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

Hoang Chinh Nguyen 1, Fu-Ming Wang 2, Kim Khue Dinh 1, Thanh Truc Pham 3, Horng-Yi Juan 3, Nguyen Phuong Nguyen 1, Hwai Chyuan Ong 4,* and Chia-Hung Su 3,*

1 Faculty of Applied Sciences, Ton Duc Thang University, Ho Chi Minh City 700000, Vietnam; nguyenhoangchinh@tdtu.edu.vn (H.C.N.); dinhkhue96@gmail.com (K.K.D.); nguyenphuongcass97@gmail.com (N.P.N.)
2 Graduate Institute of Applied Science and Technology, National Taiwan University of Science and Technology, Taipei 10607, Taiwan; mccabe@mail.ntust.edu.tw
3 Graduate School of Biochemical Engineering, Ming Chi University of Technology, New Taipei City 24301, Taiwan; ptttruc1996@gmail.com (T.T.P.); hyjuan@mail.mcut.edu.tw (H.-Y.J.)
4 School of Information, Systems and Modelling, Faculty of Engineering and Information Technology, University of Technology Sydney, Ultimo, NSW 2007, Australia
* Correspondence: ong1983@yahoo.com (H.C.O.); chsu@mail.mcut.edu.tw (C.-H.S.);
Tel.: +88-622-908-9899 (ext. 4665) (C.-H.S.)

Received: 22 March 2020; Accepted: 26 April 2020; Published: 1 May 2020

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 (R² 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, a 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:

\[ X = \frac{\text{Amount of ethyl oleate produced}}{310.51 \times \text{initial amount of oleic acid}} \]

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:

\[ aA + bB \rightleftharpoons cC + dD \]

where \( k_1 \) and \( k_2 \) denote forward and reverse reaction rate constants (L mol\(^{-1}\) 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):

\[ \frac{dX}{dt} = k_1 C_A C_B - k_2 C_C C_D \]

\[ = \frac{1}{C_A C_B} \left( k_1 C_A C_B (1 - X) C_A (\theta_B - X) - \frac{k_1 k_2}{K_e} C_A C_D (\theta_D + X) \right) \]

\[ = k_1 C_A (1 - X) (\theta_B - X) - \frac{X (\theta_D + X)}{K_e} \]
where \( C_{A0} \) is the initial oleic acid concentration; \( \theta_B \) and \( \theta_D \) 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:

\[
K_e = \frac{k_1}{k_2} = \frac{X_c(\theta_D + X_c)}{(1 - X_c)(\theta_B - X_c)}
\]  

where \( X_c \) 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 \( \ln \left[ \frac{-(1-\theta_B - \theta_D K_e + \alpha_2)X + 2\theta_B}{-(1-\theta_B - \theta_D K_e - \alpha_2)X + 2\theta_B} \right] \) versus \( \alpha_2 C_{A0} t \).

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

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

and \( \alpha_1 = 1 - \frac{1}{K_e} \)  

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

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

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

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

\[
\ln k_1 = \ln A_1 - \frac{E_a}{RT}
\]

\[
\ln K_e = \ln A_e - \frac{\Delta h}{RT}
\]

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.

![Comparison of esterification using conventional heating and microwave irradiation.](image)

**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].
was promoted \[50,51\]. This result corresponds with that reported for biodiesel production \[56\] and for pyrolysis of biomass \[51\].

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 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 \[51\].
The 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 
\[ \ln \left( \frac{\alpha_2 C_{A0} t}{X + 20X} \right) \] 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 \( k_f \) 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 \( k_f \) 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 \( k_f \) (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 \( k_f \) values than the conventional heating-based reaction (see the \( K_e \) and \( K_f \) 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 \( K_f \)) 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 \( k_f \) and 0.985 for \( K_f \)) 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 \(9.07 \times 10^8\) 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, $K_e$ (L mol$^{-1}$ min$^{-1}$) | Forward Reaction Rate Constant, $k_1$ (L mol$^{-1}$ 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$^{-1}$) | 23.59            | 65.98                 |
| Pre-Exponential Factor (L mol$^{-1}$ min$^{-1}$) | 2.27              | 9.07 × 10$^8$         |
| $R^2$                  | 0.997            | 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:

\[
\begin{align*}
K_e &= A_e \exp\left(\frac{\Delta h}{RT}\right) \\
k_1 &= A_1 \exp\left(\frac{E_a}{RT}\right) \\
A_e &= A_0^e + A_W^e W \\
A_1 &= A_0^1 + A_W^1 W
\end{align*}
\]

