

Article

Study of Solid Calcium Diglyceroxide for Biodiesel Production from Waste Cooking Oil Using a High Speed Homogenizer

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Abstract: Biodiesel has been one of the potential candidates in the field of renewable energy due to its biodegradability and non-toxicity in the natural environment. In addition, due to its high boiling point, the transportation of biodiesel is much safer than that of conventional fuel. However, the cost remains a challenge for the development of biodiesel. In this study, a homogenizer system, which can intensively minimize raw materials, is utilized as an effective approach to assist the production of both the calcium diglyceroxide (CaDG) catalyst and biodiesel. Several operational factors were evaluated to obtain the optimal conditions, and a desirable biodiesel conversion of 77.24% was achieved at a methanol-to-oil molar ratio of 7, with 2.0 g of calcium diglyceroxide, a rotation speed of 7000 rpm, a reaction temperature of 65 °C and a reaction period of 90 min.

Keywords: waste cooking oil; biodiesel; transesterification; calcium diglyceroxide; homogenizer

1. Introduction

Due to the massive use of conventional energy sources, such as coal, oil and gas, in the past, issues related to air pollution and the greenhouse effect have been on the rise in recent years [1], along with the depletion of non-renewable energy. As a result, scientists are eagerly searching for environmentally-friendly and renewable alternative sources of energy to retard the impacts of energy usage on the environment and climate. Among several potential energy sources, biodiesel, also called fatty acid methyl ester (FAME)—a clean-burning diesel—has caught the attention of scientists. Biodiesel is a monoalkyl ester of long chain fatty acids that could be produced from catalyzed transesterification of oily feedstocks with alcohols.

Because homogenous catalysts have high catalytic activity under mild operating conditions, they are commonly employed for the transesterification reaction. However, the separation procedures are complicated after the reaction, and the catalysts cannot be reused in the following steps. On the other hand, heterogeneous catalysts have appealing properties, including renewability and recyclability and the fact that they are non-corrosive and efficient. Solid calcium oxide (CaO), which can be derived from scallop shells and egg shells, etc., is employed as a potential catalyst because it is low-cost and has low solubility in methanol [2–4]. Several studies have investigated the different forms of CaO as a catalyst for transesterification [5–8]. However, some drawbacks were presented in these studies. CO₂ and H₂O easily bind with the basic sites on the CaO surface and generate by-products, including calcium hydroxide and calcium carbonate. Also, raw materials with high free fatty acids (FFAs) must undergo pretreatment, which makes biodiesel production more difficult and costly. Also, side reactions that occur after the reaction, such as saponification of the methyl esters and

acid glycerides, affect the conversion of biodiesel [9]. For the purpose of improving the stability of the catalyst, calcium diglyceroxide (CaDG) has been proposed as a viable alternative because of its resistance toward atmospheric poisoning [10]. Its outstanding physiochemical properties and good catalysis ability have been proven in various studies [11,12]. Calcium diglyceroxide (CaDG) consists of an isolated tetramer $\text{Ca}_4(\text{C}_3\text{H}_7\text{O}_3)_8$ and is bound by a complex H-bond network [13]. Compared with CaO, CaDG shows higher catalytic activity because the presence of basic oxyanions, formed due to the interruption of the surface crystal structure, which can easily extract protons from the OH groups of methanol and form methoxide ion on the surface [14]. Gupta et al. [15] investigated microwave assisted transesterification of WCO using CaDG as a catalyst. The reusability of the heterogeneous catalyst (CaDG) was reported that after the first run, the catalytic activity of CaDG decreased gradually for consecutive cycles. In the first run, a yield of 95.12% biodiesel was obtained. In the second and third cycles, the yields fell to 91.55% and 87.64%, respectively. In the fourth cycle, a yield of 79.45% was observed, which was significantly reduced due to the aggregation of the catalyst and decreased surface area and pore volume [15]. Since the fraction of the cations in calcium diglyceroxide is much less than that in the conventional calcium-based catalyst, a reduction in waste and saponification has been noted [16]. Therefore, in this study, we take advantage of the properties of calcium diglyceroxide for use as a catalyst for converting waste cooking oil (WCO) into biodiesel.

