

Article

Optimization of Biodiesel Production from Waste Cooking Oil Using Waste Eggshell as a Base Catalyst under a Microwave Heating System

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Abstract: This paper intends to explore the most affordable and environmentally friendly method for the synthesis of biodiesel. Substitute fuel is presently a significant topic all over the world, attributable to the efforts of reducing global warming, which is the result arising from the combustion of petroleum or petrol diesel fuel. Due to its advantages of being renewable and environmentally friendly, biodiesel production has the potential to become the major substitute of petrol diesel fuel. Biodiesel is non-toxic, biodegradable, is produced from renewable sources, and contributes a small amount of greenhouse gas (e.g., CO₂ and SO₂) emissions to the atmosphere. Research has established that one of the key obstacles to the commercialization of biodiesel is the high price of biodiesel production due to the shortage of suitable raw materials. However, waste-cooking-oil (WCO) is one of the most cost-effective sources of biodiesel synthesis, and can practically minimize the raw material cost. The research was carried out to produce biodiesel from waste cooking oil in order to reduce the cost, waste, and pollution associated with biodiesel production. The application of a microwave heating system towards enhancing the production of biodiesel from waste cooking oil has been given little consideration in the preceding research, particularly with the application of eggshell as a heterogeneous catalyst. However, the tentative results in this study show significant performance in terms of biodiesel production, as follows: (1) the increasing of the reaction time from 120 to 165 min considerably increased the biodiesel production, which declined with a further rise to 210 min; (2) the results of this study reveal that a methanol-to-oil molar ratio of nine is appropriate and can be used for the best production of biodiesel; (3) the production of biodiesel in this study demonstrated a significant increase in response to the further increasing of power; (4) a 120 min response time, a ratio of 9:1 methanol-to-oil molar fraction, 65 °C temperature; (5) and 5 wt % catalyst were found to be the most ideal reaction conditions during this study. In summary, recycled eggshell was re-used as a suitable catalyst to produce new biodiesel from waste cooking oil, applicable to diesel engines.

Keywords: eggshell; waste cooking oil; microwave heating system; transesterification; yields

1. Introduction

The efforts to minimize emissions arising from diesel engines without adjusting the engines have intensified the immediate growth and increase in biodiesel production. This has also been propelled

by the urgent necessity to drastically reduce the emissions from diesel engines, in the effort to help minimize global warming. Animal fats and vegetable oils have been documented as an immediate source of biodiesel production, and this has been coupled with catalysts such as methanol or ethanol through the transesterification reaction process. Using biodiesel has been associated with various major benefits, such as biodegradability, lower exhaust gas emissions, and renewability [1]. At present, many states in the USA are advocating for an expansion of the production and application of biodiesel, whereas the US central administration has adopted a credit tax system as a great motivation to enhance this initiative [2]. Several studies have discovered the discharges of polycyclic aromatic hydrocarbons (PAHs), hydrocarbons (HCs), polychlorinated dibenzo-p-dioxin/dibenzofurans, carbon monoxide (CO), and sulfur dioxide (SO₂), among others, can be significantly lowered whenever diesel engines use biodiesel as an unconventional fuel [3–15].

Biodiesel has been considered the most favorable substitute for conventional petroleum-based diesel because it is biodegradable, energy efficient, non-toxic, and most importantly, environmentally benevolent. However, one of the major impediments to biodiesel marketability has been ascribed to its high cost, because of the cost of vegetable oil. Furthermore, the biodiesel price is nearly 1.5 times greater than the diesel gasoline petroleum price [16–19]. Another disadvantage of biodiesel commercialization is linked to its combined high costs of raw material and labor incurred in production due to high-priced catalysts and feedstocks for the production of biodiesel. Thus, waste cooking oil might be utilized effectively in the production of biodiesel, so as to reduce the raw material cost. This may also help in elucidating the challenge of waste disposal arising from waste cooking oil [19–25]. Additionally, the high cost of biodiesel production can also be considerably reduced by using catalysts from waste materials. Asikin et al. [26] recognized that chicken and quail eggshells, consisting of 90% of calcium carbonate, were reliable sources of CaO [27]. A soybean biodiesel harvest ranging between 97–99% was achieved in the presence of eggshell sample crystallized beyond 800 °C. As the temperature for calcination was raised to 700 °C, a harvest of 90% was attained, while a relatively low response was detected at calcination temperatures <600 °C [27,28]. Asikin et al. also discovered a favorable performance of eggshells in the transesterification process [26]. The calcination of shell materials occurred in air at a temperature of 800 °C within an ideal interval of 2–4 h to change calcium contents found in the shells into vigorous CaO catalysts. The catalytic agent exhibited great biodiesel yields in excess of 90% fatty acid methyl ester (FAME) within 2 h [28]. A CaO catalyst reinforced by fly ash was established with eggshell as a waste for the soybean oil transesterification to produce biodiesel. The ideal bound values calculated by means of response surface methodology (RSM) consistent with the thoroughgoing (i.e., 96.97%) FAME harvest were 30 wt % stocking of CaO, 1.0 wt % catalyst, as well as a methanol/oil molar fraction of 6.9:1 [28,29]. Recently, Encinar et al. used CaTiO₃ (a metal oxide) while employing eggshell with a temperature of 1050 °C for 3.5 h for calcination purposes, producing a methyl ester portion in excess of 95% [1].

In relation to the present work, there have been several studies evaluating the promise of waste cooking oil (WCO) for biodiesel production, yet the synthesis of biodiesel using a microwave heating system as well as waste eggshell as base heterogeneous catalyst has not been studied [30,31]. Thus, our research work examines the biodiesel production from mere waste cooking oil (WCO) using cheap and recycled waste eggshell as a base catalyst under a microwave heating system that was used to decrease the reaction or response time to biodiesel production. Moreover, the impacts of the eggshell as a heterogeneous catalyst, reaction or response time, molar fraction of methanol-to-oil, and power emanating from the microwave heating system were all equally investigated.

