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Microwave-Assisted Noncatalytic Esterification of Fatty Acid for Biodiesel Production: A Kinetic Study

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Abstract: This study developed a microwave-mediated noncatalytic esterification of oleic acid for producing ethyl biodiesel. The microwave irradiation process outperformed conventional heating methods for the reaction. A highest reaction conversion, 97.62%, was achieved by performing esterification with microwave irradiation at a microwave power of 150 W, 2:1 ethanol:oleic acid molar ratio, reaction time of 6 h, and temperature of 473 K. A second-order reaction model (R^2 of up to 0.997) was established to describe esterification. The reaction rate constants were promoted with increasing microwave power and temperature. A strong linear relation of microwave power to pre-exponential factors was also established, and microwave power greatly influenced the reaction due to nonthermal effects. This study suggested that microwave-assisted noncatalytic esterification is an efficient approach for biodiesel synthesis.

Keywords: esterification; biodiesel; noncatalytic reaction; kinetic; microwave irradiation; bioenergy

1. Introduction

The energy shortage and environmental threats caused by greenhouse gas emissions have promoted the demand for renewable energy. One of the most promising alternatives is biodiesel, which is known as a biomass-derived fuel produced from the transesterification of triglycerides [1,2]. Biodiesel is a biodegradable, renewable, and green fuel and has superior combustion efficiency [3,4]. Biodiesel use can result in lower hydrocarbon, CO, CO₂, and particulate matter emissions compared with petroleum use [5,6]. Therefore, biodiesel has increasingly been used as a petroleum substitute.

Biodiesel is mainly derived from food oils [7,8], but the biodiesel produced is expensive due to the high cost of these feedstocks. To address this problem, waste and nonedible materials have been proposed as alternatives for producing biodiesel [9–11]. These oils can reduce biodiesel production cost, and they have no competition with the food supply [12,13]. Nevertheless, waste and nonedible oils contain high levels of free fatty acid, which must be reduced via esterification prior to transesterification [14,15]. Commonly, fatty acid is esterified using a liquid acid-catalyzed process [12,16]. Although this method effectively converts fatty acid into biodiesel, the downstream process for catalyst removal is difficult [17]. Notably, liquid acid catalysts cause environmental pollution

and corrosive damage to equipment, raising concerns about their use [7]. To overcome the obstacles of liquid acid catalyst use, different solid acid catalysts have been proposed for the esterification such as Propyl-SO₃H-SBA-15 [18], Amberlyst-36 [18], WO₃-USY zeolite [19], HZSM-5 [20], Amberlyst-15 [21], biocatalysts [21], and ZrO₂-TiO₂ nanorods [22]; however, these solid catalysts exhibit low stability and catalytic activity, thus requiring high catalyst quantities and long reaction times, and they result in a low conversion yield [19,20]. In addition, these catalyst residues can cause a negative impact on the environment. Consequently, the applications of those solid catalysts in the esterification reaction are still limited.

With the growing awareness regarding environmentalism, the efforts have been undertaken to develop green methods for chemical production. For several decades, the enzymatic process has been developed as a substitute for chemically catalyzed esterification for biodiesel synthesis [23,24]. Enzyme-catalyzed esterification is superior to conventional processes in terms of the mild reaction conditions, reduced environmental impact, and selectivity of enzymes toward the substrate [24,25]. However, the high price of enzymes restricts its applications [24,26]. On the other hand, the noncatalytic esterification is considered another eco-friendly process for biodiesel synthesis. This process induced the esterification of fatty acids under thermal conditions without a catalyst [27], eliminating the problems associated with both chemical and enzymatic processes. The supercritical alcohol method has been applied in noncatalytic fatty acid esterification to prepare biodiesel [28,29]. Although this process produces a high yield of esters (up to 97%) within a short reaction time (10–30 min), it proceeds at a high temperature (280–320 °C) and high pressure (10–25 MPa) and consequently requires expensive reactors and extensive safety measures [28,29]. To overcome this, Cho et al. [30] proposed another form of noncatalytic esterification for less-than-supercritical conditions to produce biodiesel. Although their process proceeded at moderate pressure (0.85–1.2 MPa), it still required a high temperature (290 °C) for the reaction [30]. Therefore, another efficient esterification method is required for biodiesel production.

