

## Article

# Enhanced Biodiesel Synthesis via a Homogenizer-Assisted Two-Stage Conversion Process Using Waste Edible Oil as Feedstock

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**Abstract:** In this study, a homogenizer in conjunction with a two-stage process was utilized to facilitate biodiesel production from waste edible oil (WEO). This paper contributes to the improvement of the yield and the shortening of the reaction time for biodiesel synthesis. Sulfuric acid was used in the first stage which was the esterification of the free fatty acids (FFA) of the WEO; then the transesterification reaction of triglycerides took place in the second stage with an alkaline catalysis. The present investigation aimed to explore the parameters affecting the reactions, including homogenizer speed, alcohol/oil molar ratio, catalyst dosage, reaction temperature, and reaction time. Under the operating conditions of the first stage (the reaction temperature was 65 °C, the homogenizer speed was 8000 rpm, the methanol/oil molar ratio was 15:1, and the amount of sulfuric acid was 4 wt%), the acid value fell to below 2 mg KOH/g after 10 min. The best base-catalyzed conditions in the second stage were: homogenizer speed of 8000 rpm, NaOH catalyst concentration of 1 wt%, methanol/oil molar ratio of 9:1 (mol/mol), reaction temperature of 65 °C, and reaction time 10 min. Consequently, the conversion rate from WEO to biodiesel achieved 97% after only 20 min, in line with the EU EN14214 standard, which requires a biodiesel production rate of at least 96.5%.

**Keywords:** biodiesel; waste edible oil; transesterification; homogenize; esterification



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## 1. Introduction

Extensive use of fossil fuels not only leads to the depletion of petroleum resources and energy crisis, but also leads to increasingly serious greenhouse effects such as global warming and climate change due to carbon dioxide emissions, further making the development of alternative fuels more and more important. The conversion of feedstocks containing triglycerides and free fatty acids (FFA), such as vegetable oils, into biodiesel is considered one of the most promising options [1]. The waste edible oil amount accumulated day by day from restaurants, fast-food stands, or families will become a significantly big source of poison to the environment if it is not effectively collected and used. Fortunately, this waste can also be reused to make biodiesel. Biodiesel shows the following general advantages: (1) it lowers dependence on imported oil; (2) it produces lower harmful emissions (especially SO<sub>x</sub>); (3) it limits greenhouse gas emissions; (4) it is a non-toxic fuel and biodegradable; (5) it can help improve the rural economy (circular economy) due to the use of agricultural residues; (6) it can be used without engine modifications; (7) it improves combustion because of the oxygen content; and (8) it provides good engine performance [1,2]. However, biodiesel has certain disadvantages, such as low calorific value [3], high viscosity [4], high NO<sub>x</sub> emission [5,6], and high fuel consumption [3,4]. Fortunately, these problems can be overcome by adding additives to the biodiesel blend to improve fuel properties [4].

The processes for synthesizing biodiesel include transesterification, microemulsions, pyrolysis, and blending [7]. Among them, the most commonly used method is transesterification. Transesterification is a catalyzed (acid-catalyzed or base-catalyzed) chemical reaction of triglycerides with alcohols to produce biodiesel, composed of fatty acid alkyl esters (FAAE), and glycerol. The alkaline process could produce high-purity, high-yield biodiesel in 30–60 min [2,8,9]. The major constituents of vegetable oils are triglycerides, consisting of three long-chain fatty acids esterified to the glycerol skeleton. The reaction of triglycerides and alcohols results in the release of three fatty acid chains from the glycerol backbone, which then combine with alcohols to synthesize fatty acid methyl esters (FAME). During this process, a by-product, glycerol, is produced [10,11]. The use of alkali catalysts possesses the advantages of low cost and high conversion rate, which is currently the most common method for synthesizing biodiesel. Unfortunately, a lot of energy consumption and wash water make glycerol recovery difficult. Additionally, when the content of FFA is higher than 0.5% by weight, FFA that cannot be converted into biodiesel causes saponification, which is a very serious problem. Conversely, acid catalysts should be used in such cases [12]. Similarly, acid catalysts also have advantages and disadvantages. Acid catalysts, such as sulfuric acid, can improve the conversion rate, but the time is longer [13]. In general, both acid- and base-catalyzed reactions possess important advantages compared to that with only raw materials [14]. Esterification and transesterification reactions may occur simultaneously in the acid-catalyzed mixtures. Consequently, feedstocks high in FFA (e.g., animal fats, waste edible oil), which are often much less expensive, can be used directly with acid catalysts [15]. Using these cheap feedstocks to produce biodiesel can reduce costs. The use of WEO as a raw material and acid-catalyzed pretreatment process should be carried out to enhance biodiesel production. When the FFA content is less than 0.5% and if the used catalyst is expected to be removed from the remaining oil easily, a solid base catalyst is chosen to complete the transesterification reaction. In general, a combined acid-base two-stage catalytic method can be considered to shorten the reaction time [16–18].

Several studies have proven that the catalyst dosage [19,20], alcohol/oil molar ratio [21–23], reaction temperature [24–26], and reaction time [25,26] greatly affected the transesterification reaction. Thus, they are important factors to be investigated. In addition, the process can also be accelerated by using ultrasound [16,27,28] or microwave [29–32] to promote the reaction. In the previous study [25], the optimal reaction conditions including methanol/oil molar ratio, catalyst dosage, reaction temperature, and reaction time were investigated to achieve the highest conversion of biodiesel. It was also found that a 1 min mixing period by ultrasound and a 2 min energizing period by closed microwave irradiation was the optimal procedure.