2. Results and Discussion

2.1. Characterization of the Heterogeneous Catalyst

2.1.1. X-ray Diffraction (XRD) Analysis of Eggshell

This experiment examined the chemical composition of waste eggshell before and after incineration using X-ray diffraction (XRD) analysis. Figure 1 shows the chemical composition before and after incineration. The peaks are located at $2\theta = 29.6^\circ$, 39.6° , 47.6° , and 57.6° for waste eggshell before burning. The spectrum for incinerated eggshell consisted of $2\theta = 32.3^\circ$, 37.5° , 54.0° , 64.3° , and 67.6° , which corresponds to the spectrum of calcium oxide (CaO) [26] as compared to the spectrum of snail shell before and after incineration using XRD. It was concluded that the spectrum of snail shell incinerated at 900°C shows the presence of calcium oxide (CaO) with peaks of 2θ located at 32.2° , 37.3° and 53.8° . The spectrum for unburnt snail shell consisted of peaks at $2\theta = 26.242^\circ$, 33.172° and 45.889° , showing that the snail shell is composed of calcium carbonate (CaCO_3) [32,33]. Said et al. studied the incineration of clam shell, burnt at 900°C for four hours [32]. The powdered clam shell became a white powder, indicating that it was chemically converted into calcium oxide. Comparing the XRD spectrum with peaks located at $2\theta = 32.46^\circ$, 37.64° , 54.12° and 62.60° against the Joint Committee on Powder Diffraction Standards (JCPDS), shows the presence of calcium oxide. The additional spectra of $2\theta = 18.22^\circ$, 34.56° , 47.20° , 50.92° , 54.12° and 64.36° correspond to the presence of calcium hydroxide, $\text{Ca}(\text{OH})_2$. The compound was formed from calcium oxide and moisture in ambient air [32,33].

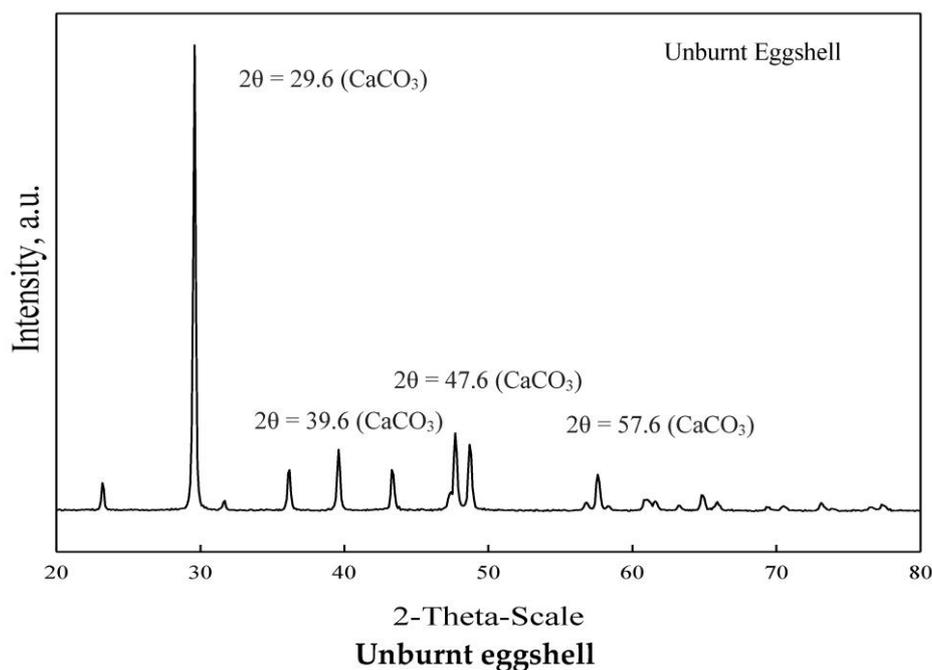


Figure 1. Cont.

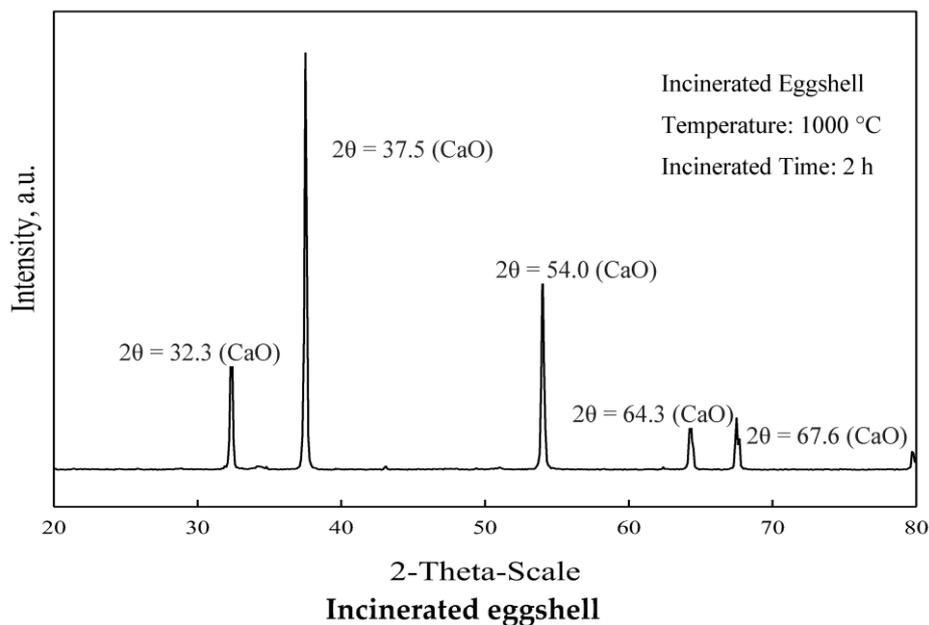


Figure 1. The X-ray Diffraction (XRD) spectrum of original (**top**) and incinerated (**bottom**) eggshell.