Transesterification for biodiesel production can be promoted through a bundle of reactors, i.e., oscillatory flow reactors, reactive distillation reactions, centrifugal contactors, ultrasonic reactors, and microwave reactors. These intensification technologies may result in better biomass characteristics, a higher conversion rate, and the optimum balance between reaction conditions and cost [17]. Homogenizers are commonly used for large-scale processing in industry. Notably, homogenizers have the potential to increase scale and effectively shorten the transesterification reaction time. However, research related to homogenizer systems for biodiesel production is relatively rare. Homogenizers are cavitation reactors that generate cavities through intense turbulence and liquid streaming [18]. A conventional homogenizer is composed of two concentric tubes with a gap in between, where the inner tube rotates at a high circumferential speed. The radical force leads to emulsion of the reactants. With the generation of small molecules, the large contact areas contribute to sufficient interaction within the reactants [19]. From the mass transfer perspective, homogenizers have been established as superior scale-up instruments compared to traditional agitation devices. Therefore, the use of high-speed homogenizers to produce biodiesel has the potential and prospects for easily expanding the capacity scale and significantly reducing the reaction time. However, as introduced above, few investigations have studied the biodiesel production using a high-speed homogenizer. In particular, there have been no experimental studies on the transesterification of WCO to biodiesel with a high-speed homogenizer and a calcium diglyceroxide catalyst.

The objective of this study is to achieve a rapid, high efficiency method for producing biodiesel from waste cooking oil with a homogenizer and a modified calcium diglyceroxide catalyst. A high-speed homogenizer plays an important role in not only the promotion of calcium diglyceroxide synthesis but also in the acceleration of the transesterification process. Making good use of waste cooking oil (WCO) as the raw material for biodiesel production significantly reduces expenses and excess pollution as well. The experiments were conducted based on several parameters, including the methanol-to-oil ratio, the amount of catalyst, the rotation speed, the reaction temperature, and the reaction period, to investigate and determine the optimal conditions for transesterification reaction.

2. Materials and Methods

2.1. Chemicals

Calcium oxide (CaO) was purchased from Riedel-De Haen (Uni-Onward Corp.). Methanol (CH_3OH ; purity: 99.8%) was obtained from Nihon Shiyaku Reagent (Nihon Shiyaku Industries,

Taipei City, Taiwan). Glycerol ($C_3H_5(OH)_3$) was acquired from Shimakyu's Pure Chemicals Co., Ltd., Osaka, Japan. Waste cooking oil (WCO) was collected from a local restaurant in Tainan City (Taiwan).

2.2. Experimental Equipment

Figure 1 shows the reactor with a high-speed homogenizer and Figure 2 shows the overall experimental schematic diagram. The reaction was carried out using a homogenizer system (Hsiangtai H-M-300, Hsiangtai Co., Ltd., New Taipei City, Taiwan), which was equipped with a thermostatic bath and a condenser used for homogenizer reactions. The high-speed homogenizer has an accuracy of $\pm 0.5\%$ of full scale at rotation speeds of 100–12000 rpm. The thermostatic bath was equipped with a special grade K-type thermocouple having an accuracy of $\pm 1.1\text{ }^\circ\text{C}$ provided by Omega Engineering Inc.

The biodiesel samples were investigated using a Clarus 600 GC mass spectrometer (PerkinElmer, Shelton, CT, USA) equipped with a capillary column (SPB7M-WAX, $30\text{ m} \times 0.75\text{ mm} \times 1.0\text{ }\mu\text{m}$) and a flame ionization detector (FID). The method for GC calibration was shown in a previous study [20]. To ensure the reliability of the experimental data for the gas chromatography (GC), the correlation coefficient for the calibration curve regression should be equal to or greater than 0.995.



Figure 1. The experimental setup.

