The washing stage is meticulously carried out on methyl ester, separated from glycerol, using distilled water with a volume ratio of 1:1 between methyl ester and distilled water. Washing is repeated diligently until the color of the biodiesel layer is clear and easily separated from the filtered water layer and impurities. This rigorous washing aims to ensure the removal of any catalyst or other impurities contained in the methyl ester. The top layer of washing results is methyl ester, and the bottom layer is distilled water. Next, the methyl ester is separated from the distilled water. The next stage is drying after the methyl ester is separated from distilled water.

The drying process is of utmost importance as it aims to significantly reduce the water content of the methyl ester after washing with distilled water. If the water content of methyl ester is high, it can cause serious problems when applied to machines. Drying uses a magnetic stirrer hotplate set at around 100°C with a medium rotation speed. The results of the transesterification process will show a noticeable color difference from reddish yellow to clear yellow, indicating the successful removal of water content.

2.2.3 Characterization

The characterization carried out in this study includes:

Free Fatty Acid (FFA) level test

Testing of FFA levels is carried out using the titration method, which refers to SNI 01-3555-1998. This test was carried out on Nyamplung oil before and after the titration.

FAME-level test

The FAME content in raw biodiesel products was tested using GC with a flame ionization detector (FID). The values of FFA and FAME levels obtained from this experiment were used to calculate the reaction rate constant and the activation energy of the transesterification reaction.

2.2.4 Determination of a constant value of reaction rate and activation energy

The Arrhenius equation was used to determine the constant value of the reaction rate. Furthermore, the activation energy was calculated using regular reaction rate data at different temperatures.

$$k = Ae^{-Ea/RT} \tag{1}$$

Or, by making right and left sides in the form of log normal:

$$\ln k = \ln A - \frac{Ea}{R} \frac{1}{T}$$
$$-\ln k = \frac{\frac{Ea}{R}}{T} - \ln A$$
$$-\ln k = \frac{Ea}{R} \frac{1}{T} - \ln A$$
(2)

$$y = ax + b \tag{3}$$

where:

A = collision factor (L/mol. sec) Ea = activation energy (kJ/mol), and R = ideal gas constant (8.314 L.atm/mol.K). Eq. (3) is a straight-line equation where the x-axis is (1/T), the y-axis is ln k, and the slope is the intercept of (-Ea/R) and ln k.

3 Reuslts

3.1 Transesterification Results

Transesterification was carried out to determine and analyze the results of the characteristics test of Nyamplung oil biodiesel in the form of FFA, FAME, viscosity, and density. It was obtained from the esterification result with an FFA content of 1.65% and was used as the primary raw material in the transesterification process (Figure 2) [7]. Figure 3 shows one of the test records at 65°C, which lasted for a very short period, i.e., 0.43 minutes, while the characteristics of transesterified Nyamplung oil are shown in Table 1.

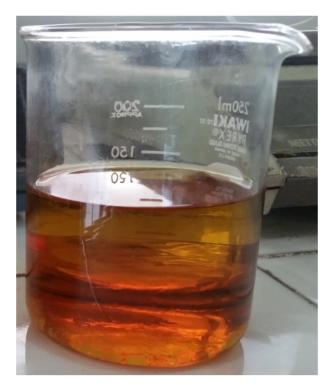


Figure 2. Nyamplung biodiesel

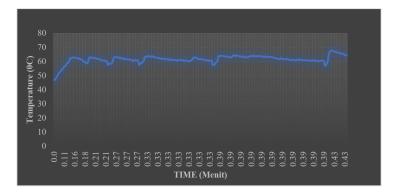


Figure 3. Recording results of transesterification time data

No.	Parameter	Time (min)	Score	SNI*	ASTM 6751**
1.	FAME (%)	0.43	65.9	-	-
		0.73	65.12	-	-
		1.03	64.89	-	-
2.	Density (gr/cm^3)	-	0.882	0.85 - 0.90	0.87 - 0.9
3.	Viscosity (mm^2/s)	-	5.54	2.3 - 6.0	1.9 - 6.0
4.	Acid numbers	-	0.87	0.8	0.8

Table 1. Key parameters of our model

* = Standard Nasional Indonesia (Indonesian National Standard)

** = American Standard Testing and Material

Table 1 shows the conversion of triglycerides to FAME for each time variable at temperatures up to 650C. It was observed that the conversion process decreased with increasing reaction time. Notably, for the time variation from 0.43 to 1.03 minutes, the FAME conversion decreased from 65.96% to 64.89% as the transesterification reaction time increased. The use of shorter heating times in the Nyamplung oil transesterification process using electromagnetic induction compared to the hot plate heating method and microwaves has been reviewed in a previous paper by Kurniati et al. [17]. This paper has tested the advantages of induction heating in a short time, starting with the degumming, esterification, and transesterification processes in processing biodiesel from Nyamplung oil. Apart from that, the table shows that the density, viscosity, and acid number values of biodiesel produced using the electromagnetic induction method meet the standards of SNI 04-7182-2006 and ASTM D6571.