2.1.2. Fourier Transform Infrared Spectroscopy Analysis of Eggshell

This experiment examined the chemical composition of eggshell using Fourier transform infrared spectroscopy (FTIR) analysis. Figure 2 shows the absorption bands of unburnt and incinerated eggshell, with incineration occurring at 1000 °C for two hours. The pre-incineration absorption bands centered at 1421, 875 and 713 cm^{-1} , and this spectrum is due to the presence of carbonate, CO_3^{2-} , species on the catalyst surface [4,26,34,35]. Meanwhile, the post-incineration absorption bands centered at 3643, 1415, 1049, 524 and 430 cm^{-1} . The FTIR spectra obtained during the study are consistent with the reported results in preceding studies [35].

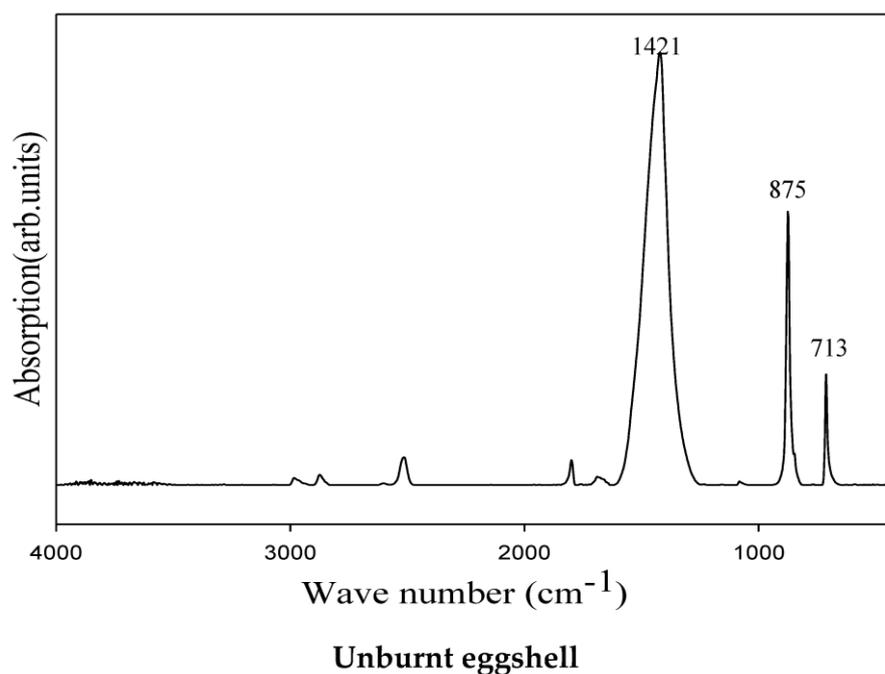


Figure 2. Cont.

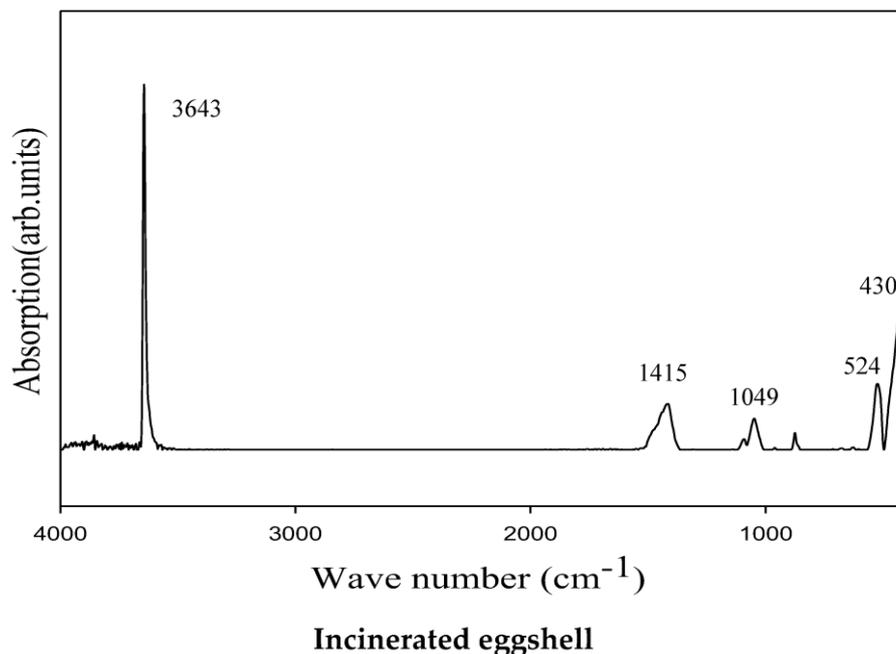


Figure 2. The Fourier transform infrared spectroscopy (FTIR) spectrum of original (top) and incinerated (bottom) eggshell.