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 (\( A_0^e \) and \( A_0^1 \)) and the coefficients (\( A_W^e \) and \( A_W^1 \)) 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)]:

\[
\frac{K_e}{e^{-\Delta h/RT}} = A_0^e + A_W^e W
\]

\[
\frac{k_1}{e^{-E_a/RT}} = A_0^1 + A_W^1 W
\]

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 (\( A_0^0 \) and \( A_0^1 \)) could therefore be determined from the slope and intercept of each regression line. The value of \( A_W^e \) and \( A_W^1 \) for the equilibrium reaction was 4.11 \times 10^6 \, W^{-1} \) and 3.69 \times 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} \) and 1.5282 \, \text{L mol}^{-1} \text{min}^{-1} .

![Figure 6](image-url)  

**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 |
|--------------------|------------------|----------------------|
| \( A_{10} \) \( \text{(L mol}^{-1}\text{min}^{-1}) \) | 1.5282            | 3.69 \( \times 10^8 \) |
| \( A_{1W} \) \( \text{(L mol}^{-1}\text{min}^{-1} \text{W}^{-1}) \) | \( 4.40 \times 10^{-3} \) | 4.11 \( \times 10^6 \) |
| \( R^2 \)          | 0.997            | 0.951                |
| \( A_{e0} \) \( \text{(W}^{-1}) \) |                     |                      |
| \( A_{eW} \) \( \text{(W}^{-1}) \) |                     |                      |

Linear relationship of pre-exponential factors to microwave power: \( A_1 = A_{10} + A_{1W}W \); \( A_e = A_{e0} + A_{eW}W \).

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., \( \text{H}_2\text{SO}_4 \)) [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 ecfriendly and efficient process to produce biodiesel.
Table 4. Oleic acid esterification using different methods for producing biodiesel.

| Catalyst                  | Catalyst Loading (%, \text{w/w}) | Conversion (%) | References |
|---------------------------|----------------------------------|----------------|------------|
| \(\text{H}_2\text{SO}_4\)  | 1                                | 99.9           | [16]       |
| \(\text{HZSM-5}\)         | 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.

Author Contributions: Conceptualization, H.C.N., H.C.O., and C.-H.S.; methodology, H.C.N., H.C.O., and C.-H.S.; validation, F.-M.W., K.K.D., and H.-Y.J.; formal analysis, H.C.N., F.-M.W., and K.K.D.; investigation, F.-M.W., K.K.D., T.T.P., H.-Y.J., and N.P.N.; resources, C.H.-S. and H.C.O.; writing—original draft preparation, H.C.N., H.C.O., and C.-H.S.; writing—review and editing, C.-H.S. and H.C.O.; supervision, C.-H.S. and H.C.O.; project administration, C.-H.S.; funding acquisition, C.-H.S. and H.C.O. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Ministry of Science and Technology of Taiwan, R.O.C.

Conflicts of Interest: The authors declare no conflict of interest.
References

1. Nguyen, H.C.; Liang, S.-H.; Chen, S.-S.; Su, C.-H.; Lin, J.-H.; Chien, C.-C. Enzymatic production of biodiesel from insect fat using methyl acetate as an acyl acceptor: Optimization by using response surface methodology. *Energy Convers. Manag.* **2018**, *158*, 168–175. [CrossRef]

2. Santos, S.; Nobre, L.; Gomes, J.; Puna, J.; Quinta-Ferreira, R.; Bordado, J. Soybean oil transesterification for biodiesel production with micro-structured calcium oxide (CaO) from natural waste materials as a heterogeneous catalyst. *Energies* **2019**, *12*, 4670. [CrossRef]

3. Choi, K.; Park, S.; Roh, H.G.; Lee, C.S. Combustion and emission reduction characteristics of GTL-biodiesel fuel in a single-cylinder diesel engine. *Energies* **2019**, *12*, 2201. [CrossRef]

4. Mahlia, T.M.I.; Syazmi, Z.A.H.S.; Mofijur, M.; Abas, A.E.P.; Bilad, M.R.; Ong, H.C.; Silitonga, A.S. Patent landscape review on biodiesel production: Technology updates. *Renew. Sustain. Energy Rev.* **2020**, *118*, 109526. [CrossRef]

5. Suresh, M.; Jawahar, C.; Richard, A. A review on biodiesel production, combustion, performance, and emission characteristics of non-edible oils in variable compression ratio diesel engine using biodiesel and its blends. *Renew. Sustain. Energy Rev.* **2018**, *92*, 38–49. [CrossRef]