Homogenizers are often used in large-scale processing industries. It has been recently reported that homogenizers have the potential to be easily scaled up and significantly shorten the reaction time of transesterification [33–35]. However, there are relatively few studies related to homogenizer systems for biodiesel production, especially using a two-stage synthesis method. In this investigation, enhancement in biodiesel synthesis was achieved using a two-step catalyzed process via a homogenizer. This method can be used when ultrasound or microwave equipment cannot be afforded. To reduce the high cost of biodiesel synthesis, various ideas were proposed such as the use of WEO [36–38], the development of various catalysts [39–43], and the modification of the manufacturing process [44,45]. Here, WEO was chosen as the raw material. This investigation mainly aimed to find the optimal operating conditions to synthesize biodiesel via a homogenizer in conjunction with a two-stage process.

## 2. Materials and Methods

Experimental substances were all purchased from excellent suppliers. Sodium hydroxide 99%, sulfuric acid 99%, and methanol 99.8% were purchased from Shiyaku Company; zinc oxide (ZnO) 99.8% was purchased from Mallickrodt Company, and Fluka Company was the supplier of Methyl laurate and acetic acid. Waste edible oils utilized herein were

gathered from local restaurants in Tainan, Taiwan. Food remaining in the waste edible oil was first removed by a filtering process. The acid value (AV) and saponification value (SV) were determined by a standard titrimetry method (AOCS: American Oil Chemists' Society). The acid value determination included the following steps: 5 g oil was put into a 250 mL cone bottle together with 150 mL mixture of alcohol and ether (volume ratio 1:1 *v/v*); next several drops of 1% phenolphthalein indicator were added and finally 0.1 N potassium hydroxide for titration was added. The saponification value (SV) determination steps were: 2 g oil was put into a 250 mL cone bottle; next 0.5 N potassium hydroxide alcohol solution was added and mixed well in 1 h before some drops of 1% phenolphthalein indicator were added, and finally 0.5 N hydrochloric acid solution was added for titration. Then, the SV was determined using Equation (1) [29,30], and the AV was calculated via Equation (2) [33–35]. Where *W* is the oil weight (g), *B* designates blank titration amount (mL), *S* is sample titration amount (mL), *V*<sub>NaOH</sub> denotes the volume (mL) of the NaOH titrant.

$$SV = \frac{(B - S) \times 56.1 \times 0.5}{W}, \quad (1)$$

$$AV = \frac{5.61 \times V_{NaOH}}{W}. \quad (2)$$

After determining the saponification value (SV) and acid value (AV), which were 287.36 and 4.36 mg KOH/g, respectively, the molecular weight (MW) of WEO could be calculated as 585.67 using Equation (3) [33–35].

$$MW = 56.1 \times 1000 \times \frac{3}{(SV - AV)}. \quad (3)$$

In the first stage of the reaction process, a homogenizer model Hsiangtai HM-300 Power (Figure 1), whose speed could be set at 3000–9000 rpm, was utilized to improve the uniformity of the reactants. Additionally, the molar ratio (MeOH to WEO) was controlled ranging from 6:1 to 18:1, the catalyst dosage was from 1 to 5 wt% and the reaction temperature was from 50 to 90 °C. The homogenizing process was carried out for 2 to 12 min until the reaction completed. After being washed with ionized water several times, the product was collected to get ready for the second-stage reaction. The reaction conditions in the second stage were: alcohol/oil ratio 6:10; catalyst dosage 0.5–1.5%; reaction temperature 55–70 °C and reaction time 2.5–12.5 min. After the reaction finished, the FAME layer that floated up to the top of the mixture was removed in a separating funnel. The methyl ester biodiesel product was washed at least three times with acetate 30% and deionized water and finally dried at 105 ± 3 °C in an oven.

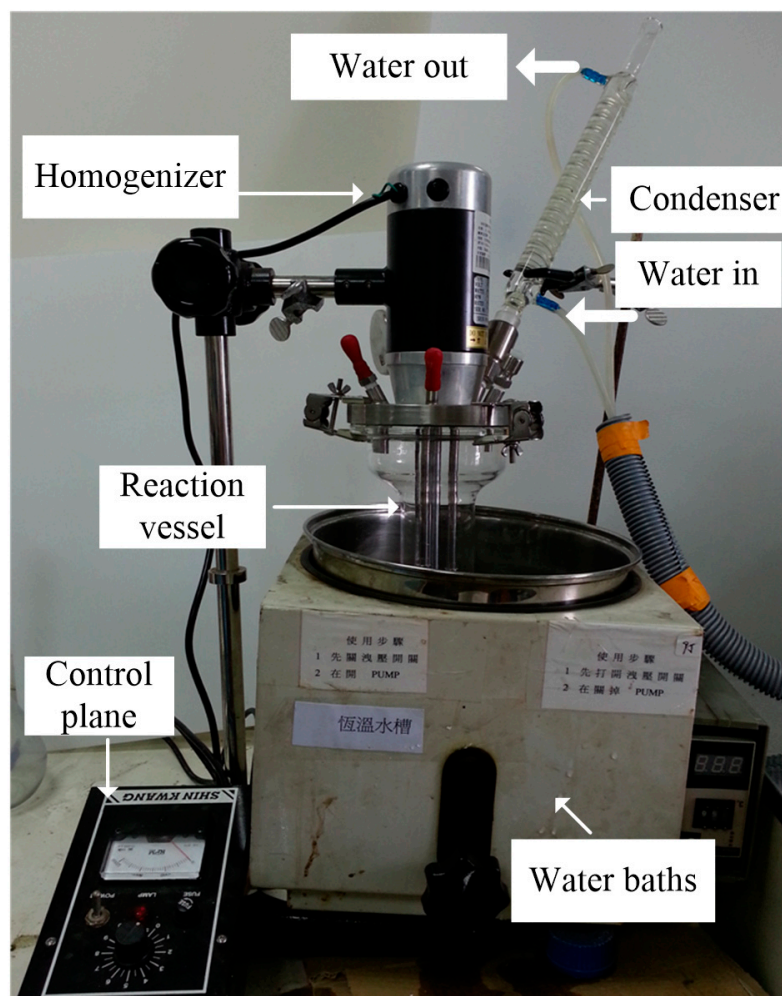


Figure 1. Experimental apparatus [33–35].