3.2 Fatty Acid Composition Testing (GC-MS Testing)

GC-MS analysis determines the components and levels of fatty acids in Nyamplung seed oil biodiesel, which reacts with electromagnetic induction radiation. Table 2 shows the results of testing the components of the Nyamplung oil biodiesel compound.

Component	Peak	Detection Time	Identified Compound	Molecular Formulas	Percentage (%)
Ι	6, 7	35.06, 35.109	Methyl ester linoleate	$C_{19}H_{34}O_2$	16.78 +17.17 =33.95
II	8	35.388	Methyl ester oleate	$C_{19}H_{36}O_2$	20.06
III	9	35.997	Methyl ester stearate	$C_{19}H_{38}O_2$	18.62
IV	3	28.563	Methyl ester palmitate	$C_{17}H_{34}O_2$	17.12
V	Compounds minor (Impurity)			10.25	
	Total 100.00				100.00

Table 2. Major components based on GC-MS results

Based on this table, it can be seen that the significant components mostly found in Nyamplung biodiesel, such as linoleic methyl ester ($C_{19}H_{34}O_2$), are 33.95% with a molecular mass of 294. The percentage of the second major component of methyl ester oleate ($C_{19}H_{36}O_2$) is 20.06%, with a molecular mass of 296. Furthermore, methyl ester stearate ($C_{19}H_{38}O_2$), which produces a peak of 298 m/z, and methyl ester palmitate ($C_{17}H_{34}O_2$), which produces a peak of 2970 m/z, are the third and fourth-largest components at 18.62% and 17.12%, respectively.

3.3 Activation Energy of Transesterification Reaction

The activation energy of the transesterification reaction was determined from the graph of ln k against 1/T, according to Figure 4.

In the same way, as has been done by previous studies, the determination of the activation energy of the transesterification process can be done using a linear graph of the relationship between -ln k and 1/T [18–20]. Based on the straight-line equation of -128.57x + 34.102, as shown in Figure 4, it is found that ln A = 34.102, so the collision factor (A) is 6.46×10^{14} L/mol minute. The value of Ea/R = 128.57, with R = 8.314 J/mol. L, the activation energy (Ea) is 1,068 kJ/mol. The value of k at various transesterification temperatures can be expressed using equation (1). Thus, the equation for the rate constant of the reaction becomes (k) = $6.46 \times 10^{14} e^{(-1,068.93/RT)}$. Since the transesterification reaction rate of Nyamplung oil is rT = k [ME], where k is the rate of the transesterification reaction and [ME] is the concentration of methyl ester formed, it is obtained $rT = 6.46 \times 10^{14} e^{(-1,068.93/RT)}$ [ME].

According to Arhenius's law, the relationship between activation energy and reaction rate is inversely proportional. The greater the activation energy, the slower the reaction rate, because the minimum energy required for the reaction to occur is more significant. The smaller the lnK value, the larger the average 1/T value. This proves that the higher the temperature, the smaller the activation energy and the less time it takes, so it will increase the value of the reaction

rate. Table 3 compares activation energy (Ea) values based on energy sources and types of biodiesel. Based on this table, the activation energy value of the transesterification reaction by electromagnetic induction is smaller than that of the microwave heating system. Previously, other researchers used an energy source from a microwave, which lowered the activation energy value of the transesterification reaction compared to the direct heating method [21-24]. These results indicate that using electromagnetic induction is a novelty that can reduce activation energy compared to other energy sources.

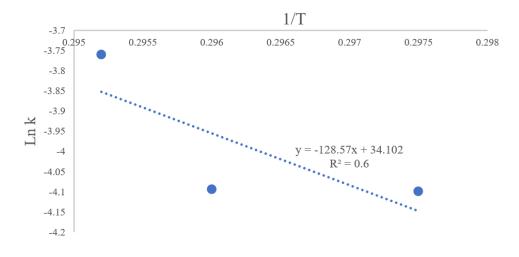


Figure 4. Plot of ln k against 1/T

No.	Energy Sources	Activation Energy (Ea), kJ/mol	Collision (A), L.mol/min	Types of Biodiesel	Ref.
1.	Hotplate	28.8	5.424	Jathropa	[20]
2.	Microwave	18.91	2001.4	Jathropa	[21]
3.	Hotplate	4.83	0.3772	NT	[22]
	Microwave	2.58	1.0611	Nyamplung	
4.	Microwave	3.87	32.23×10^3	Nyamplung	[23]
5.	Electromagnetic Induction	1.07	6.46×10^{14}	Nyamplung	In this work