6. Ong, H.C.; Masjuki, H.H.; Mahlia, T.M.I.; Silitonga, A.S.; Chong, W.T.; Yusaf, T. Engine performance and emissions using *Jatropha curcas*, *Ceiba pentandra* and *Calophyllum inophyllum* biodiesel in a CI diesel engine. *Energy* **2014**, *69*, 427–445. [CrossRef]

7. Selvaraj, R.; Praveen Kumar, R.; Moorthy, I.G. A comprehensive review of biodiesel production methods from various feedstocks. *Biofuels* **2019**, *10*, 325–333. [CrossRef]

8. Almasi, S.; Ghobadian, B.; Najafi, G.H.; Yusaf, T.; Dehghani Soufi, M.; Hoseini, S.S. Optimization of an ultrasonic-assisted biodiesel production process from one genotype of rapeseed (TERI (OE) R-983) as a novel feedstock using response surface methodology. *Energies* **2019**, *12*, 2656. [CrossRef]

9. Nguyen, H.C.; Liang, S.-H.; Doan, T.T.; Su, C.-H.; Yang, P.-C. Lipase-catalyzed synthesis of biodiesel from black soldier fly (*Hermetia illucens*): Optimization by using response surface methodology. *Energy Convers. Manag.* **2017**, *145*, 335–342. [CrossRef]

10. Khan, I.U.; Yan, Z.; Chen, J. Optimization, transesterification and analytical study of *Rhus typhina* non-edible seed oil as biodiesel production. *Energies* **2019**, *12*, 4290. [CrossRef]

11. Hsiao, M.-C.; Chang, L.-W.; Hou, S.-S. Study of solid calcium diglyceroxide for biodiesel production from waste cooking oil using a high speed homogenizer. *Energies* **2019**, *12*, 3205. [CrossRef]

12. Su, C.-H.; Nguyen, H.C.; Pham, U.K.; Nguyen, M.L.; Juan, H.-Y. Biodiesel production from a novel nonedible feedstock, soursoe (*Annona muricata* L.) seed oil. *Energies* **2018**, *11*, 2562. [CrossRef]

13. Silitonga, A.S.; Masjuki, H.H.; Mahlia, T.M.I.; Ong, H.C.; Chong, W.T.; Boosroh, M.H. Overview properties of biodiesel blends from edible and non-edible feedstock. *Renew. Sustain. Energy Rev.* **2013**, *17*, 346–360. [CrossRef]

14. Li, Q.; Zheng, L.; Cai, H.; Garza, E.; Yu, Z.; Zhou, S. From organic waste to biodiesel: Black soldier fly, *Hermetia illucens*, makes it feasible. *Fuel* **2011**, *90*, 1545–1548. [CrossRef]

15. Ong, H.C.; Milano, J.; Silitonga, A.S.; Hassan, M.H.; Shamsuddin, A.H.; Wang, C.-T.; Indra Mahlia, T.M.; Siswantor, J.; Kusumo, F.; Sutrison, J. Biodiesel production from *Calophyllum inophyllum-Ceiba pentandra* oil mixture: Optimization and high speed homogenizer. *J. Clean. Prod.* **2019**, *219*, 183–198. [CrossRef]

16. Lucena, I.L.; Saboya, R.M.; Oliveira, J.F.; Rodrigues, M.L.; Torres, A.E.; Cavalcante, C.L., Jr.; Parente, E.J., Jr.; Silva, G.F.; Fernandes, F.A. Oleic acid esterification with ethanol under continuous water removal conditions. *Fuel* **2011**, *90*, 902–904. [CrossRef]

17. Mardhiah, H.H.; Ong, H.C.; Masjuki, H.; Lim, S.; Lee, H. A review on latest developments and future prospects of heterogeneous catalyst in biodiesel production from non-edible oils. *Renew. Sustain. Energy Rev.* **2017**, *67*, 1225–1236. [CrossRef]

18. Melero, J.A.; Bautista, L.F.; Morales, G.; Iglesias, J.; Sánchez-Vázquez, R. Biodiesel production from crude palm oil using sulfonic acid-modified mesostructured catalysts. *Chem. Eng. J.* **2010**, *161*, 323–331. [CrossRef]