Microwave irradiation has been successfully applied in chemical reactions to enhance the reaction rate [31,32]. This method employs microwaves, which are electromagnetic waves, to transfer energy to the reactants [33]. Through relaxation or resonance generated by microwaves, reactant molecules are induced to vibrate at extremely high frequencies, resulting in fast molecular mobility of reaction species [34,35]. Consequently, microwave irradiation increases reaction rate and conversion yield whilst decreasing energy consumption and reaction time [33,36]. Furthermore, microwave-mediated processes are effective for large-scale operations [37]. Such advantages mean that the microwave approach has been extensively applied in catalytic transesterification and esterification for producing biodiesel [38–40]. Recently, our previous studies have demonstrated the potential use of microwave-mediated noncatalytic/autocatalytic synthesis of fatty acid [41], phytosterol esters [42], and ethyl levulinate [43]. However, its use in noncatalytic esterification to produce biodiesel remains limited.

This study proposed noncatalytic esterification of fatty acid with ethanol using microwave irradiation as an environmentally friendly and energy-efficient method to produce ethyl biodiesel. The esterification was performed under selected microwave powers to enhance the reaction conversion. Ethanol (95%) was used as an acyl acceptor instead of methanol for biodiesel synthesis because ethyl biodiesel is superior to methyl biodiesel due to its oxidation stability, calorific value, cetane number, and cold flow properties [44,45]. Oleic acid was chosen as a model molecule for the esterification, because it is a predominant fatty acid presented in animal fats and vegetable oils [46]. The reaction parameter effect on the reaction conversion was investigated. Furthermore, a mathematical model was proposed for representing the kinetics of noncatalytic esterification reactions.

2. Materials and Methods

2.1. Chemicals

Ethanol (95%), oleic acid (98%), and other reagents were obtained from Tokyo Chemical Industry (Tokyo, Japan).

2.2. Effects of Different Heating Processes

The effect of two heating approaches (conventional heating and microwave irradiation) on the noncatalytic esterification of oleic acid with ethanol was examined. For microwave-assisted esterification, 10-mL glass reactor containing the reaction solution (5 mL, 2:1 molar ratio of ethanol to oleic acid) was sealed and placed in a CEM 908005 microwave oven (Matthews, NC, USA). The microwave was equipped with a gas cooling system to maintain the temperature at a desired level. The reaction was then carried out at a microwave power of 150 W, 433 K, and different reaction times (60–360 min) with stirring. The reaction using conventional heating was undertaken in a 10 mL-sealed stainless-steel reactor placed in an oil bath under the same reaction conditions: 2:1 molar ratio of ethanol to oleic acid, 433 K, and different reaction times (60–360 min). After the reaction was completed, the sample was withdrawn to determine the oleic acid conversion. Each experiment was independently performed in triplicate for each reaction time.

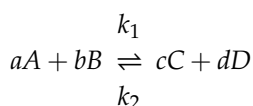
2.3. Analysis

The amount of ethyl oleate synthesized was quantified using a Gas Chromatograph system (GC-2014, Shimadzu, Japan) equipped with a flame ionization detector and Stabilwax column (60 m × 0.25 mm id, 0.25 µm film thickness; Restek, Bellefonte, PA, USA) [1]. Nitrogen was used as the carrier gas and set at 1.0 mL/min. The temperatures of detector and injector were maintained at 250 and 220 °C, respectively. The column temperature was held at 140 °C for 5 min, increased to 240 °C with a ramp rate of 4 °C/min, and maintained for 15 min. Ethyl oleate standard (Sigma-Aldrich, Louis, MO, USA) was used to identify and determine the amount the produced ethyl oleate. One mol of oleic acid could stoichiometrically produce 1 mol of ethyl oleate; the oleic acid conversion (X) was consequently calculated as follows:

$$\begin{aligned} \text{Oleic acid conversion, } X &= \frac{\text{Ethyl oleate conversion}}{\text{Amount of oleic acid reacted}} \\ &= \frac{\text{Initial amount of oleic acid}}{282.47 \times \text{amount of ethyl oleate produced}} \\ &= \frac{310.51 \times \text{initial amount of oleic acid}}{\text{amount of ethyl oleate produced}} \end{aligned} \quad (1)$$

2.4. Kinetics of Noncatalytic Esterification Using Microwave Irradiation

Noncatalytic esterification of oleic acid (A) with ethanol (B) to produce ethyl oleate (C) and water (D) is demonstrated as follows:



The model established for depicting esterification is considered elementary and reversible. The rate law is therefore as follows:

$$-\frac{dC_A}{dt} = k_1 C_A^a C_B^b - k_2 C_C^c C_D^d \quad (2)$$

where k_1 and k_2 denote forward and reverse reaction rate constants ($\text{L mol}^{-1} \text{min}^{-1}$), respectively; C_A , C_B , C_C , and C_D are concentrations of oleic acid, ethanol, ethyl oleate, and water, respectively; a , b , c , and d are the reaction orders of involved species. The reaction is assumed to follow the second-order kinetics ($c = d = a = b = 1$), the rate law is shown in terms of oleic acid conversion (X) as follows Equation (3):

$$\begin{aligned} \frac{dX}{dt} &= \frac{1}{C_{A0}} (k_1 C_A C_B - k_2 C_C C_D) \\ &= \frac{1}{C_{A0}} \left[k_1 C_{A0} (1 - X) C_{A0} (\theta_B - X) - \frac{k_1}{K_e} C_{A0} X C_{A0} (\theta_D + X) \right] \\ &= k_1 C_{A0} \left[(1 - X)(\theta_B - X) - \frac{X(\theta_D + X)}{K_e} \right] \end{aligned} \quad (3)$$

where C_{A0} is the initial oleic acid concentration; θ_B and θ_D are the initial ethanol:oleic acid molar ratio and the initial molar ratio of water to oleic acid, respectively; and K_e is the equilibrium rate constant. The reaction rate (dX/dt) will be zero at equilibrium, and K_e is then calculated as follows:

$$K_e = \frac{k_1}{k_2} = \frac{X_e(\theta_D + X_e)}{(1 - X_e)(\theta_B - X_e)} \quad (4)$$

where X_e is the equilibrium conversion of oleic acid. After determination of K_e , Equation (3) can be integrated into Equation (5) using the derivation described by Su [47]. Equation (5) can subsequently be used for determining the rate constant k_1 by linearly plotting $\ln \left[\frac{(-1 - \theta_B - \frac{\theta_D}{K_e} + \alpha_2)X + 2\theta_B}{(-1 - \theta_B - \frac{\theta_D}{K_e} - \alpha_2)X + 2\theta_B} \right]$ versus $\alpha_2 C_{A0} t$.

$$\ln \left[\frac{(-1 - \theta_B - \frac{\theta_D}{K_e} + \alpha_2)X + 2\theta_B}{(-1 - \theta_B - \frac{\theta_D}{K_e} - \alpha_2)X + 2\theta_B} \right] = \alpha_2 C_{A0} k_1 t \quad (5)$$

$$\text{where } \alpha_2 = \left[\left(1 + \theta_B + \frac{\theta_D}{K_e} \right)^2 - 4\alpha_1 \theta_B \right]^{\frac{1}{2}} \quad (6)$$

$$\text{and } \alpha_1 = 1 - \frac{1}{K_e} \quad (7)$$

The relationship between temperature and the rate constants are represented by the Arrhenius equation:

$$k_1 = A_1 \exp\left(-\frac{E_a}{RT}\right) \quad (8)$$

$$K_e = A_e \exp\left(-\frac{\Delta h}{RT}\right) \quad (9)$$

where A_e and A_1 ($\text{L mol}^{-1} \text{ min}^{-1}$), respectively, denote pre-exponential factors for the equilibrium and forward rate constants; Δh (J mol^{-1}) and E_a (J mol^{-1}), respectively, represent the molar reaction heat and activation energy of forward reaction; T (K) and R ($\text{J mol}^{-1} \text{ K}^{-1}$) are the reaction temperature and the ideal gas constant, respectively. These parameters (A_1 , A_e , E_a , and Δh) can be obtained from the Arrhenius–Van't Hoff plot [Equations (10) and (11)]:

$$\ln k_1 = \ln A_1 - \frac{E_a}{RT} \quad (10)$$

$$\ln K_e = \ln A_e - \frac{\Delta h}{RT} \quad (11)$$

3. Results and Discussion

3.1. Effect of Various Heating Processes

This study compared noncatalytic esterification using microwave irradiation and conventional heating. As demonstrated in Figure 1, conventional heating resulted in low oleic acid conversions (27.13%–67.13%). This finding is consistent with other works in that conventional heating needed long reaction time to achieve a satisfactory reaction conversion [48]. Conventional heating is an inefficient form of heat transfer, because heat is delivered to the reaction solution by convection, radiation, and conduction from the surface of the reactor, causing heat loss [38,39]. To increase the heat transfer and reaction efficiency, microwave approach was employed as a replacement for the reaction. Results indicated that the oleic acid conversion significantly increased and reached high levels (60.61%–90.18%) with microwave irradiation. Remarkably, at a given reaction time, microwave irradiation exhibited significantly higher oleic acid conversion than conventional heating, signifying

that microwave irradiation is preferable to conventional heating for performing the esterification. This result corresponds to the study of Aguilar–Reynosa et al. [49]. Microwave irradiation minimizes loss of heat and additionally provides a nonthermal activation influence on the esterification [50]. Microwaves strongly induce movement, collision, and oscillation of reactant molecules, promoting the reaction efficiency [49,51]. As a result, microwave irradiation is superior than traditional heating regarding to reaction time [43,52]. Therefore, microwave approach was selected for more extensive study.