Some samples were taken for analysis with a Perkin Elmer GC Clarus 600 equipped with a capillary column (SPBTM-WAX, 30 m × 0.75 m × 1.0 μm) and a flame ionization detector (FID). Methyl laurate was added to the crude biodiesel as an internal standard, and then the sample was injected under the following conditions: carrier gas nitrogen; injector temperature 280 °C with a split ratio of 1:20; and temperature of the detector 300 °C. The oven temperature started at 210 °C for 4 min, then increased to 240 °C at a rate of 4 °C/min, and finally maintained at 240 °C for 8 min [39]. Equation (4) could be used to calculate the conversion rate of the crude biodiesel [16,29,30] as follows:

$$\text{Conversion(\%)} = \frac{\left( \frac{\text{area of FAME}}{\text{area of reference}} \right) \times \text{weight of reference}}{\text{weight of crude oil}}. \quad (4)$$

### 3. Results and Discussion

#### 3.1. Factors Affecting the Esterification Reaction in the First Stage

##### 3.1.1. Effect of Rotational Speed on the Acid Value

The use of a homogenizer at different speeds to facilitate the transesterification reaction did result in different acid value levels, as shown in Table 1 (operation conditions: catalyst (sulfuric acid) amount 3 wt%, methanol/oil molar ratio 12:1, reaction time 10 min, reaction temperature 65 °C). The acid value decreased as the speed increased. For example, at the speed of 8000 rpm, the acid value reduced to 3.46 mg KOH/g. However, increasing the

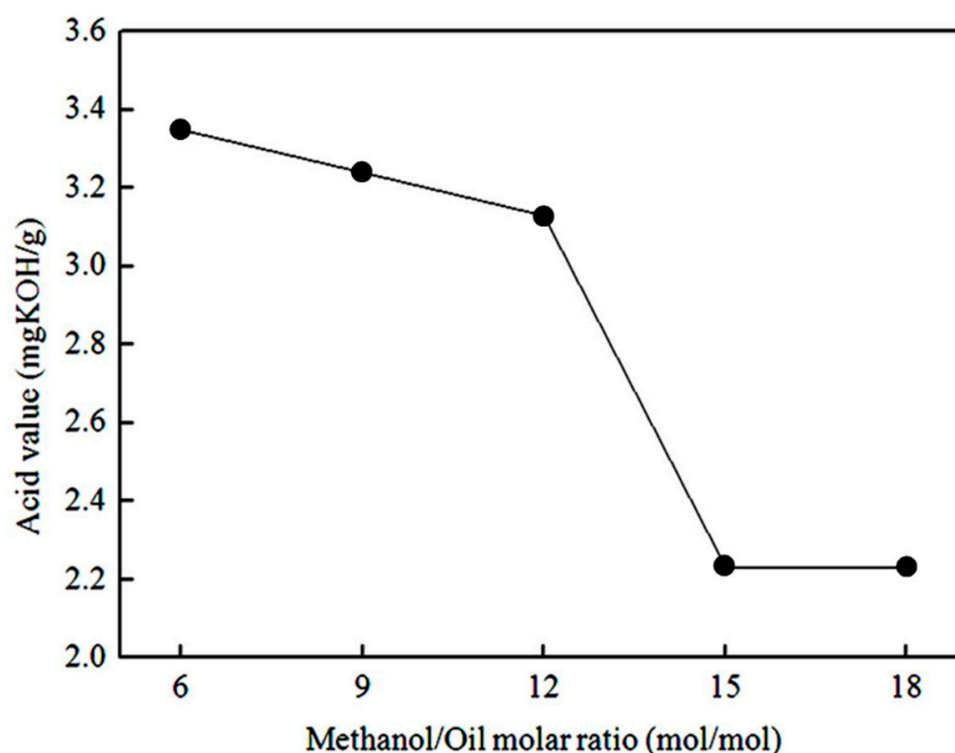
speed further to 9000 rpm could not reduce the acid value faster. It was because the speed of 8000 rpm was good enough for the reactants to be fully mixed with each other.

**Table 1.** Effect of rotational speed on the acid value.

Revolution (rpm)	Acid Value (mg KOH/g)
3000	4.12
5000	3.59
7000	3.57
8000	3.46
9000	3.46

### 3.1.2. Effect of Methanol/Oil Molar Ratio on the Acid Value

The methanol/oil molar ratio greatly affects the acid value, as shown in Figure 2. Operation conditions were: homogenizer speed 8000 rpm, catalyst (sulfuric acid) amount 3 wt%, reaction time 10 min, and reaction temperature 65 °C. Figure 2 depicts the decrease in acid value with increasing methanol/oil molar ratio, which is consistent with the study by Hsiao et al. [16]. More specifically, as the ratio was changed from 6:1 to 18:1, the acid value decreased dramatically. At a 6:1 molar ratio, the acid value was 3.35 mg KOH/g. With increasing the molar ratio to 9:1 or 12:1, the acid value decreased slowly and remained above 3 mg KOH/g. However, at a 15:1 molar ratio, it decreased more rapidly to 2.23 mg KOH/g. There was almost no change in the acid value at a higher molar ratio of 18:1. Consequently, for economic considerations and reduction of unnecessary waste, a 15:1 molar ratio (MeOH to WEO) was the most suitable.