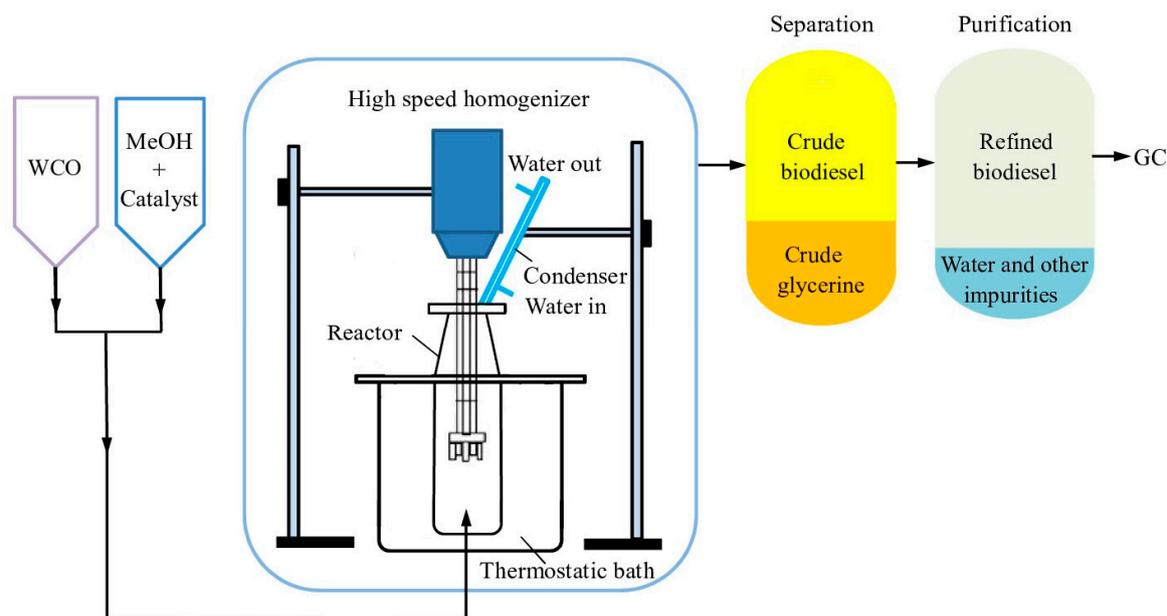


Figure 2. The overall experimental schematic diagram.

2.3. Experimental Procedure

2.3.1. Synthesis Procedure for the Calcium Diglyceroxide Catalyst

The calcium diglyceroxide was synthesized using the mixture of calcium oxide (9.0 g), methanol (132.0 g) and glycerol (30.0 g) in the same mass ratio (1:14.667:3.333) as in the literature [15]. This mixture was placed into a reactor and mixed evenly through a homogenizer with a rotation speed of 7000 rpm at 60 °C for 90 min. When the solution turned light yellow, which indicates the formation of CaDG [15], it was transferred into a centrifuge (Hermle, Z200A, Labnet International, Inc., NJ, USA) for the purification process. The centrifuge was set with a rotation speed of 4000 rpm for 5 min. Afterwards, the supernatant was discarded, leaving the precipitation, which was washed twice with methanol. Finally, solid calcium diglyceroxide ($\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2$) was obtained after vacuum-drying for 8 h and was ready for further experimental use.

2.3.2. Transesterification Reaction Procedure

Methanol (14.3 g) and waste cooking oil (100 g) were chosen as the raw materials for the transesterification reaction, and the synthesized calcium diglyceroxide (1.0 g) served as the catalyst. The reaction was carried out using a homogenizer system (Figure 1) and evaluated under several operation conditions, including a comparison between calcium oxide and calcium diglyceroxide, five levels of methanol-to-oil molar ratio (4, 5, 6, 7 and 8), five levels of amount of catalyst (0.5, 1, 1.5, 2 and 2.5 g), five levels of rotation speed (5000, 6000, 7000, 8000 and 9000 rpm), five levels of reaction temperature (50, 55, 60, 65 and 70 °C), and five levels of reaction time (30, 45, 60, 75 and 90 min). As shown in Figure 2, after the reaction was completed, the mixture was poured into a separatory funnel, and then glycerin was separated from the biodiesel. Subsequently, the biodiesel was heated and purified using an oven at a temperature of 105 °C for 2 h. Finally, after the completion of purification, two layers could be observed: upper layer—biodiesel, and lower layer—water and other impurities.

2.4. Analytical Methods

The acid value (AV) of WCO was calculated using Equation (1) [21]:

$$AV = \frac{5.61 \times V_{\text{NaOH}}}{W}, \quad (1)$$

where V_{NaOH} is the volume of the sodium hydroxide titrant (mL) and W is the oil weight (g).

The saponification value (SV) of the waste cooking oil was calculated from the formula Equation (2) [22,23] below:

$$SV = \frac{(B - S) \times 56.1 \times 0.5}{W}, \quad (2)$$

where B is blank titration amount (mL), S is sample titration amount (mL), and W is oil weight (g).

The molecular weight (MW) of WCO was calculated from its SV and AV using Equation (3) [20,24]:

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

where SV and AV are in units of mg KOH/g. The AV , SV and MW of the WCO calculated using Equations (1)–(3) are 2.132 mg KOH/g, 188.395 mg KOH/g, and 883.34, respectively.