Table 3. Comparison of the value of activation energy (Ea) based on energy source and type of biodiesel

4 Discussion

The effect of the induced radiation came from two events: the interaction of the induced radiation with reactants and a dipolar polarization. It was observed that with increasing temperature, molecular polarity (such as a solvent) and the effect of induced radiation were in direct proportion. Methanol is an organic solvent with high polarity and a large absorption capacity for induced radiation. It undergoes dipolar polarization due to the molecular level of interaction of induced radiation with the reaction mixture, which results in dipolar rotation and ionic conduction. This interaction (triglycerides and methanol) led to a significant decrease in the activation energy due to increased dipolar polarization, which was influenced by the medium and reaction mechanism. Methanol has a permanent dipole moment due to the asymmetry of its molecular structure. This dipole moment can be affected by temperature. At low temperatures, the orientation of methanol dipoles is more regular, resulting in higher dipolar polarization. As the temperature increases, the movement of methanol molecules becomes more random, so its dipolar polarization decreases. The absorption of electromagnetic radiation by methanol depends on its dipolar polarization. Electromagnetic radiation with a frequency corresponding to the dipole transition energy of the methanol molecule is absorbed. The higher the dipolar polarization, the greater the chance of radiation being absorbed.

Here, fast superheating played a role in lowering the activation energy. Higher temperatures increase the kinetic energy of methanol molecules, leading to more random rotation and orientation of the dipoles. This reduces the total dipolar polarization of methanol. Higher temperatures increase the internal energy of methanol molecules, allowing them to absorb lower-frequency radiation. This increases the probability of electronic transitions and, therefore, radiation absorption. On the other hand, it can increase the dipolar polarization of methanol by aligning the molecular dipoles. This can increase transesterification efficiency by increasing the possibility of interactions between methanol and other reactants. In addition, Kumar et al. [25] explained that the rate constant (k) varies

depending on the fatty acid oil composition (FFA), reaction conditions, and the heating technology used for biodiesel production. However, there are differences in the raw materials and methods used with a molar ratio of 6:1, and the reaction temperature is the same at 65°C. Another difference is the transesterification process of P. pinnata oil with the assistance of microwaves and NaOH and KOH as catalysts, with a reaction time of 5 minutes.

Furthermore, the vibrations in the molecules caused by induced heat radiation will produce uniform heat in the molecules. That is, the heat produced is not only on the surface but can penetrate the molecule evenly. Induction heating radiation can speed up the reaction by rapidly vibrating the reactant molecules. The longer the radiation time is applied to the transesterification reaction, the greater the heat generated by the vibrations of the reactant molecules, so that, at a particular time, the transesterification reaction will reach its optimum state. The collision value is tremendous, based on the analysis results obtained from the Arrhenius equation. That shows that collisions occur more frequently, which causes an increase in the reaction rate. Because the motion is getting faster, more kinetic energy will be converted into vibration energy. In other words, the kinetic energy is significant, and the colliding molecules will vibrate strongly, causing the chemical bonds to break. According to Susilo et al. [26], the formation of a reaction product must begin with a quick chemical breakdown. That means the initial kinetic energy is small; the molecule will bounce off and remain intact.

5 Conclusions

(1) Induction heating is a new method in the production process of Nyamplung oil biodiesel with a transesterification reaction rate constant faster than the microwave irradiation method. In the transesterification process, Nyampung oil biodiesel processing only takes 0.43 minutes for 70 ml, 2% KOH, with a methanol to oil ratio of 6:1.

(2) The activation energy of the transesterification reaction using electromagnetic induction radiation was less than microwave assistance. Electromagnetic induction radiation can be used for biodiesel processing in other oil materials.

Author Contributions

Conceptualization, S.K. and S.S.; methodology, S.K.; software, N.; validation, S.K., S.S. and N.; formal analysis, W. F. G.; investigation, N.; resources, S.S.; data curation, W. F. G.; writing—original draft preparation, S.K.; writing—review and editing, S.S.; visualization, S.K.; supervision, S.K.; project administration, N.; funding acquisition, S.S.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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Nomenclature

GC-MS	Gas Chromatography-Mass Spectrometry
FAME	Fatty Acid Methyl Ester
FID	Flame Ionization Detector
ASTM	American Standard Testing and Material