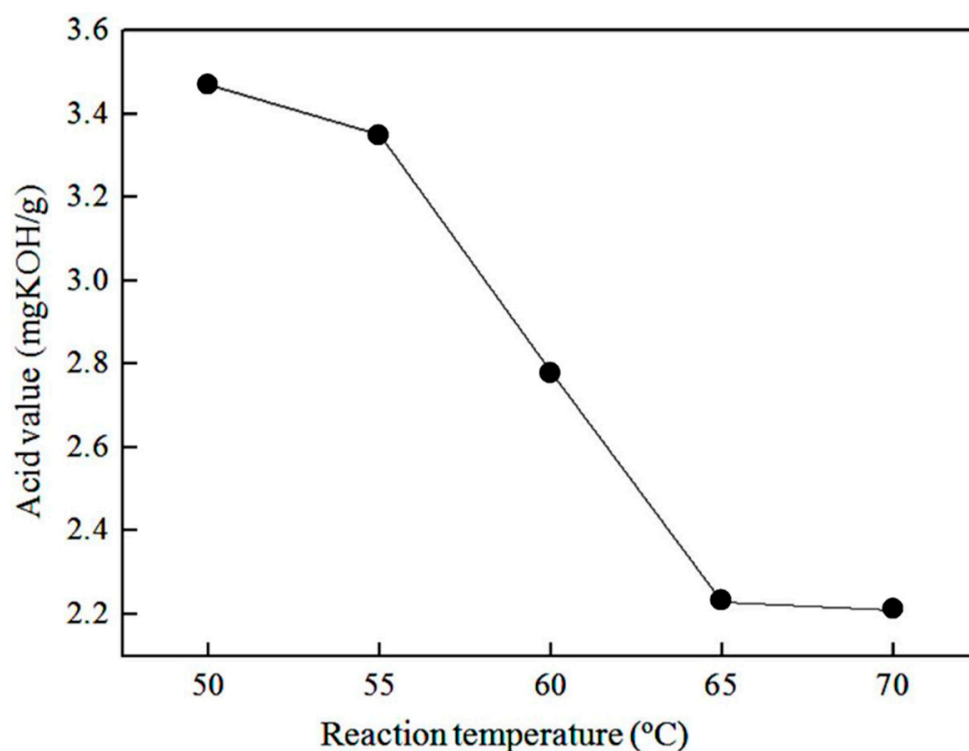


**Figure 2.** Effect of methanol/oil molar ratio on the acid value.



### 3.1.3. Effect of Reaction Temperature on the Acid Value

Figure 3 indicates the acid value as a function of temperature (50–70 °C) under the experimental conditions: homogenizer speed 8000 rpm, methanol/oil molar ratio 12:1, added sulfuric acid amount 3 wt%, reaction time 10 min. Results showed that the acid value of waste edible oil was reversely proportional to the reaction temperature. This trend is consistent with the findings of Hsiao et al. [16] and Sadaf et al. [46]. With increasing the reaction temperature, the solubility of methanol in the oil increased and the homogeneous level reaction system enhanced. This led to an increase in the reaction between free fatty acids and methanol. Thus, the mass transfer resistance of the two-phase reaction system is reduced. When the temperature exceeded 65 °C, however, the acid value did not drop significantly. This was mainly because of the 64.5 °C boiling point of methanol. When the reaction temperature got over 65 °C, methanol evaporated and escaped quickly from the reaction mixture. This evaporation slowed down the esterification reaction. Therefore, the acid value did not significantly reduce at reaction temperatures higher than 65 °C. Additionally, 65 °C could be the most suitable reaction temperature.

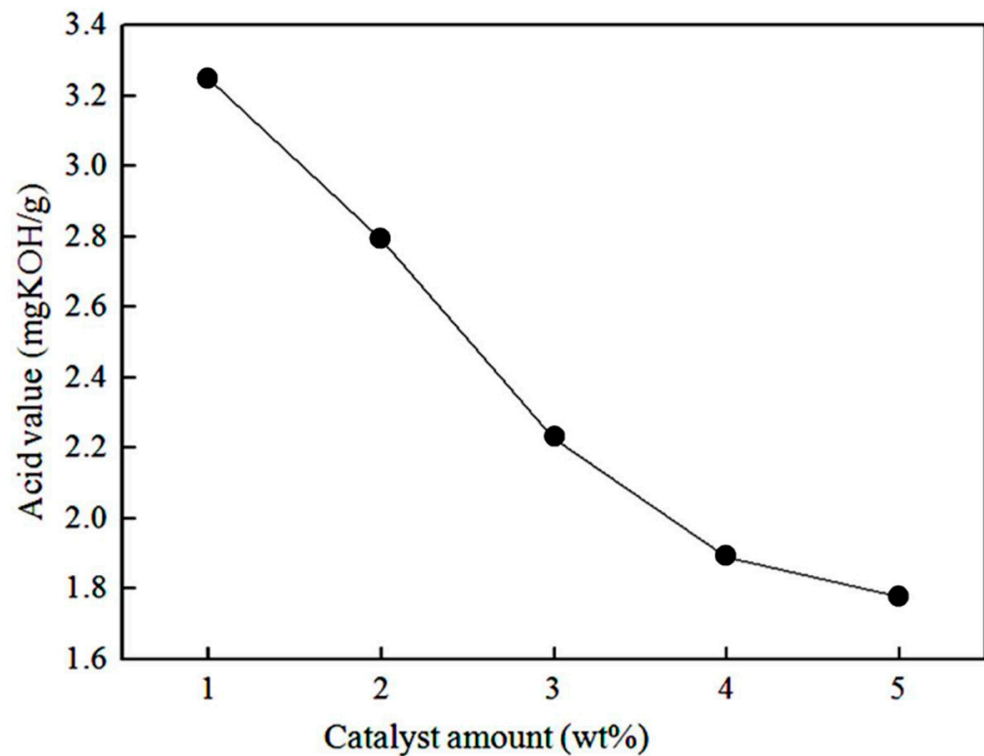


**Figure 3.** Effect of reaction temperature on the acid value.

### 3.1.4. Effect of Catalyst Amount on the Acid Value

Figure 4 demonstrates that catalyst amount also has an important effect on the acid value. The catalyst adopted was sulfuric acid because it not only acted as a catalyst but also removed esterification impurities such as phospholipids. Thus, it could help simplify the transesterification of the final product and the biodiesel purification. Furthermore, using sulfuric acid as a catalyst, the esterification reaction of free fatty acid and methanol occurred. Although the transesterification reaction of oil and methanol also took place, the reaction was very slow and could be ignored in the acid catalyst. In Figure 4, the experimental conditions were: homogenizer speed 8000 rpm, methanol/oil molar ratio 15:1, reaction time 10 min, and reaction temperature 65 °C. The acid value decreased with the increase in catalyst dosage, as found in the previous study [16]. When the amount of sulfuric acid added was varied from 1 to 5 wt%, the acid value showed a downward trend, from more than 3.2 mg KOH/g to below 1.8 mg KOH/g (Figure 4). Since an acid value of