19. Costa, A.A.; Braga, P.R.; de Macedo, J.L.; Dias, J.A.; Dias, S.C. Structural effects of WO₃ incorporation on USY zeolite and application to free fatty acids esterification. *Micropor. Mesopor. Mat.* **2012**, *147*, 142–148. [CrossRef]
20. Vieira, S.S.; Magriotis, Z.M.; Santos, N.A.; Saczk, A.A.; Hori, C.E.; Arroyo, P.A. Biodiesel production by free fatty acid esterification using lanthanum (La\(^{3+}\)) and HZSM-5 based catalysts. Bioresour. Technol. 2013, 133, 248–255. [CrossRef]

21. Álvarez-Mateos, P.; García-Martín, J.; Guerrero-Vacas, F.; Naranjo-Calderón, C.; Barrios-Sánchez, C.; Pérez Camino, M.D.C. Valorization of a high-acidity residual oil generated in the waste cooking oils recycling industries. Grasas y Aceites 2019, 70, e335. [CrossRef]

22. Fan, M.; Si, Z.; Sun, W.; Zhang, P. Sulfonated \(\text{ZrO}_2\)-\(\text{TiO}_2\) nanorods as efficient solid acid catalysts for heterogeneous esterification of palmitic acid. Fuel 2019, 252, 254–261. [CrossRef]

23. Selvakumar, P.; Sivashanmugam, P. Ultrasound assisted oleaginous yeast lipid extraction and garbage lipase catalyzed transesterification for enhanced biodiesel production. Energy Convers. Manag. 2019, 179, 141–151. [CrossRef]

24. Nguyen, H.C.; Huang, D.T.M.; Juan, H.-Y.; Su, C.-H.; Chien, C.-C. Liquid lipase-catalyzed esterification of oleic acid with methanol for biodiesel production in the presence of superabsorbent polymer: Optimization by using response surface methodology. Energies 2018, 11, 1085. [CrossRef]

25. Amini, Z.; Ilham, Z.; Ong, H.C.; Mazaheri, H.; Chen, W.-H. State of the art and prospective of lipase-catalyzed transesterification reaction for biodiesel production. Energy Convers. Manag. 2017, 141, 339–353. [CrossRef]

26. Budžáki, S.; Miljić, G.; Sundaram, S.; Tisma, M.; Hessel, V. Cost analysis of enzymatic biodiesel production in small-scaled packed-bed reactors. Appl. Energy 2018, 210, 268–278. [CrossRef]

27. Rani, K.N.P.; Neeharika, T.S.V.R.; Kumar, T.P.; Satyavathi, B.; Sailu, C. Kinetics of non-catalytic esterification of free fatty acids present in Jatropha oil. J. Oleo Sci. 2016, 65, 441–445. [CrossRef]

28. Alenezi, R.; Leeke, G.; Winterbottom, J.; Santos, R.; Khan, A. Esterification kinetics of free fatty acids with supercritical methanol for biodiesel production. Energy Convers. Manag. 2010, 51, 1055–1059. [CrossRef]

29. Tsai, Y.-T.; Lin, H.-M.; Lee, M.-J. Biodiesel production with continuous supercritical process: Non-catalytic transesterification and esterification with or without carbon dioxide. Bioresour. Technol. 2013, 145, 362–369. [CrossRef]

30. Cho, H.J.; Kim, S.H.; Hong, S.W.; Yeo, Y.-K. A single step non-catalytic esterification of palm fatty acid distillate (PFAD) for biodiesel production. Fuel 2012, 93, 373–380. [CrossRef]

31. Martinez-Guerra, E.; Howlader, M.S.; Shields-Menard, S.; French, W.T.; Gude, V.G. Optimization of wet microalgal FAME production from \textit{Nannochloropsis} sp. under the synergistic microwave and ultrasound effect. Int. J. Energy Res. 2018, 42, 1934–1949. [CrossRef]

32. Thakkar, K.; Shah, K.; Kodgire, P.; Kachhwaha, S.S. In-situ reactive extraction of castor seeds for biodiesel production using the coordinated ultrasound–microwave irradiation: Process optimization and kinetic modeling. Ultrason. Sonochem. 2019, 50, 6–14. [CrossRef] [PubMed]

33. Encinar, J.; González, J.; Martínez, G.; Sánchez, N.; Pardal, A. Soybean oil transesterification by the use of a microwave flow system. Fuel 2012, 95, 386–393. [CrossRef]