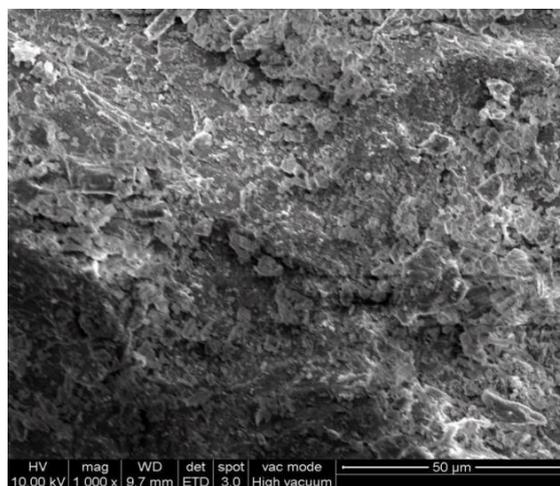
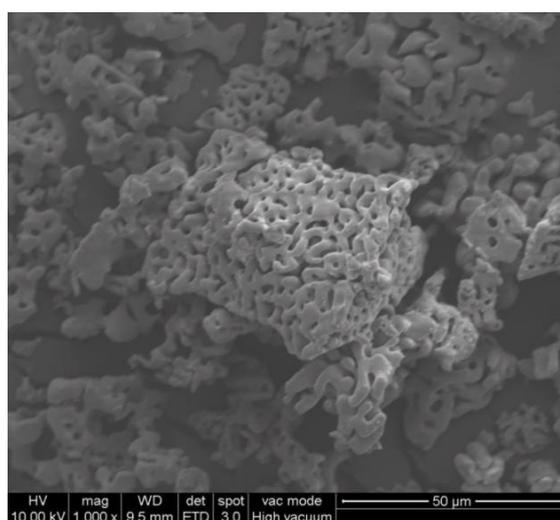
2.1.3. Composition of Eggshell

It was pointed out in several studies that the incineration temperature affects the extent of conversion of calcium carbonate into calcium oxide. Li et al. studied the effects of incineration temperature (between 200 and 1000 °C) on the soybean oil transesterification process [36]. It was concluded that the catalyst performance is optimized by incinerating the eggshell at 800 °C. Ali et al. pointed out, with a Thermogravimetric analysis (TG)/Differential thermal analysis (DTA) (TG/DTA) analysis, that complete conversion of calcium carbonate to calcium oxide can be attained by incinerating the eggshell at a temperature between 800 and 1000 °C [7]. If incineration occurs at an ambient temperature of less than 700 °C, the conversion of calcium carbonate into calcium oxide will be incomplete [18,36,37]. In order to guarantee complete conversion, all incineration presented in this study was conducted at 1000 °C for a duration of two hours. An Energy Dispersive Spectroscopy (EDS) analysis was conducted to examine the composition of eggshell, which shows that the shells mainly contain calcium and oxygen, supplemented by minor elements such as carbon and magnesium. The detailed composition of eggshell is shown in Table 1. Quantitative analysis carried out by EDS composition showed that eggshell elements consist mainly of carbon, oxygen, magnesium and calcium components. The detailed composition of pre- and post-incinerated eggshell is shown in Table 1.

Figure 3 shows the material texture of eggshell, before and after incineration at high temperature, the images were taken using an environmental scanning electron microscope (ESEM). The pore structures in the eggshell showed extensive variations before and after incineration. After incineration, there were obvious alterations in the mechanical structures of the shell, indicating that the calcium carbonate was converted into calcium oxide.

Table 1. Detailed composition of (a) pre-and (b) post-incinerated eggshell.

(a) Pre-incinerated eggshell		
Element	Wt %	At %
Carbon (C)	17.74	29.95
Nitrogen (N)	3.17	4.59
Oxygen (O)	33.49	42.46
Iron (Fe)	1.53	0.56
Magnesium (Mg)	0.45	0.37
Calcium (Ca)	43.62	22.07
(b) Post-incinerated eggshell		
Element	Wt %	At %
Carbon (C)	6.25	13.85
Nitrogen (N)	2.53	4.81
Oxygen (O)	20.52	34.12
Iron (Fe)	2.28	1.09
Magnesium (Mg)	1.65	1.8
Calcium (Ca)	66.77	44.33

**Unburnt eggshell****Incinerated eggshell****Figure 3.** Material texture of eggshell, before and after incineration at high temperature.

2.1.4. BET Surface Area Measurements and Porosity Characterization

The specific surface areas of prepared eggshell catalyst was determined by Brunauer–Emmett–Teller (BET) measurements (Quantachrome Instruments Trading Company Limited, Shanghai, China) of eggshell catalyst. The porosity and surface area of the eggshell catalyst were determined via the BET method of adsorption of nitrogen gas with the help of a Micromeritics instrument (ASAP 2020, Micromeritics Instrument Corp., Norcross, GA, USA), whereas, the total pore volume and the average pore size of the eggshell catalyst were measured by the Barret–Joyner–Halenda (BJH) method. A FTIR spectrophotometer (Thermo-Nicolet iS10, Thermo Fisher Scientific, Taipei, Taiwan) equipped with attenuated total reflectance (ATR) was used to identify the active surface. Basic analysis and the surface morphology of the catalyst were determined using an energy dispersive X-ray spectrophotometer (EDX, YKT (Taiwan) Corporation, Taipei City, Taiwan), which measured for the sample mounted on the microscope using an environmental scanning electron microscope (Philips XL30 ESEM FEG, Thermo Fisher Scientific, Taipei, Taiwan). BET analysis indicated that the catalyst specific surface area was $0.7334 \text{ m}^2/\text{g}$ with an average BJH adsorption pore width (4V/A by BET) or pore diameter of 9.66773 nm (see Table 2).

Table 2. Brunauer–Emmett–Teller (BET) surface area measurements and porosity characterization.