To determine the content of the biodiesel, the Taiwan CNS-15051 standard was set as a reference [25]. A gas chromatograph (GC) was employed to analyze the conversion rate of the biodiesel. The preparation of the sample for the GC analysis is discussed as follows: The biodiesel sample (0.5 g), methyl laurate (0.05 g, internal standard) and hexane (10 mL) were homogeneously mixed. Then, 1 μL of the mixture was injected into the gas chromatograph under the following conditions: injection port temperature of 280 $^{\circ}\text{C}$, nitrogen flow rate of 45 mL/min, air flow rate of 450 mL/min, split ratio of 1:20, and a detector temperature of 300 $^{\circ}\text{C}$. The heating programs were controlled as follows: The oven temperature was maintained at 210 $^{\circ}\text{C}$ for 4 min with a stable rate of increase of 4 $^{\circ}\text{C}/\text{min}$ until it was raised to 240 $^{\circ}\text{C}$, after which it was maintained at 240 $^{\circ}\text{C}$ for 8 min. Finally, the peak areas were compared with the internal standard (reference), for which the calculation for the conversion rate of the biodiesel was defined as Equation (4) suggested by Wang et al. [26].

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

The data on conversion rate were obtained by averaging three individual measurements, and the standard deviations were shown with error bars. The reported values of conversion rate are the average with experimental errors in the range of $\pm 2.5\%$.

3. Results and Discussion

3.1. Effects of Methanol-to-Oil Molar Ratio and Catalyst Type on the Conversion Rate of Biodiesel

Calcium oxide has been reported to be a mature basic heterogeneous catalyst for transesterification. However, its sensitivity toward moisture and carbon oxide is one of the greatest concerns during the reaction and recycling. Therefore, in this study, calcium diglyceroxide, which was modified from commercialized calcium oxide, was applied in the experiment to compare its catalytic ability. The effects of commercialized calcium oxide and synthesized calcium diglyceroxide on the transesterification reaction are shown in Figure 3. The conversion of biodiesel was enhanced with increases in the methanol-to-oil molar ratio and reached its culmination point at a methanol-to-oil molar ratio of 7. Moreover, the reaction assisted with calcium diglyceroxide was found to be more effective than that with calcium oxide. The conversion rate reached 51.49% with calcium diglyceroxide while it only reached 33.72% with calcium oxide. Interestingly, when the methanol-to-oil molar ratio was raised to 8, the conversion rate declined. This phenomenon could be attributed to the excess amount of methanol, which diluted the concentration of the catalyst and led to the promotion of a reverse transesterification reaction [27,28]. Therefore, calcium diglyceroxide was chosen as the active catalyst with a collocation of a methanol-to-oil molar ratio 7 in the further experiments.

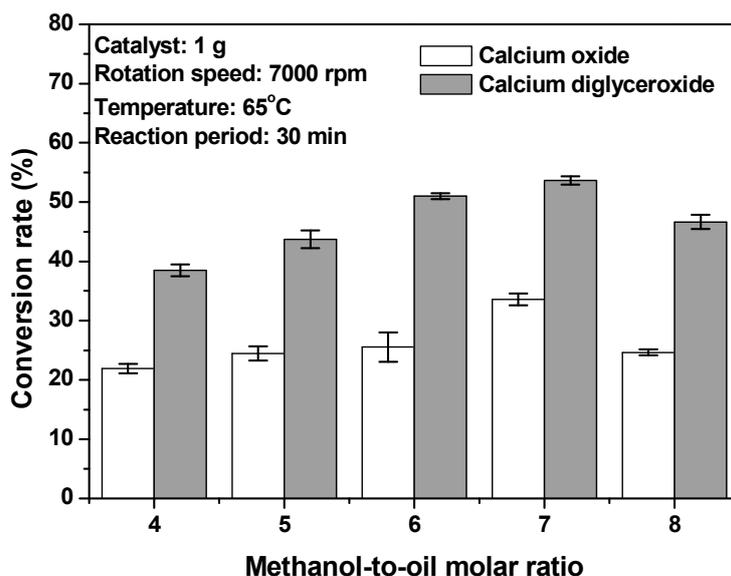


Figure 3. Effects of the methanol-to-oil ratio and catalyst type (calcium oxide and calcium diglyceroxide) on the transesterification reaction. Reaction conditions: methanol-to-oil molar ratio ranging from 4–8, 1 g of catalyst, rotation speed of 7000 rpm, reaction temperature of 65 °C, and a reaction period of 30 min.