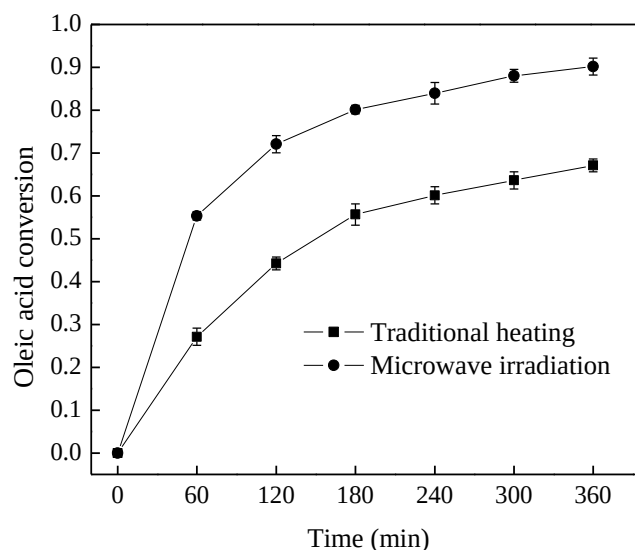


Figure 1. Comparison of esterification using conventional heating and microwave irradiation. Reaction conditions occurred with an ethanol:oleic acid molar ratio of 2:1, temperature of 433 K, and microwave power of 150 W (for microwave irradiation). Vertical bars illustrate the standard deviation of three replicates.

3.2. Influence of Reactant Molar Ratio

This work investigated the impact of reactant molar ratio on the reaction by undertaking the reaction at 433 K, at a microwave power of 150 W, and at various ethanol:oleic acid molar ratios (1:1–8:1). As demonstrated in Figure 2, the oleic acid conversion was promoted when molar ratios of the reactants were increased from 1:1 to 2:1. Nevertheless, additional increase in ethanol:oleic acid molar ratio resulted in decreased oleic acid conversion. This may be because large quantities of ethanol used to dilute oleic acid, which plays a role as a catalyst for the esterification reaction, may lower the reaction rate [53,54]. This result corresponds to that of the biodiesel production study by Minami and Saka [54].

3.3. Temperature Effect on Esterification

The impact of temperature on reaction was evaluated by conducting the reaction at a microwave power of 150 W, an ethanol:oleic acid molar ratio of 2:1, and various temperatures (413–473 K). Figure 3 presents the progress over time of the oleic acid esterification at different temperatures. Results showed that higher temperature provided a greater conversion of oleic acid, with the highest conversion of 97.62% obtained at 473 K and 6 h. This is because high temperature enhances reaction rate [12], increasing the reaction conversion. This finding is similar to those of other works [12,14,55].

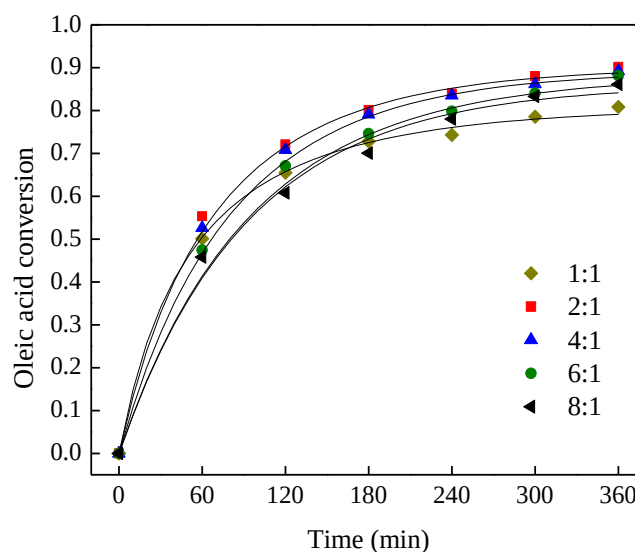


Figure 2. Influence of molar ratio of ethanol to oleic acid on esterification reaction. Reactions occurred at a temperature of 433 K and with microwave power of 150 W.