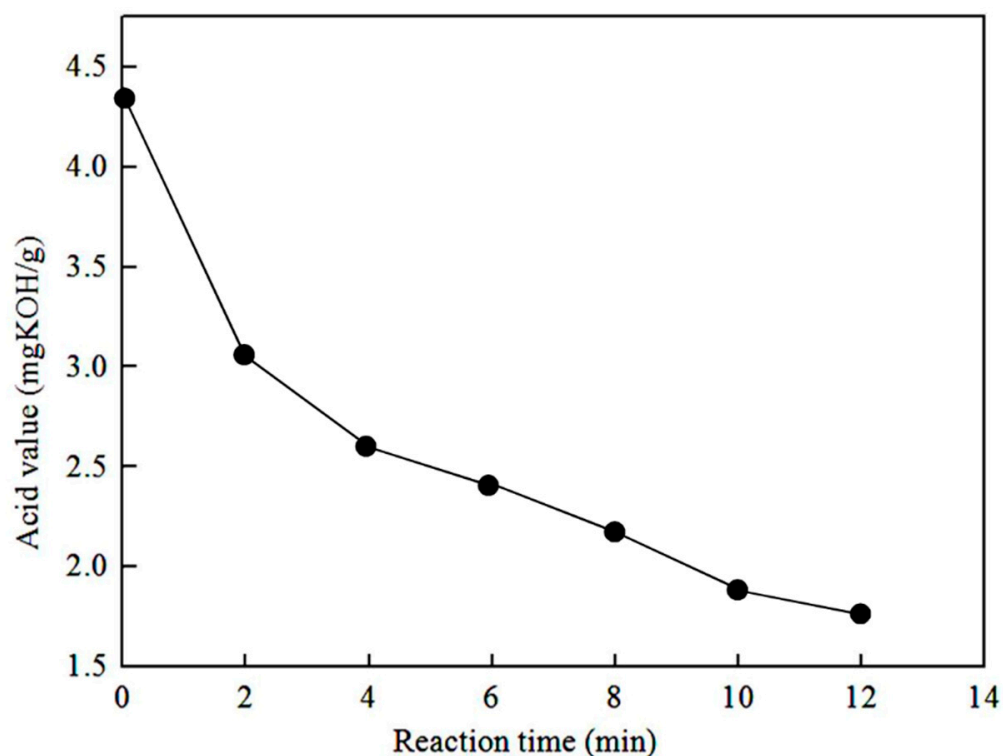
2 mg KOH/g meets the requirement for the transesterification reaction (second stage), it is recommended to add 4 wt% sulfuric acid.



**Figure 4.** Effect of catalyst amount on the acid value.

### 3.1.5. Effect of Reaction Time on the Acid Value

Figure 5 demonstrates the acid value versus reaction time under the following experimental conditions: homogenizer speed 8000 rpm, methanol/oil molar ratio 15:1, added catalyst (sulfuric acid) 4 wt%, reaction temperature 65 °C. The reaction time varied from 2–12 min. It was found that the longer the reaction time, the lower the acid value. As both the waste edible oil and methanol had different polarities, they could not automatically fully mix. However, when the reaction time increased, more monoglyceride, glycerol, and fatty acid methyl esters were formed, and they improved the uniformity of the reaction system. The homogeneous catalytic transesterification reaction was supported and took place faster. When the reaction time reached 10 min, the acid value dropped below 2.0 mg KOH/g. Thus, the best reaction period should be 10 min. This optimal reaction time is shorter than the 40 min found in Hsiao et al.'s study [16] and the 60 min reported in He et al.'s study [17].



**Figure 5.** Effect of reaction time on the acid value.

### 3.2. Factors Affecting the Transesterification Reaction in the Second Stage

According to the above results, the optimal esterification reaction parameters to reduce the acid value of waste edible oil below 2 mg KOH/g were the conditions required for the second stage reaction: homogenization speed 8000 rpm, alcohol/oil ratio 15:1, catalyst dosage 4 wt%, reaction temperature 65 °C and reaction period 10 min. Figures 6–8 show the effects of different parameters on the conversion rate of transesterification in the second phase of the overall process.

#### 3.2.1. Effect of methanol/oil molar ratio on the biodiesel conversion

Figure 6 shows the effect of the methanol/oil molar ratio on the biodiesel conversion rate under the operating conditions: homogenizer speed 8000 rpm, catalyst amount 1 wt%, reaction time 10 min, reaction temperature 65 °C. In this step, the methanol/oil molar ratio was set at 6:1–10:1 for testing. The trend of the methanol/oil molar ratio affecting biodiesel conversion is similar to previous studies [16,17]. As can be seen, the reaction was not complete at a 6:1 molar ratio and the conversion rate was very low, only 76.78%. Thus, an additional amount of methanol (corresponding to a larger molar ratio of methanol to oil) is suggested. At a 9:1 molar ratio, the conversion rate reached 97% and met the standard EU EN14214 which required the biodiesel production rate to be at least 96.5%. Based on cost considerations, the molar ratio of 9:1 was considered an acceptable value.