Catalyst Type	Temperature (°C)	BET Surface Area (m^2/g)	Adsorption Pore Diameter (nm)
Eggshell	1000	0.1992 ± 0.0645	1.1930
Eggshell	1000	0.7372 ± 0.0769	9.66773
Eggshell	1000	0.7334 ± 0.0673	9.31039

2.1.5. Effects of Incineration on the pH-Value of Eggshell

With the purpose of examining the significance of incineration on the pH value of the eggshell, a pre-determined amount of the tested eggshell was well-mixed with deionized water to produce 1 M solution. The consequential solution was then tested using a pH meter for its pH value. The pH value for eggshell increased from 9.69 before incineration to 12.32 after incineration. The results show that incineration increases the alkalinity of the substance. In actual fact, incinerated eggshells have strong alkali, which can be used as an effective catalyst [38].

2.1.6. The Effects of Catalytic Agent on the Production of Biodiesel Using a Microwave Heating System

Experiments were conducted by means of a diverse catalyst amount loaded, in an attempt to examine their impact on biodiesel production. A microwave heating system was used, with a 165 min reaction time, $65 \text{ }^\circ\text{C}$ temperature and a proportion of nine methanol-to-oil molar fraction. The amounts of the catalyst loaded were 3, 4, 5, 6, and 7 wt %, respectively. As shown in Figure 4, the yields of biodiesel were found to be $84.4 \pm 0.4\%$, $85.1 \pm 0.6\%$, $87.8 \pm 0.4\%$, $86.4 \pm 0.6\%$, and $85.6 \pm 0.3\%$ for 3, 4, 5, 6, and 7 wt % catalyst amounts from waste eggshell, respectively. The biodiesel yield or production improved with an increasing amount of catalyst loaded for catalyst absorption of 3 wt % to 5 wt %, and from that moment it then declined from 5 wt % to 7 wt %. The maximum yield was reached by the 5 wt % catalyst amount loaded. These outcomes show that even if extra catalyst might increase the biodiesel yield (production), the volume of glycerin yield is similarly improved as a result of saponification, instigating a further decrease of biodiesel synthesis. A further increase in catalyst absorption did not affect the catalyst performance on biodiesel yield, but it then resulted in further expenses attributed to its inference from the reaction intermediate at the peak of the procedure [3,39]. Moreover, Sirisomboonchai et al. resolved that the accumulation of an inconsistent quantity of alkali catalyst intensifies the creation of a suspension, which increases stickiness and causes the gels' formation [34]. This alone deters the separation of glycerin, then consequently, there is a

reduction of ethyl esters and the supposed ester yield reduces [40]. To this end, the optimum biodiesel production (yield) was accomplished by 5 wt % catalyst from waste eggshell for waste cooking oil.

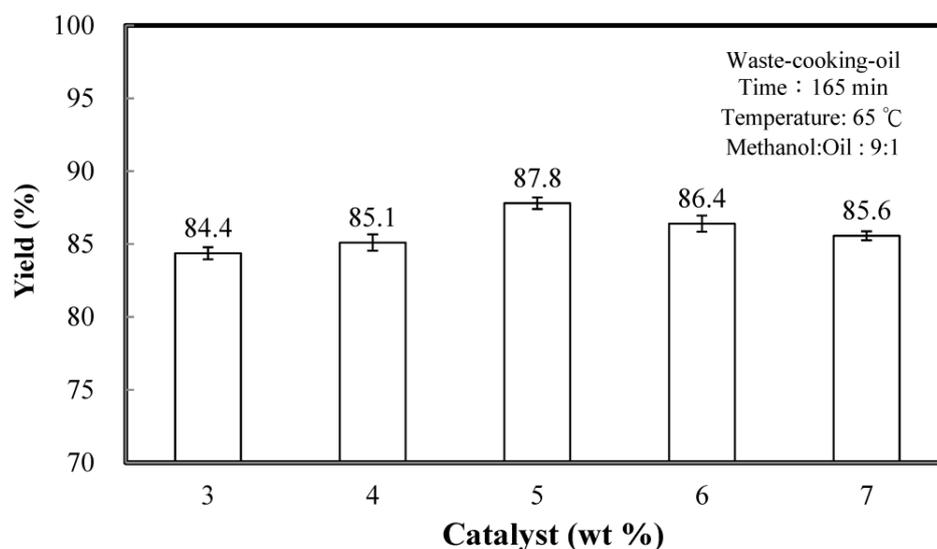


Figure 4. Effects of catalyst on the harvest (production) of biodiesel under a microwave system.

2.1.7. Effect of Reaction Time

A 5 wt % catalyst was used during the experiments, a temperature of 65 °C, a fraction of 9, methanol-to-oil molar proportion, and assorted response times (120–210 min) to examine the influence and effect of response time with regards to biodiesel production. As depicted in Figure 5, the production of biodiesel from waste cooking oil was observed to be $78.4 \pm 0.5\%$, $81.3 \pm 0.6\%$, $84.4 \pm 0.5\%$, $87.8 \pm 0.4\%$, $87.2 \pm 0.6\%$, $86.3 \pm 0.6\%$, and $85.5 \pm 0.8\%$ for reaction times of 120, 135, 150, 165, 180, 195, and 210 min, respectively. Whereas the increase in response (reaction) time at 120 to 165 min triggered a substantial rise of biodiesel production, this subsequently declined with a further increase to 210 min. The outcomes to this end may perhaps be attributed to the imperfect transesterification response amid methanol and oil with a slighter response; despite the fact that, the lengthier reaction had a longer reaction temperature, developing into more glycerin solubility [7,41–45].