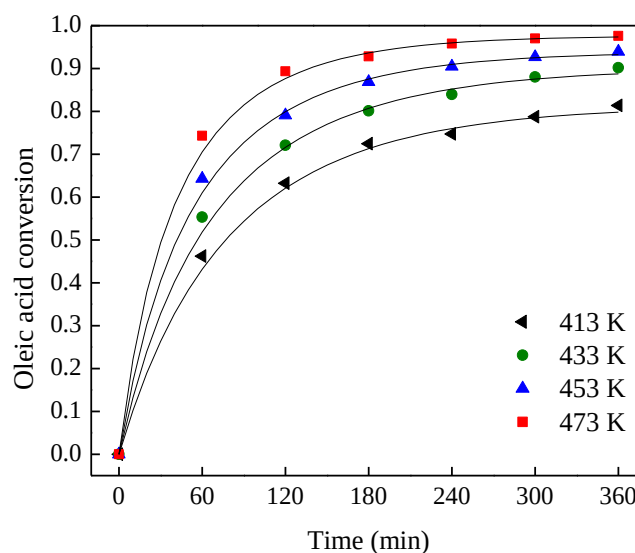


Figure 3. Influence of temperature on esterification reaction. Reactions occurred at a molar ratio of ethanol to oleic acid of 2:1 and microwave power of 150 W.

3.4. Effect of Microwave Power on Reaction

To determine the impact of microwave power on the reaction, the esterification was carried out at different microwave power levels (120–210 W) while maintaining other factors at a constant level. As illustrated in Figure 4, increasing microwave power led to an increase in the oleic acid conversion. This might have been because higher energy generated by higher microwave power resulted in higher activation effects (nonthermal effects), causing faster molecular mobility; therefore, the reaction rate was promoted [50,51]. This result corresponds with that reported for biodiesel production [56] and for pyrolysis of biomass [51].

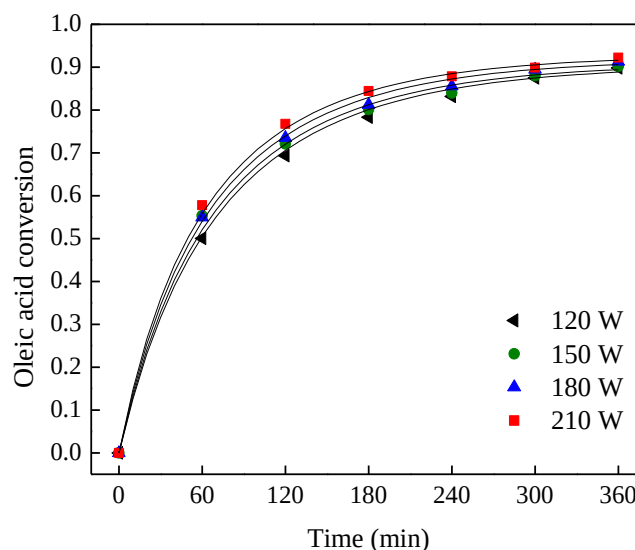


Figure 4. Influence of microwave power on esterification reaction. Reactions occurred at a molar ratio of ethanol to oleic acid of 2:1 and at a temperature of 433 K.

3.5. Kinetic Model Development

3.5.1. Determination of Reaction Rate Constant

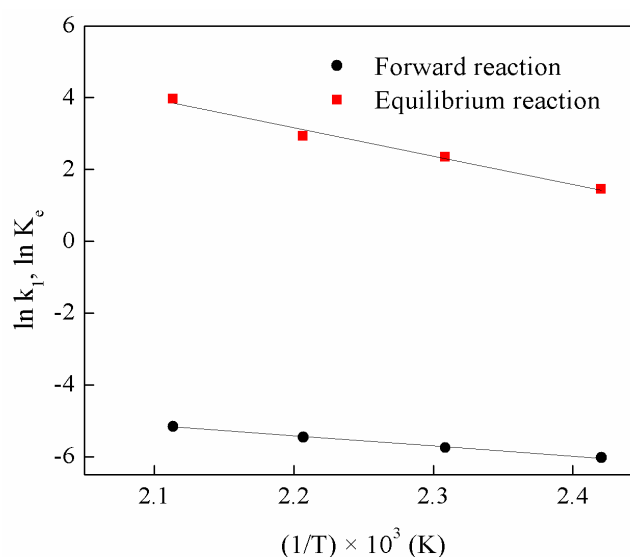
Figures S1–S3 (in the Supplementary Material), respectively, provide a linear plot of $\ln \left[\frac{(-1-\theta_E - \frac{\theta_D}{K_e} + \alpha_2)X + 2\theta_E}{(-1-\theta_E - \frac{\theta_D}{K_e} - \alpha_2)X + 2\theta_E} \right]$ versus $\alpha_2 C_{A0} t$ at different microwave powers, temperatures, and ethanol:oleic acid molar ratios. As illustrated in Table 1, correlation coefficients (R^2) of the regression lines were in the range of 0.972–0.997, indicating the reliability and correction of the second-order reaction model. Table 1 (runs 1–5) shows that rate constants K_e and k_1 both decreased when the molar ratio of ethanol to oleic acid increased, indicating the negative influence of high ethanol:oleic acid molar ratio on the reaction conversion [53,54]. Nevertheless, the rate constants K_e and k_1 accelerated with increasing temperature (Table 1, runs 6–9), signifying that the reaction is endothermic [47]. Furthermore, increasing microwave power enhanced the rate constants K_e and k_1 (Table 1, runs 10–13), which was similar to the results of other studies [51,56]. This result indicated a positive effect from microwave power on the reaction. Notably, at any ethanol:oleic acid molar ratio and temperature, microwave-based reaction had much higher K_e and k_1 values than the conventional heating-based reaction (see the K_e and k_1 values for the conventional heating-based reaction in the Table S1 in the Supplementary Material). These results indicated that microwave irradiation enhanced the equilibrium rate constant and forward reaction rate constant. Therefore, microwave irradiation is more efficient than conventional heating for conducting the ethyl oleate synthesis.