34. Thakkar, K.; Shah, K.; Kodgire, P.; Kachhwaha, S.S. In-situ reactive extraction of castor seeds for biodiesel production using the coordinated ultrasound–microwave irradiation: Process optimization and kinetic modeling. Ultrason. Sonochem. 2019, 50, 6–14. [CrossRef] [PubMed]

35. Srivastava, G.; Sivasankar, N.; Aroua, M.K. Microwave-assisted transesterification of industrial grade crude glycerol for the production of glycerol carbonate. Chem. Eng. J. 2016, 284, 469–477. [CrossRef]

36. Silitonga, A.S.; Shamsuddin, A.H.; Mahlia, T.M.; Milano, J.; Kusumo, F.; Siswanto, J.; Dharma, S.; Sebayang, A.H.; Masjuki, H.H.; Ong, H.C. Biodiesel synthesis from \textit{Ceiba pentandra} oil by microwave irradiation-assisted transesterification: ELM modeling and optimization. Renew. Energy 2020, 146, 1278–1291. [CrossRef]

37. Teng, W.K.; Ngoh, G.C.; Yusoff, R.; Aroua, M.K. Microwave-assisted transesterification of industrial grade crude glycerol for the production of glycerol carbonate. Chem. Eng. J. 2016, 284, 469–477. [CrossRef]

38. Silitonga, A.S.; Shamsuddin, A.H.; Mahlia, T.M.; Milano, J.; Kusumo, F.; Siswanto, J.; Dharma, S.; Sebayang, A.H.; Masjuki, H.H.; Ong, H.C. Biodiesel synthesis from \textit{Ceiba pentandra} oil by microwave irradiation-assisted transesterification: ELM modeling and optimization. Renew. Energy 2020, 146, 1278–1291. [CrossRef]

39. Milano, J.; Ong, H.C.; Masjuki, H.H.; Silitonga, A.S.; Chen, W.-H.; Kusumo, F.; Dharma, S.; Sebayang, A.H. Optimization of biodiesel production by microwave irradiation-assisted transesterification for waste cooking oil-\textit{Calophyllum inophyllum} oil via response surface methodology. Energy Convers. Manag. 2018, 158, 400–415. [CrossRef]

40. Cui, Y.; Liang, Y. Direct transesterification of wet \textit{Cryptococcus curvatus} cells to biodiesel through use of microwave irradiation. Appl. Energy 2014, 119, 438–444. [CrossRef]

41. Ye, W.; Gao, Y.; Ding, H.; Liu, M.; Liu, S.; Han, X.; Qi, J. Kinetics of transesterification of palm oil under conventional heating and microwave irradiation, using CaO as heterogeneous catalyst. Fuel 2016, 180, 574–579. [CrossRef]

42. Teo, C.L.; Idris, A. Evaluation of direct transesterification of microalgae using microwave irradiation. Bioresour. Technol. 2014, 174, 281–286. [CrossRef]
40. Ye, J.; Zhu, H.; Yang, Y.; Huang, K.; Raghavan, G.V. Dynamic analysis of a continuous-flow microwave-assisted screw propeller system for biodiesel production. *Chem. Eng. Sci.* 2019, 202, 146–156. [CrossRef]

41. Nguyen, H.C.; Lee, H.-Y.; Su, C.-H.; Shih, W.-J.; Chien, C.-C. Green process for fatty acid production from soybean oil through microwave-mediated autocatalytic synthesis. *Chem. Eng. Process.* 2020, 147, 107782. [CrossRef]

42. Nguyen, H.C.; Ong, H.C.; Pham, T.T.T.; Dinh, T.K.K.; Su, C.H. Microwave-mediated noncatalytic synthesis of ethyl levulinate: A green process for fuel additive production. *Int. J. Energy Res.* 2019, 44, 1698–1708. [CrossRef]

43. Nguyen, H.C.; Ong, H.C.; Pham, T.T.T.; Dinh, T.K.K.; Su, C.H. Microwave-mediated noncatalytic synthesis of ethyl levulinate: A green process for fuel additive production. *Int. J. Energy Res.* 2019, 44, 1698–1708. [CrossRef]

44. Knothe, G. Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters. *Fuel Proces. Technol.* 2005, 86, 1059–1070. [CrossRef]

45. Li, Q.; Xu, J.; Du, W.; Li, Y.; Liu, D. Ethanol as the acyl acceptor for biodiesel production. *Renew. Sustain. Energy Rev.* 2013, 25, 742–748. [CrossRef]