3.2. Effects of the Amount of Catalyst on the Conversion Rate of Biodiesel

The experiment was intended to evaluate the optimal amount of catalyst for the transesterification reaction conducted under the various amounts of calcium diglyceroxide catalysts (0.5, 1.0, 1.5, 2.0, 2.5 g), with a methanol-to-oil molar ratio of 7, a rotation speed of 7000 rpm, a reaction temperature of 65 °C, and a reaction period of 30 min. It can be clearly seen from Figure 4 that the conversion rate of biodiesel increased from 32.06 to 59.46% when the amount of catalyst was raised from 0.5 to 2.0 g. The conversion rate slightly decreased to 58.08%, when the amount of catalyst was adjusted to 2.5 g. This was attributed to the enhanced collision between the catalyst and the reactants. Also, a similar trend was also found by Mohamad et al. [29]. Therefore, from the results, we concluded that 2.0 g of the catalyst is sufficient for the transesterification reaction.

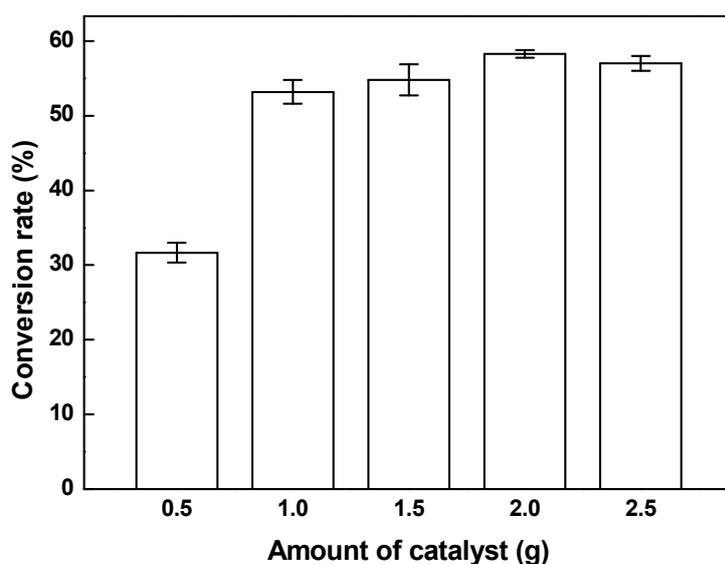


Figure 4. Effect of amount of catalyst on the transesterification reaction. Reaction conditions: 0.5–2.5 g of calcium diglyceroxide, a methanol-to-oil molar ratio of 7, a rotation speed of 7000 rpm, a reaction temperature of 65 °C, and a reaction period of 30 min.

3.3. Effect of Rotation on the Conversion Rate of Biodiesel

Based on the results shown in Figures 3 and 4, the experiment was carried out at a methanol-to-oil molar ratio of 7 with 2.0 g of calcium diglyceroxide to investigate the influence of various rotation speeds of 5000, 6000, 7000, 8000 and 9000 rpm. Figure 5 demonstrates that the conversion rate of biodiesel escalated with incremental increases in the rotation speed. The reactants did not fully react at the low rotation speed of 5000 rpm; thus, the conversion rate was sustained at 40.04%. On the other hand, when the rotation speed was elevated from 6000 to 9000 rpm, the conversion rate was significantly enhanced from 56.68 to 63.84%. A homogenizer was used as the hydrodynamic cavitation reactor [30]. Based on the structure of the homogenizer, the narrow gap on the probe results in the generation of a cavity force and shear force, which have the ability to microminiaturize the waste cooking oil, methanol, and the calcium diglyceroxide catalyst. The enhanced contact area and homogeneous mixing significantly increased the conversion rate. Therefore, according to the result shown in Figure 5, the conversion rate increased as the number of revolutions increased. At a rotational speed of 9000 rpm, the conversion was 63.84%, which was higher than the conversion rate at 7000 rpm (56.68%) or 8000 rpm (57.32%). However, taking into consideration the homogenizer overheating problem and the issue of reducing energy consumption, we concluded that the most suitable rotation speed is 7000 rpm for the experiments. In the subsequent experiments, the rotation speed was fixed at 7000 rpm to optimize the conditions for the highest transesterification rate.