3.5.2. Determination of Pre-Exponential Factor and Activation Energy

The influence of temperature on reaction rate constants (K_e and k_1) is represented using the Arrhenius equation [Equations (8) and (9)]. The activation energy, pre-exponential factor, and molar reaction heat of the reaction were calculated using the Arrhenius–van’t Hoff plots. As illustrated in Figure 5 and in Table 2, high R^2 of the regression lines (0.997 for k_1 and 0.985 for K_e) were achieved; therefore, the model parameters can be determined from the straight line. Results showed that the activation energy of the forward reaction was 23.59 kJ mol^{−1}, and the molar reaction heat was 65.98 kJ mol^{−1}. The pre-exponential factors were calculated to be 2.27 L mol^{−1} min^{−1} and 9.07×10^8 for forward and equilibrium reactions, respectively.

Table 1. Forward reaction rate constant k_1 and equilibrium rate constant K_e for esterification under different reaction conditions.

Run	Molar Ratio of Ethanol to Oleic Acid	Temperature (K)	Microwave Power (W)	Equilibrium Constant, K_e	Forward Reaction Rate Constant, k_1 ($\text{L mol}^{-1} \text{min}^{-1}$)	R^2
1	1:1	433	150	21.5253	6.50×10^{-3}	0.972
2	2:1	433	150	10.3897	3.18×10^{-3}	0.986
3	4:1	433	150	4.1905	1.59×10^{-3}	0.993
4	6:1	433	150	2.7692	1.06×10^{-3}	0.990
5	8:1	433	150	1.9294	0.92×10^{-3}	0.978
6	2:1	413	150	4.2537	2.41×10^{-3}	0.989
7	2:1	433	150	10.3897	3.18×10^{-3}	0.986
8	2:1	453	150	18.7094	4.23×10^{-3}	0.994
9	2:1	473	150	52.7582	5.75×10^{-3}	0.992
10	2:1	433	120	9.8958	3.02×10^{-3}	0.984
11	2:1	433	150	10.3897	3.18×10^{-3}	0.986
12	2:1	433	180	12.0860	3.39×10^{-3}	0.983
13	2:1	433	210	13.8671	3.59×10^{-3}	0.997

**Figure 5.** Arrhenius–Van't Hoff plot for equilibrium rate constant and forward reaction rate constant of esterification reaction.**Table 2.** Activation energy, molar reaction heat, and pre-exponential factor for oleic acid esterification with ethanol using microwave approach.

Forward Reaction			Equilibrium Reaction		
Activation Energy (kJ mol^{-1})	Pre-Exponential Factor ($\text{L mol}^{-1} \text{min}^{-1}$)	R^2	Molar Reaction Heat (kJ mol^{-1})	Pre-Exponential Factor	R^2
23.59	2.27	0.997	65.98	9.07×10^8	0.985

3.5.3. Relation of Microwave Power to Pre-Exponential Factor

The modified Arrhenius equation reported by Su et al. [57] was used to determine the influence of microwave heating on the kinetic model:

$$K_e = A_e \exp\left(-\frac{\Delta h}{RT}\right)$$

$$k_1 = A_1 \exp\left(-\frac{E_a}{RT}\right)$$

$$A_e = A_0^e + A_W^e \cdot W \quad (12)$$

$$A_1 = A_0^1 + A_W^1 \cdot W \quad (13)$$

where W is the microwave power; A_W^e and A_W^1 , respectively, denote the coefficient for representing the effect of power on the equilibrium and forward reaction; A_0^e and A_0^1 , respectively, denote the constant for representing the effect of power on the equilibrium and forward reaction. The pre-exponential factors (A_e and A_1) were assumed to obey linear functions with the microwave power. Both the constants (A_0^1 and A_0^e) and the coefficients (A_W^1 and A_W^e) can therefore be determined by linearly plotting $\frac{K_e}{e^{-\Delta h/RT}}$ versus microwave power W [Equation (14)] or $\frac{k_1}{e^{-E_a/RT}}$ versus microwave power W [Equation (15)]:

$$\frac{K_e}{e^{-\Delta h/RT}} = A_0^e + A_W^e \cdot W \quad (14)$$

$$\frac{k_1}{e^{-E_a/RT}} = A_0^1 + A_W^1 \cdot W \quad (15)$$

Figure 6a,b, respectively, represents a linear relationship between $\frac{K_e}{e^{-\Delta h/RT}}$ and W and $\frac{k_1}{e^{-E_a/RT}}$ and W for the equilibrium reaction and forward reaction. The high R^2 value of the regression line (0.951–0.997) signified that the developed model is reliable, and the assumption is correct. The coefficients (A_W^e and A_W^1) and constants (A_0^e and A_0^1) could therefore be determined from the slope and intercept of each regression line. The value of A_W^e and A_0^e for the equilibrium reaction was $4.11 \times 10^6 \text{ W}^{-1}$ and 3.69×10^8 , respectively (Table 3). For the forward reaction, the values of A_W^1 and A_0^1 were respectively determined to be $4.4 \times 10^{-3} \text{ L mol}^{-1} \text{ min}^{-1} \text{ W}^{-1}$ and $1.5282 \text{ L mol}^{-1} \text{ min}^{-1}$.

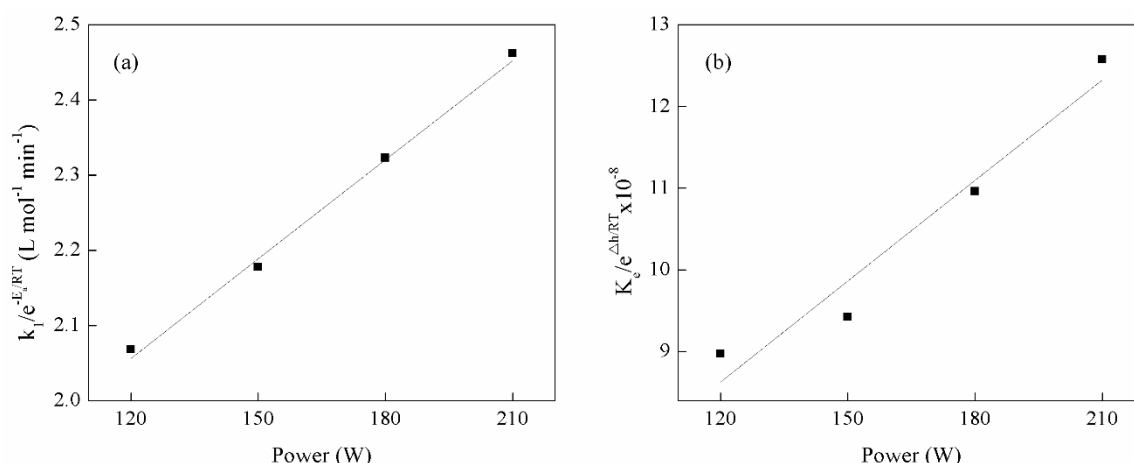


Figure 6. Linear regression of the experimental data for determining microwave power constants and coefficients for forward reaction (a) and equilibrium reaction (b).

Table 3. Constants and power coefficients for describing the relationship between microwave power and pre-exponential factors.

Forward Reaction			Equilibrium Reaction		
A_0^1 (L mol ⁻¹ min ⁻¹)	A_W^1 (L mol ⁻¹ min ⁻¹ W ⁻¹)	R ²	A_0^e	A_W^e (W ⁻¹)	R ²
1.5282	4.40×10^{-3}	0.997	3.69×10^8	4.11×10^6	0.951

Linear relationship of pre-exponential factors to microwave power: $A_1 = A_0^1 + A_W^1 \cdot W$; $A_e = A_0^e + A_W^e \cdot W$.