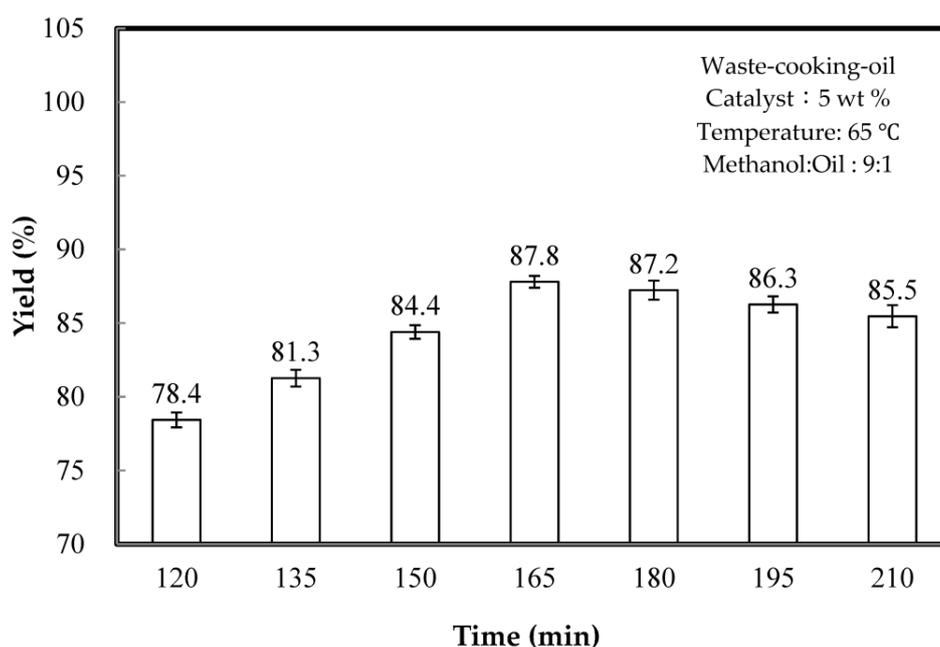


Figure 5. Effects of reaction time.

2.1.8. Effects of Microwave Temperature

A catalyst amount of 5 wt % was used during the experiment in this study, a response period of 165 min, a proportion of 9 methanol-to-oil molar share, as well as diverse microwave temperature (45, 55, 65, 75, and 85 °C) to examine the influence of the microwave heating system temperature on biodiesel production. Figure 6 records the biodiesel production or synthesis from waste cooking oil, which were $73.7 \pm 0.7\%$, $83.9 \pm 0.6\%$, $87.8 \pm 0.4\%$, $86.9 \pm 0.8\%$, and $84.0 \pm 0.5\%$ for temperatures of 45, 55, 65, 75, and 85 °C, respectively. The biodiesel production increased with an increased temperature from 45 to 65 °C, and then decreased with a further increase of temperature to 85 °C; this is also confirmed by other studies [18,36,43–49]. These optimized conditions (weight of catalyst, reaction time and molar ratio) were established according to a preeminent temperature 65 °C [50,51]. Yet, the assessment of the effects of reaction temperature on reaction performance might give us information of relevance with regards to the catalyzed reaction mechanism of the biodiesel production process [44].

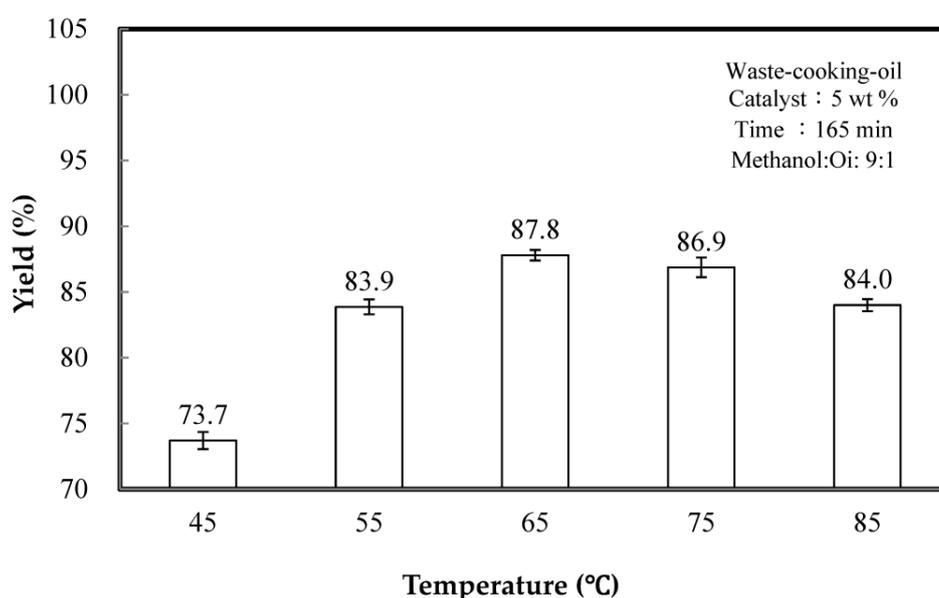


Figure 6. Effects of microwave temperature.

2.1.9. Effects of Molar Fraction of Methanol-to-Oil

During this stage, an amount of 5 wt % catalyst was used in the experiments, a microwave heating system temperature of 65 °C, a response time of 165 min, as well as several methanol-to-oil molar fractions (7, 8, 9, 10, and 11) to examine the impact of this fraction on the biodiesel synthesis (production). As indicated in Figure 7, an increase in relation to molar proportion ranging between 7 to 9 prompted a substantial increase in biodiesel production from 85.3% to 87.8%; while when the molar fraction was enhanced to 11, the biodiesel production declined from 87.8% to 83.7%. Hence, a molar proportion of 9 is the furthestmost appropriate of the production of biodiesel from waste cooking oil under a microwave heating system, especially with the application of an eggshell catalyst. Hypothetically, every mole of biodiesel is a result of one mole of methanol and 1/3 of a triglyceride mole from the transesterification response. Equally, and in rehearsal, an advanced molar fraction is required for the response, since the transesterification reaction is revocable. Besides, glycerol and biodiesel are capable of being mixed because of the use of superfluous methanol as described in the literature [45–47]. Furthermore, methanol is a robust intermediate for captivating and captivating microwaves, and then consequently the additional methanol might enthrall microwave energy and decrease the microwave power [52]. Therefore, the methanol-to-oil molar fraction ought not to be disproportionate, and 9 was contemplated as the furthestmost appropriate level of this investigational approach to this study.