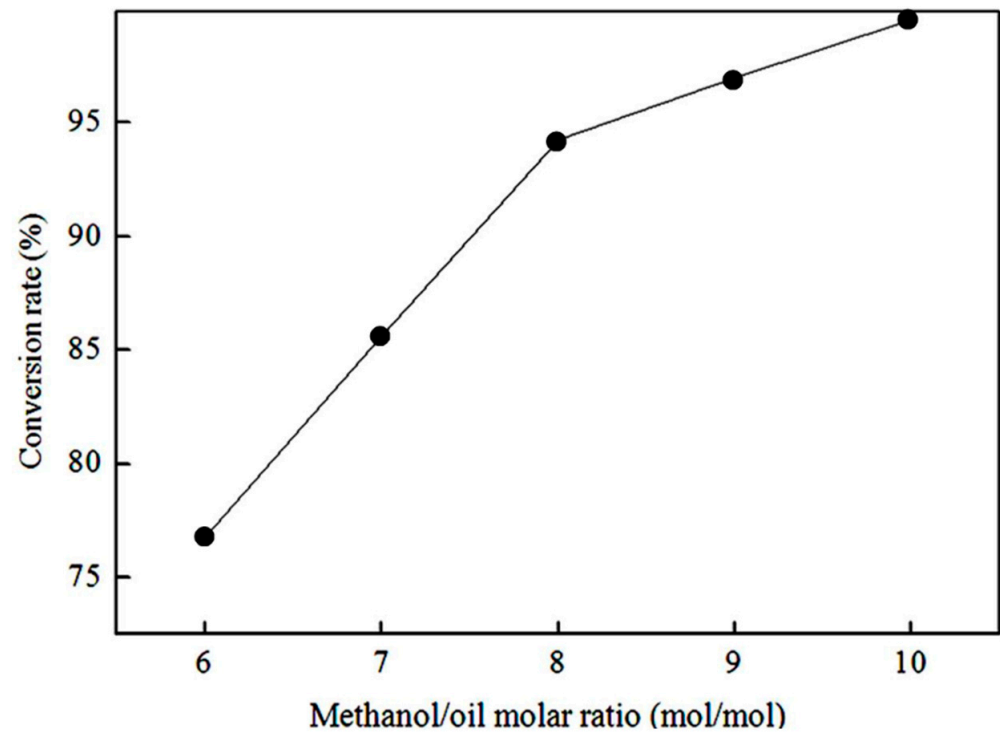


Figure 6. Effect of methanol/oil molar ratio on the biodiesel conversion.

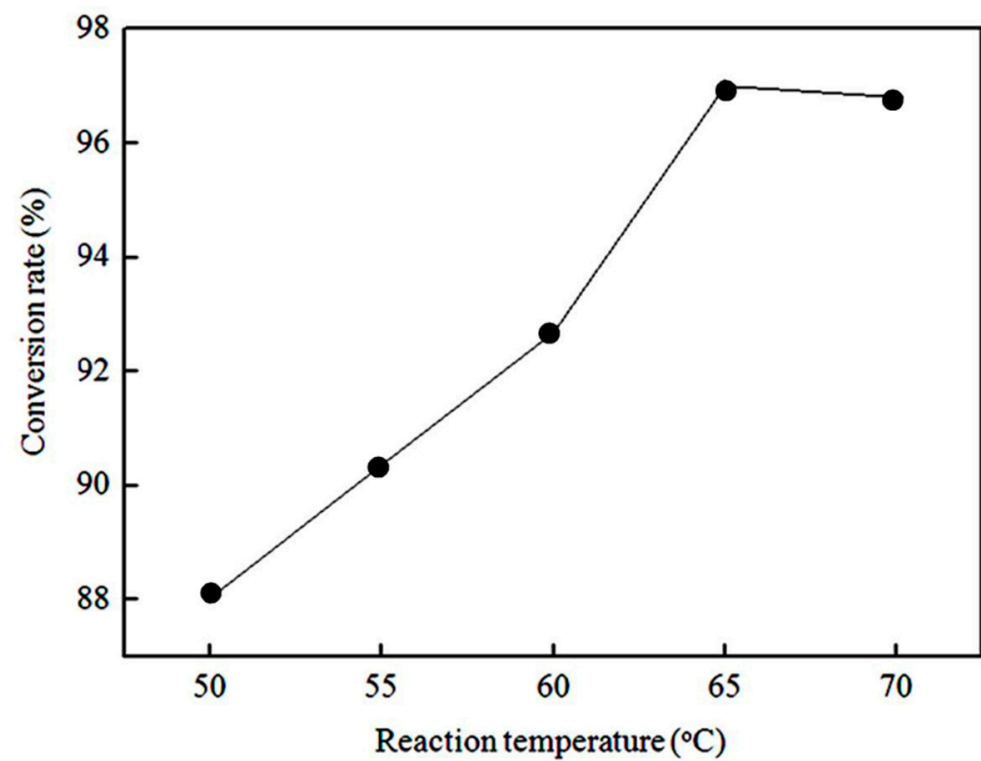
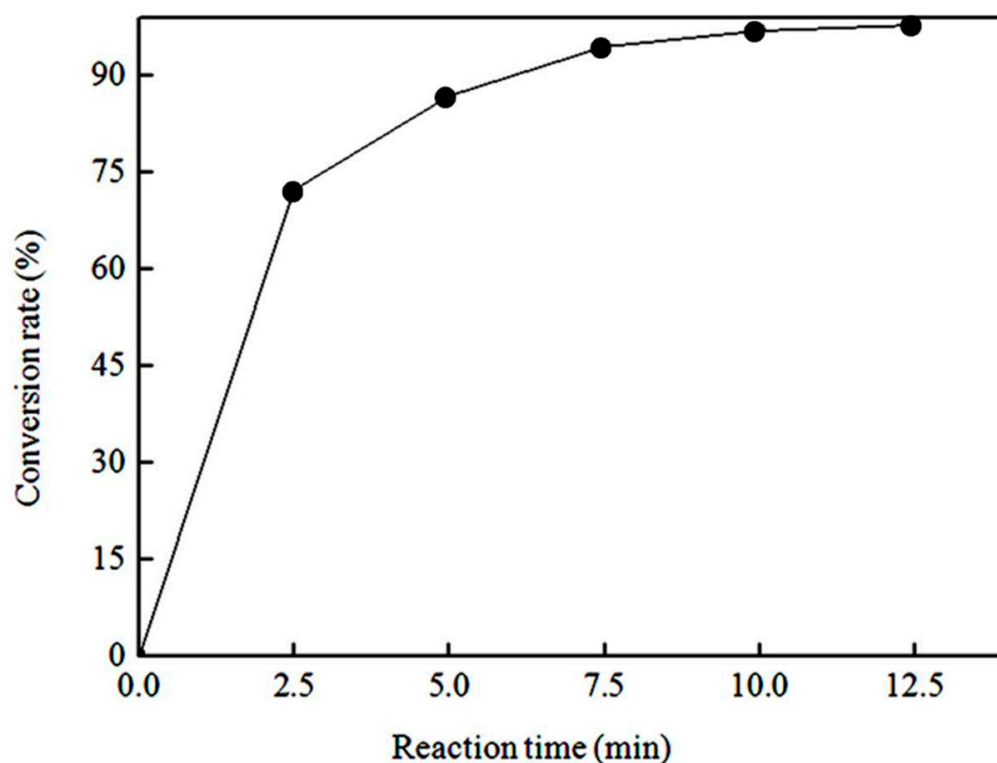