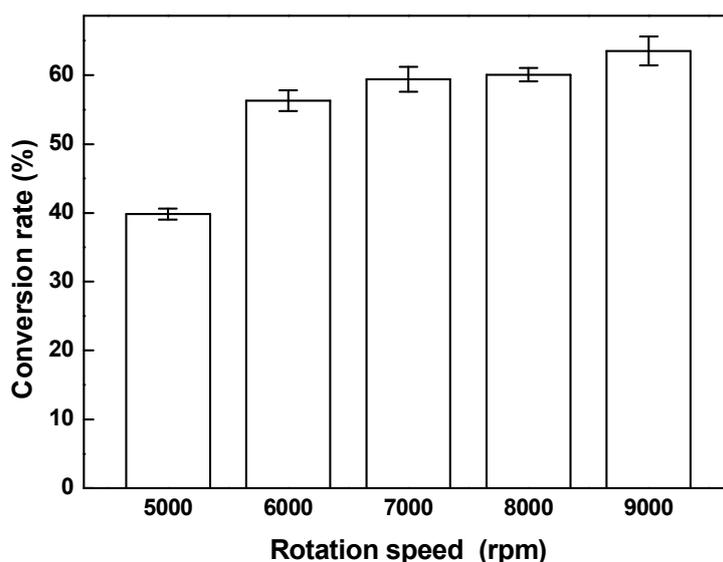


Figure 5. Effect of rotation speed on the transesterification reaction. Reaction conditions: a rotation speed of 5000–9000 rpm, 2.0 g of calcium diglyceroxide, a methanol-to-oil molar ratio of 7, a reaction temperature of 65 °C, and a reaction period of 30 min.

3.4. Effect of Reaction Temperature on the Conversion Rate of Biodiesel

The experiment was conducted with a methanol-to-oil molar ratio of 7, 2.0 g of calcium diglyceroxide, a rotation speed of 7000 rpm, with various reaction temperatures of 50, 55, 60, 65 and 70 °C. Figure 6 shows that an increase in reaction temperature from 50 and 65 °C caused an obvious increase in conversion, but the conversion slightly decreased with a further increase in the reaction temperature at 70 °C. Since the conversion rates were 38.42 and 43.31% at 50 and 55 °C, respectively, it was inferred that the system did not react completely. When the system temperature reached to 60 °C, the conversion rate significantly increased to 57.18%. Furthermore, the conversion obtained was 59.46% at 65 °C, which is slightly above the boiling point of methanol of 64.7 °C. The phase transformation from liquid to vapor causes disturbance in the system and agitates the reaction, which is known as cavitation formation. Also, increasing temperatures lead to lower viscosity in the oil phase and

therefore, promotes the miscibility of the reactants. However, overheating leads to the vaporization of the methanol, which is seen as the dampening of the cavitation effect [31]. Thus, when the reaction temperature was increased to 70 °C, the conversion rate slightly decreased to 57.93%. In this experiment, it was concluded that at a temperature of 65 °C, the transesterification reaction exhibited the best performance.

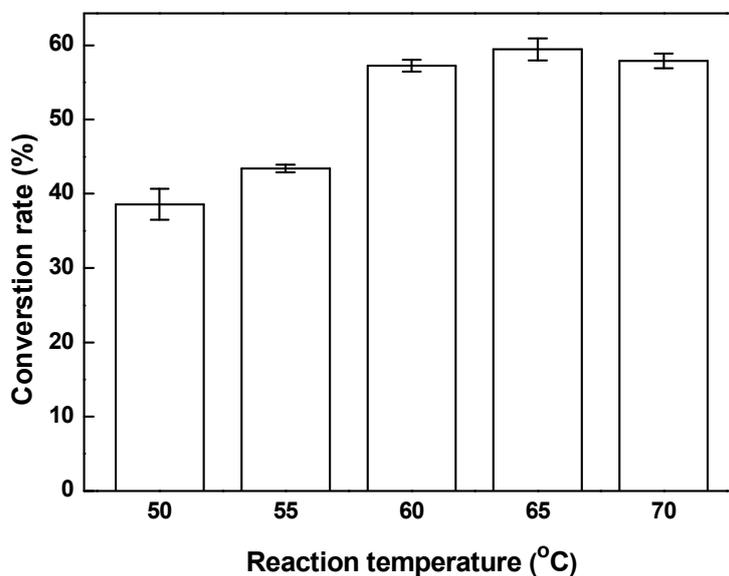


Figure 6. Effect of reaction temperature on the transesterification reaction. Reaction conditions: a reaction temperature of 50–70 °C, 2.0 g of calcium diglyceroxide, a methanol-to-oil molar ratio of 7, a rotation speed of 7000 rpm, and a reaction period of 30 min.