46. Pan, Y.; Alam, M.A.; Wang, Z.; Wu, J.; Zhang, Y.; Yuan, Z. Enhanced esterification of oleic acid and methanol by deep eutectic solvent assisted Amberlyst heterogeneous catalyst. *Bioresour. Technol.* 2016, 220, 543–548. [CrossRef] [PubMed]

47. Su, C.-H. Kinetic study of free fatty acid esterification reaction catalyzed by recoverable and reusable hydrochloric acid. *Bioresour. Technol.* 2013, 130, 522–528. [CrossRef] [PubMed]

48. Warrand, J.; Janssen, H.-G. Controlled production of oligosaccharides from amylose by acid-hydrolysis under microwave treatment: Comparison with conventional heating. *Carbohydr. Polym.* 2007, 69, 353–362. [CrossRef]

49. Aguilar-Reynosa, A.; Romaní, A.; Rodríguez-Jasso, R.M.; Aguilar, C.N.; Garrote, G.; Ruiz, H.A. Comparison of microwave and conduction-convection heating autohydrolysis pretreatment for bioethanol production. *Bioresour. Technol.* 2017, 243, 273–283. [CrossRef]

50. Loong, T.C.; Idris, A. Rapid alkali catalyzed transesterification of microalgae lipids to biodiesel using simultaneous cooling and microwave heating and its optimization. *Bioresour. Technol.* 2014, 174, 311–315. [CrossRef]

51. Huang, Y.-F.; Chiueh, P.-T.; Kuan, W.-H.; Lo, S.-L. Microwave pyrolysis of lignocellulosic biomass: Heating performance and reaction kinetics. *Energy* 2016, 100, 137–144. [CrossRef]

52. Gole, V.L.; Gogate, P.R. Intensification of glycerolysis reaction of higher free fatty acid containing sustainable feedstock using microwave irradiation. *Fuel Process. Technol.* 2014, 118, 110–116. [CrossRef]

53. Zanuttini, M.S.; Pisarello, M.; Querini, C.A. *Butia Yatay* coconut oil: Process development for biodiesel production and kinetics of esterification with ethanol. *Energy Convers. Manag.* 2014, 85, 407–416. [CrossRef]

54. Minami, E.; Saka, S. Kinetics of hydrolysis and methyl esterification for biodiesel production in two-step supercritical methanol process. *Fuel* 2006, 85, 2479–2483. [CrossRef]

55. Ramadhas, A.S.; Jayaraj, S.; Muraleedharan, C. Biodiesel production from high FFA rubber seed oil. *Fuel* 2005, 84, 335–340. [CrossRef]

56. Singh, V.; Sharma, Y.C. Low cost guinea fowl bone derived recyclable heterogeneous catalyst for microwave assisted transesterification of *Annona squamosa* L. seed oil. *Energy Convers. Manag.* 2017, 138, 627–637. [CrossRef]

57. Su, C.H.; Fu, C.C.; Gomes, J.; Chu, L.; Wu, W.T. A heterogeneous acid-catalyzed process for biodiesel production from enzyme hydrolyzed fatty acids. *AIChE J.* 2008, 54, 327–336. [CrossRef]

58. Melo-Júnior, C.A.; Albuquerque, C.E.; Fortuny, M.; Dariva, C.; Egues, S.; Santos, A.F.; Ramos, A.L. Use of microwave irradiation in the noncatalytic esterification of C18 fatty acids. *Energy Fuels* 2009, 23, 580–585. [CrossRef]

59. De la Hoz, A.; Diaz-Ortiz, A.; Moreno, A. Microwaves in organic synthesis. Thermal and non-thermal microwave effects. *Chem. Soc. Rev.* 2005, 34, 164–178. [CrossRef]

60. Lin, Z.-R.; Zeng, X.-A.; Yu, S.-J.; Sun, D.-W. Enhancement of ethanol–acetic acid esterification under room temperature and non-catalytic condition via pulsed electric field application. *Food Bioprocess Technol.* 2012, 5, 2637–2645. [CrossRef]
61. Gude, V.G.; Patil, P.; Martinez-Guerra, E.; Deng, S.; Nirmalakhandan, N. Microwave energy potential for biodiesel production. *Sustain. Chem. Process.* **2013**, *1*, 5. [CrossRef]

62. Mutyala, S.; Fairbridge, C.; Paré, J.J.; Bélanger, J.M.; Ng, S.; Hawkins, R. Microwave applications to oil sands and petroleum: A review. *Fuel Process. Technol.* **2010**, *91*, 127–135. [CrossRef]

© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).