Figure 7. Effect of reaction temperature on the transesterification reaction.



**Figure 8.** Effect of reaction time on the transesterification reaction.

### 3.2.2. Effect of Catalyst Amount on the Biodiesel Conversion

Table 2 demonstrates how the biodiesel conversion rate varied with the catalyst amount. As is widely recognized, in the transesterification process, highly efficient catalysts are usually used, such as alkali metal oxides and hydroxides. In this article, homogenizer speed 8000 rpm and sodium hydroxide were used for an economic point of view. The reaction conditions were: catalyst amount 0.5–1.5 wt%, methanol/oil molar ratio 9:1, reaction temperature 65 °C for ten minutes. At 1.0 wt% catalyst, the conversion rate reached the highest, 97%, and it was lower when the catalyst dosage was less than or greater than 1.0 wt%. With a catalyst dosage above 1.0 wt%, a small amount of biodiesel was gel-like, which caused more alkali saponification reactions and more colloidal substances. The viscosity of the mixture increased and even the liquid eventually turned into a gel, making separation of the final product more difficult. This also added a water-washing step, resulting in more wastewater. The optimal catalyst dosage (1.0 wt%) is the same as the study by Hsiao et al. [16].

**Table 2.** Effect of catalyst amount on the biodiesel conversion.

Catalyst Amount (wt%)	Conversion (%)
0.5	78.02
0.8	90.34
1.0	97.00
1.2	88.45
1.5	80.25

### 3.2.3. Effect of Reaction Temperature on the Biodiesel Conversion

During the entire process, the reaction temperature affects not only the performance of the first stage, but also that of the second stage. The reaction temperature is generally close to the boiling point of methanol, but can also be below room temperature, in the transesterification reaction. To explore how temperature affected the transesterification process, experiments were performed with a temperature setting of 50–70 °C. Furthermore, the operating conditions were set as follows: the rotating speed of the homogenizer was 8000 rpm, the methanol/oil molar ratio was 9:1, the addition amount of sodium hydroxide was 1 wt%, and the reaction time was 10 min. Figure 7 depicts that raising the temperature below 65 °C helped to improve the conversion. At temperatures above 65 °C (greater than the boiling point of methanol), however, disturbances appeared. The higher the temperature was, the more quickly methanol evaporated. At this time, the original mixed reactants were separated, methanol and oil could not be mixed well, and the conversion rate decreased. Hence, 65 °C was the optimal reaction temperature, which is in agreement with previous studies [16,30].

### 3.2.4. Effect of Reaction Time on the Biodiesel Conversion

Figure 8 depicts that the role of the reaction time on the transesterification reaction is also considerable. The operating conditions were as follows: homogenizer speed 8000 rpm, methanol/oil molar ratio 9:1, catalyst amount 1 wt%, reaction temperature 65 °C. As can be seen, the oil conversion rate was only 72.3% after the reaction time of 2.5 min. With a prolonged time period, the conversion increased rapidly. Based on the reaction mechanism of transesterification, the reaction was reversible. After a certain reaction time, the equilibrium of the forward and reverse reaction rates would be reached. In this case, further prolonging the reaction time could not effectively increase the conversion. Note that the conversion rate was 97% within a 10 min reaction time, which meets the standard specification of biodiesel (EU EN14214). In addition, after the time period exceeded 10 min, the reaction gradually achieved equilibrium, and the conversion rate did not increase significantly. This optimal reaction time (10 min) obtained in the second stage (transesterification) is much shorter than the results of previous studies, which were 40 min and 50 min in [16] and [46], respectively.

In summary, the conventional acid-catalyzed method took at least 4 h to synthesize biodiesel from waste edible oil [47], while the whole process of the enhanced method in this study only took 20 min in total, which is much shorter. Furthermore, the optimal reaction time (20 min) obtained in this study via a homogenizer-assisted two-stage conversion process was also much shorter compared to the 140 min reported by Hsiao et al. [16]. Their study also used a two-stage catalytic process, but with traditional mechanical stirring methods.

### 3.2.5. Reaction Rate Constant $k$

In this study, the reaction was considered to have a single direction, and this first-order reaction could be expressed as [30]:



where ME is methyl ester, uME is unreacted matter, and GL is glycerol.