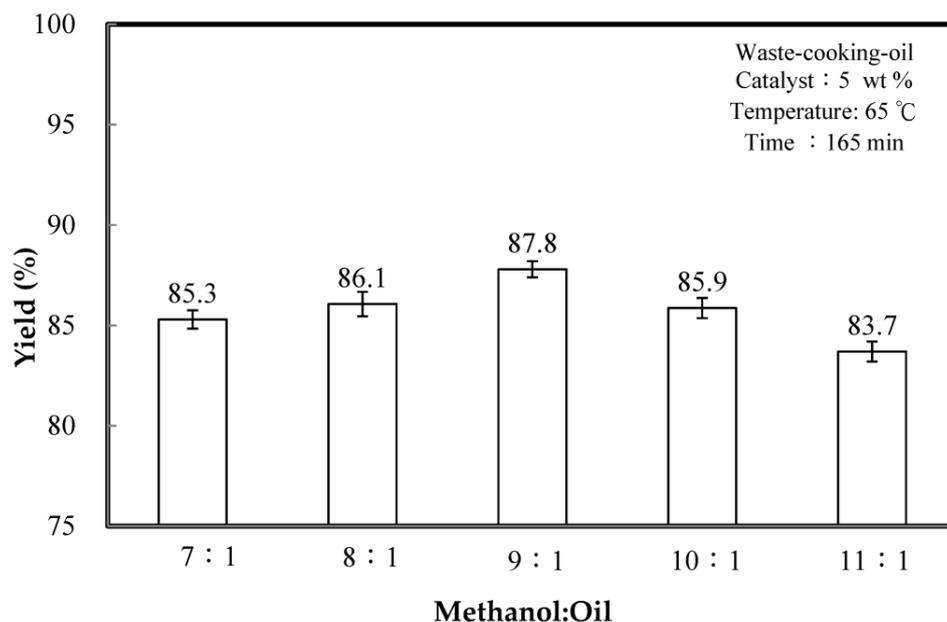


Figure 7. Effects of methanol-to-oil molar fraction.

2.2. Comparison of Catalytic Performance for Transesterification Reaction over the CaO Catalysts Derived from Different Sources

This experiment used eggshell as a catalyst, waste cooking oil as a feedstock for transesterification, and the operating conditions were set at a catalyst amount of 5 wt %. The reaction time of 165 min, reaction temperature of 65 °C and the ratio of methanol to oil of 9:1, were the most favorable conditions yielding biodiesel of 87.8%. According to the research in other related literature, as shown in Table 3, the best yield of this research study is slightly better than that of other scholars.

The highest yield of FAME obtained using the CaO catalyst prepared from the eggshell waste was compared with the highest FAME yields obtained from different studies, using the CaO catalysts prepared from different waste that were reported in the literature (as presented in Table 3) and it was found that the CaO catalyst prepared from eggshell waste has comparable catalytic performance for biodiesel production.

Table 3. Comparison of catalytic performance for transesterification reaction over the CaO catalysts derived from different sources.

Feedstock	Source of Catalyst	Operating Conditions	Yield (%)	References
Waste Cooking Oil	Chicken bones (CaO) (5 wt %)	Reaction time = 4 h Temperature = 65 °C Methanol: Oil = 15:1	89.3	[51]
Waste Cooking Oil	Snail shell (CaO) (2 wt %)	Reaction time = 7 h Temperature = 60 °C Methanol: Oil = 6.03:1	87.3	[52]
Waste Cooking Oil	River snail shell (CaO) (3 wt %)	Reaction time = 1 h Temperature = 65 °C Methanol: Oil = 9:1	92.5	[53]
Waste Cooking Oil	CaO catalysts prepared from chicken manure (7.5 wt %)	Reaction time = N/A Temperature = 65 °C Methanol: Oil = 15:1	90.8	[54]
Waste Cooking Oil	Sr/ZrO ₂ (2.7 wt %)	Reaction time = 2 h Temperature = 115.5 °C Methanol: Oil = 29:1	79.7	[55]

Table 3. Cont.

Feedstock	Source of Catalyst	Operating Conditions	Yield (%)	References
Waste Cooking Oil	CaO/ZrO ₂ (10 wt %)	Reaction time = 2 h Temperature = 65 °C Methanol: Oil = 30:1	92.1	[56]
Waste Cooking Oil	Ba/CaO (3 wt %)	Reaction time = 3 h Temperature = 65 °C Methanol: Oil = 9:1	88.0	[57]
Waste Cooking Oil	Scallop shell (CaO) (5 wt %)	Reaction time = 120 min Temperature = 65 °C Methanol: Oil = 6:1	86	[58]
Waste Cooking Oil	Sea sand (CaO) (7.5 wt %)	Reaction time = 6 h Temperature = 65 °C Methanol: Oil = 12:1	97.5	[59]
Waste Cooking Oil	Eggshell (5 wt %)	Reaction time = 165 min Temperature = 65 °C Methanol: Oil = 9:1	87.8	This study

3. Experimental Section

3.1. The Transesterification Procedures

For this experiment, the waste cooking oil used as a feedstock was provided (at no cost) by a food outlet in Kaohsiung City, Taiwan. However, upon measuring the acid value in waste cooking oil, it was found to be a lesser amount of 2 mg of KOH g⁻¹, whereas there was a high-performance liquid chromatography (HPLC) grade with regards to the methanol. The experimental arrangement for this experiment is displayed in Figure 8. In addition to this, a microwave blend reactor (Pree Kem APEX, Pree Kem Scientific Instruments Co., Ltd., Shanghai, China), outfitted with an automated stirrer and a condenser (LC-10, Hi-point Co., Ltd., Taiwan) was also designed for the microwave reactions. A stirrer was used at around 600 rpm through a captivating (magnetic) center. Several catalyst amounts (3–7 wt % waste eggshell as catalyst), reaction time (120–210 min), a (7–11) fraction of methanol-to-oil molar proportions, and a temperature response of (45–85 °C) were investigated during this study. Moreover, a conservative heating system (HTS-1003, Laboratory & Medical Supplies Co., Ltd., Tokyo, Japan) furnished and coupled with a power-driven stirrer along with a condenser (LC-10, Hi-point Co., Ltd., Kaohsiung City, Taiwan) was also used.