3.5. Effect of Reaction Period on the Conversion Rate of Biodiesel

The reaction period is also a critical aspect of a chemical reaction. The experiment was performed under the following conditions: a methanol-to-oil molar ratio of 7, 2.0 g calcium diglyceroxide, a rotation speed of 7000 rpm, a reaction temperature of 65 °C, with and various reaction periods of 30, 45, 60, 75 and 90 min. Figure 7 demonstrates that the trend leveled steadily with the prolongation of the reaction time. When the reaction period was 30 min, the conversion rate was 59.46%. During the transesterification reaction, a longer reaction time provided more opportunities for collision between the reactants and the catalyst. Finally, the conversion rate of biodiesel reached its highest point, 77.24%, when the reaction period was set at 90 min. Based on the results, 90 min was considered to be the most suitable reaction time.

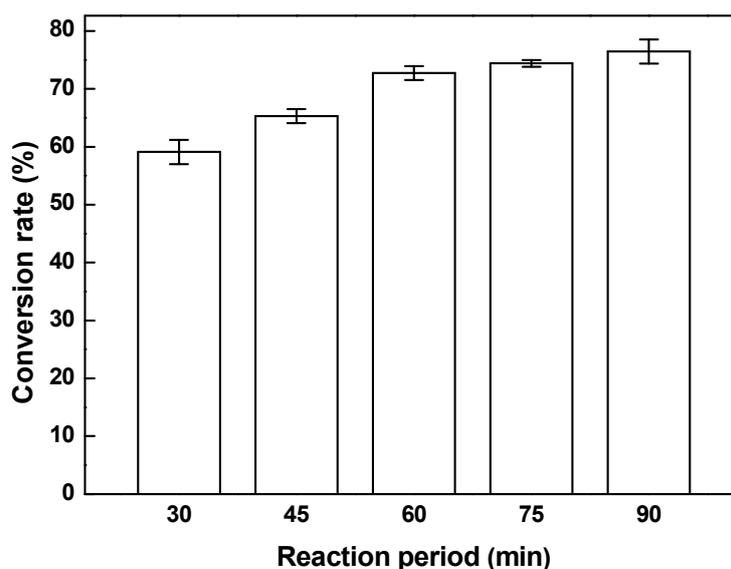


Figure 7. Effect of reaction period on the transesterification reaction. Reaction conditions: a reaction period 30–90 min, 2 g of calcium diglyceroxide, a methanol-to-oil molar ratio of 7, a rotation speed of 7000 rpm, and a reaction temperature of 65 °C.

4. Conclusions

The main contribution of this study is the achievement of a rapid, high efficiency method for producing biodiesel from waste cooking oil using a homogenizer and a calcium diglyceroxide catalyst. An effective calcium diglyceroxide catalyst was synthesized from calcium oxide through the use of a homogenizer. Also, calcium diglyceroxide significantly promoted the transesterification reaction, where the results indicated a higher conversion to biodiesel than was the case with calcium oxide. A high-speed homogenizer was proven to play an important role in not only the promotion of calcium diglyceroxide synthesis but also in the acceleration of the transesterification process. In addition, different controllable factors in the transesterification reaction were investigated. It was concluded that the reaction condition was optimized at a methanol-to-oil molar ratio 7, with 2.0 g calcium diglyceroxide, a rotation speed of 7000 rpm, a reaction temperature of 65 °C, and a reaction period of 90 min. Making good use of WCO as the raw material for biodiesel production greatly reduces expenses and excess pollution as well. It is noteworthy that the choice of a combination of waste cooking oil, a homogenizer and a calcium diglyceroxide catalyst creates a potentially viable technology for waste treatment and industrial scale-up processes, thus supporting commercialization of biodiesel into the market.

Author Contributions: M.-C.H. contributed to the generation of ideas, as well as the format, structure, organization, and presentation of the work. L.-W.C. performed the experiments and analyzed the results. S.-S.H. contributed to generating ideas, designing the experiments, analyzing the results, and preparing and editing the manuscript.

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

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