3.6. Comparison with Other Works

Table 4 illustrates the comparison of reaction conditions for oleic acid esterification using various processes. The esterification was mainly conducted using a liquid acid catalyst (e.g., H₂SO₄) [16]. This process provides a high conversion yield (99.9%), but it severely corrodes equipment, requires a complicated process for catalyst removal from the reaction solution, and pollutes the environment [16,17]. To avoid the complications associated with homogeneous catalysts, Vieira et al. [20] used HZSM-5 as a solid catalyst for the reaction. Nevertheless, the heterogeneous catalyst demonstrated low catalytic activity, thus requiring large quantities of catalyst (20%) and a long reaction time (7 h), and lowering reaction conversion (80%) [20]. Enzymatic esterification is proposed as a substitute for chemically catalyzed esterification to facilitate environmentally friendly biodiesel production. Nguyen et al. [24] successfully esterified oleic acid with methanol using Eversa Transform lipase for producing biodiesel. Although this process showed high reaction conversion (96.73%), the high cost of enzymes limits its industrial application. Tsai et al. [29] developed another green process called the noncatalytic process using supercritical methanol for oleic acid esterification to eliminate the problems associated with both enzyme- and chemical-catalyzed methods. This efficiently converted oleic acid to esters (97%) within a short reaction time (15 min), but the reaction proceeded at a high temperature (593 K) and high pressure (25 MPa) [29]; it thus required expensive reactors and extensive safety precautions. Melo-Júnior et al. [58] proposed a noncatalytic esterification of fatty acid using microwave irradiation. However, the reaction conversion obtained in their study was low (only 35%), because microwave power was not maintained in their study, leading to lack of microwave-induced nonthermal effect for promotion of the reaction rate [59]. Therefore, the microwave irradiation used in their study is similar to conventional heating. In this study, we proposed another noncatalytic method using microwave irradiation for the oleic acid esterification with ethanol under constant microwave powers to enhance the reaction conversion. The result was a high reaction conversion of 97.62%. The use of microwave irradiation for esterification was more efficient and rapid than conventional heating-based esterification, reducing energy consumption and reaction time. In the reaction mixture, oleic acid and ethanol exist under molecular cage with hydrogen bonding [60]. With the application of microwaves, oleic acid and ethanol absorb the energy from the electromagnetic field, which consequently induces the oscillation of reaction molecule and hydrogen bond variation between ethanol and oleic acid [59]. Resonance is subsequently generated and causes the hydrogen bonds breakage and formation of free small molecules due to reactant molecules escaping from the molecular cage. Consequently, the number of activation molecules is promoted, enhancing the reaction rate [60]. This work signifies that microwave-assisted noncatalytic esterification can be an ecofriendly and efficient process to produce biodiesel.

Table 4. Oleic acid esterification using different methods for producing biodiesel.

Catalyst	Catalyst Loading (% <i>w/w</i>)	Conversion (%)	References
H ₂ SO ₄	1	99.9	[16]
HZSM-5	20	80	[20]
Eversa Transform lipase	11.98	96.73	[24]
Catalyst free (supercritical methanol)	-	97.0	[29]
Catalyst free (microwave irradiation)	-	35	[58]
Catalyst free (traditional heating)	-	67.13	This study
Catalyst free (microwave irradiation)	-	97.62	This study

The potential applications of microwave approach in the large-scale biodiesel production have been widely discussed in literatures [61,62]. Although microwave is superior to conventional heating in the terms of energy consumption and reaction time, the use of microwave for industrial application has several limitations regarding to the control of temperature and safety of the pressurized vessel [61,62]. To address these concerns, the design of microwave reactor is crucial. Studies have showed that the design of microwave reactor for enhancing the temperature and pressure monitoring, safety features, and cooling features is possible [61]. In addition, microwave-based process has been successfully implemented in many industries such as polymers processing, minerals processing, and powder processing [61]. Therefore, the microwave process has a potential application for industrial biodiesel production. However, microwave process has not been used commercially for biodiesel production yet. Further studies are consequently required to evaluate the application of microwave in large-scale biodiesel production.

4. Conclusions

This study developed the noncatalytic oleic acid esterification with ethanol using microwave irradiation for biodiesel production. The microwave-mediated esterification was more efficient than conventional-heating-based esterification. The oleic acid conversion decreased with increasing molar ratio of ethanol to oleic acid but increased by enhancing the temperature, reaction time, and microwave power levels. The high R^2 values of the second-order kinetic model were established in describing the esterification. In addition, a linear relation of microwave power to pre-exponential factors was observed, in which microwave power positively influenced the reaction. This work suggested that microwave-assisted noncatalytic esterification is an ecofriendly and energy-efficient approach for biodiesel synthesis.

Supplementary Materials: The following are available online at <http://www.mdpi.com/1996-1073/13/9/2167/s1>, Figure S1: Kinetic model for calculating forward reaction rate constant of esterification of oleic acid with ethanol at different reactant molar ratios, Figure S2: Kinetic model for calculating forward reaction rate constant of esterification of oleic acid with ethanol at different temperatures, Figure S3: Kinetic model for calculating forward reaction rate constant of esterification of oleic acid with ethanol at different microwave power levels, Table S1: Forward reaction rate constant k_1 and equilibrium rate constant K_e for esterification using conventional heating.

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