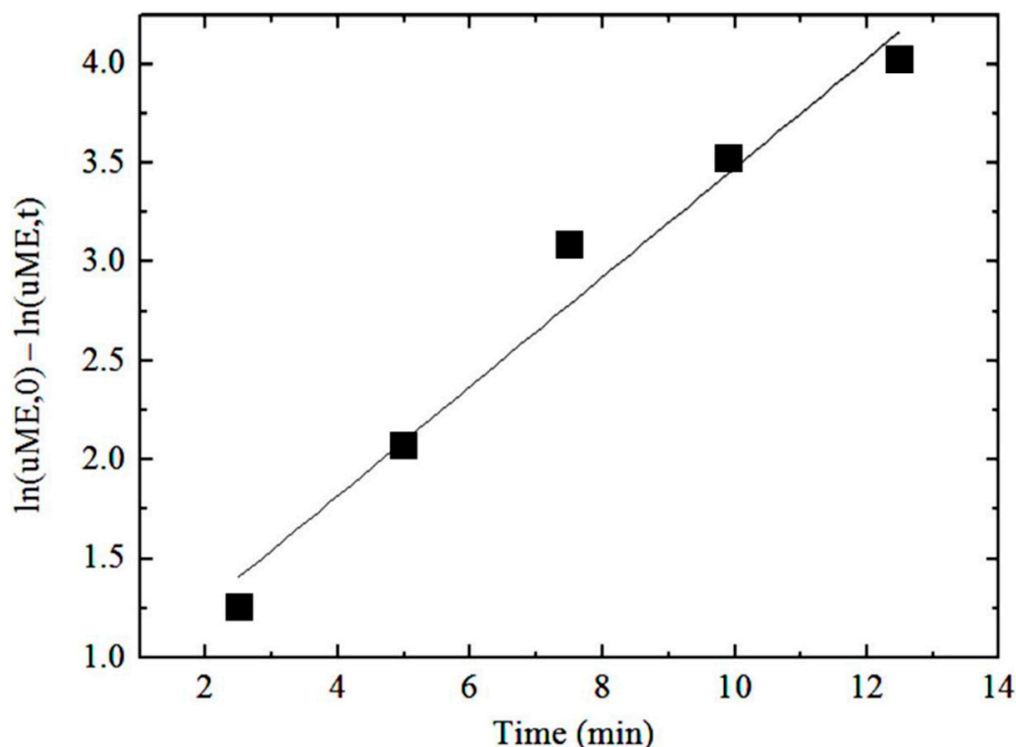
Equation (5) could be rewritten as:

$$-\frac{d[uME]}{dt} = k[uME]. \quad (6)$$

Merging Equations (5) and (6) led to:

$$\ln[uME, 0] - \ln[uME, t] = kt, \quad (7)$$

wherein  $[uME, 0]$  and  $[uME, t]$  were the initial waste oil concentration and the concentration of the unreacted waste oil at time  $t$ . Equation (7) was adopted to calculate the reaction rate constant  $k$  [48]. Equation (7) also depicted the value of  $(\ln[uME, 0] - \ln[uME, t])$  as a linear function in terms of time  $t$ , as shown in Figure 9. The results in Figure 9 could be employed to calculate the  $k$  value according to temperature given in Table 3.



**Figure 9.** Plot of the value of  $(\ln[uME, 0] - \ln[uME, t])$  of waste edible oil converted to biodiesel as a linear function of time  $t$ .

**Table 3.** Reaction rate constant  $k$  versus reaction temperature.

Temperature ( $^{\circ}\text{C}$ )	Rate Constants $k$ ( $\text{min}^{-1}$ )
50	0.2116
55	0.2324
60	0.2599
65	0.3515
70	0.3437

Table 3 illustrates the reaction rate constant  $k$  as a function of temperature for the NaOH-catalyzed transesterification reaction of WEO. Raising the temperature from 50 to 60  $^{\circ}\text{C}$  led to a slight augmentation in  $k$  from 0.2116 to 0.2599  $\text{min}^{-1}$ . However, the  $k$  value significantly increased to 0.3515  $\text{min}^{-1}$  at 65  $^{\circ}\text{C}$ . This was mainly due to the increase in the average molecular kinetic energy, which made the collisions between molecules more efficient, and the reaction accelerated. In addition, at this temperature, the reaction system reached the boiling point of methanol, so the disturbance in the system started to increase. With further raising the temperature to 70  $^{\circ}\text{C}$ , however, the reaction rate constant decreased as the reaction system approached equilibrium. Additionally, methanol began to leave out of the reaction system at this time. Therefore, the reaction rate constant began to decline above 65  $^{\circ}\text{C}$ .

#### 4. Conclusions

- (1) When waste edible oil was used to produce biodiesel by a two-stage transesterification process assisted by a homogenizer, in the first step (acid-catalyzed stage) the acid value was effectively decreased lower than 2 mg KOH/g within only 10 min with the following suggested operating conditions: homogenizer speed 8000 rpm, methanol/oil molar ratio 15:1, added catalyst amount 4 wt% (sulfuric acid) and reaction temperature 65 °C.
- (2) In the second step (the base-catalyzed stage), the conversion rate of biodiesel reached 97% after 10 min and met the standard value (at least 96.5%) of EN 14214 with the following reaction conditions: homogenizer speed 8000 rpm, alcohol/oil molar ratio 9:1 (mol/mol), sodium hydroxide addition level 1 wt% and reaction temperature at 65 °C.
- (3) Additionally, by increasing the reaction temperature from 60 to 65 °C, the reaction rate constant changed significantly from 0.2599 to 0.3515 min<sup>-1</sup>.
- (4) Synthesizing biodiesel from waste edible oil took at least 4 h via the conventional acid-catalyzed approach [47], while the whole process of the improved method in this study only took 20 min in total, which is a very considerable time reduction. Note that the optimal reaction time (20 min) herein is also much shorter compared to the 140 min reported by Hsiao et al. [16], who also utilized the two-stage catalytic process, but instead used a conventional mechanical stirring approach.

**Author Contributions:** All authors (M.-C.H., P.-H.L., K.-C.Y., N.V.L. and S.-S.H.) contributed equally to this paper in acquiring and interpreting the data and analyzing the results. Additionally, it is worth noting that S.-S.H. contributed significantly to the writing and editing of manuscript preparation. All authors have unanimously agreed to this paper for publication. All authors have read and agreed to the published version of the manuscript.

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

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