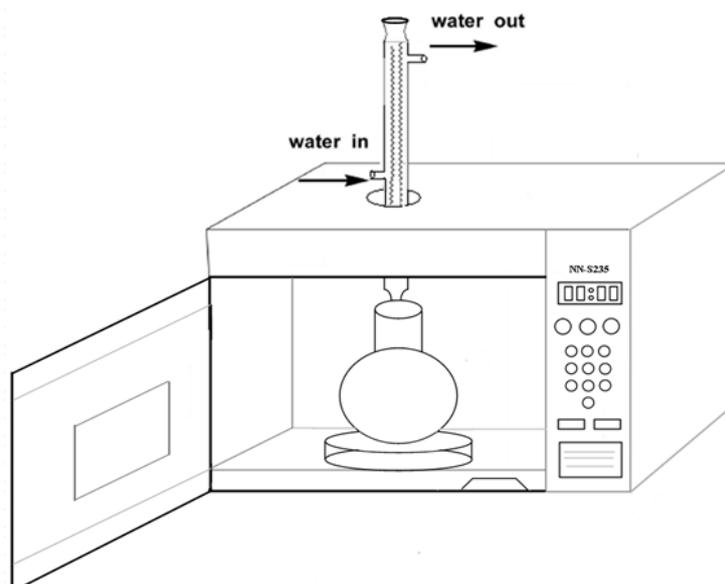


Figure 8. Experimental arrangement.

3.2. Separation and Purification

During this experimental stage, the transesterification process was assumed to have happened once the content of methyl ester was above 95%. Subsequently, the assortment and blend at the conclusion of the transesterification method was isolated by means of a filter (CN-1040; Hsiangtai, Taiwan) which was operated at 2000 rpm for a period of 10 min causing the materialization of an upper phase, entailing methyl ester, and then a lower phase, comprising glycerin. This also resulted in surplus methanol in the methyl ester phase, dispersed through heating system at a temperature of 80°C. The silica gel was added in order to remove the catalyst and water was also added to remove impurities. As such, the biodiesel was eventually obtained.

3.3. Product Assessment

This study used the analytic methods stipulated in the Taiwan CNS15051 to regulate the content of methyl ester. Moreover, the methyl ester content was also significantly established by the application of a Gas Chromatography (GC) system outfitted by a flame ionization detector (FID). The inoculation port and indicator temperature were fixed at a temperature of 250 and 260 °C, respectively. The temperature of the oven was automated to start at 50 °C for a period of 2 min, and afterward the temperature was elevated to 150 °C at a proportion of 10 °C min⁻¹, then paused for 2 min. The temperature was subsequently increased to 200°C at a rate of 4 °C min⁻¹, paused for 4 min, and ultimately increased to 230 °C at a degree of 1 °C min⁻¹, then held for 5 min. The inoculation capacity was 1 µL in the split-less booster mode. The passageway pillar (capillary) was a HP-INNOWAX 19091N-133, 30 m × 0.25 mm I.D, and the film breadth was 0.25 µm. The spilt rate was 1:60, whereas the velocity of the carrier gas (He) was 19 cm s⁻¹. The methyl ester proportion (content) is expressed as follows:

$$\text{Methyl ester content} = C = \frac{(\sum A) - A_{EI}}{A_{EI}} \times \frac{C_{EI} \times V_{EI}}{m} \times 100\% \quad (1)$$

where ΣA is the sum of the peak area of fatty acid methyl ester from C₁₄ to C_{24:1}; A_{EI} is the peak area of the interior standard, methyl heptadecanoate (C₁₈H₃₆O₂); C_{EI} is the concentration of methyl heptadecanoate (mg mL⁻¹); V_{EI} is the volume of methyl heptadecanoate (mL⁻¹); and m is the mass of input biodiesel (g).

The methyl ester yield is expressed as follows:

$$\text{Methyl ester yield} = \text{methyl ester content} \times \text{biodiesel yield} = C \times \frac{W_B}{W_{oil}} \times 100\% \quad (2)$$

where C is the methyl ester content (%); W_B is the weight of biodiesel production (g); and W_{oil} is the weight of the initial amount of WCO (g). Hence, the biodiesel production was analyzed and calculated in relation to the preliminary quantity of waste cooking oil by weight. This was also found in comparable studies [39,48,49].

4. Conclusions

The findings in this study provide evidence that biodiesel production was enhanced due to the application of a microwave heating system. The biodiesel yield was improved by increasing the catalyst loading amount of 3 wt % to 5 wt %, and ultimately declined by increasing the catalyst loading amount of 0.75 wt % to 1.50 wt %. It should, however, be noted that the best performance was recorded at below 3 wt % and 5 wt % of the waste eggshell catalyst, for biodiesel production from waste cooking oil. However, the obtained catalyst from waste eggshell exhibited high catalytic performance for the production of biodiesel from the transesterification reaction of waste cooking oil and methanol (i.e. up to 87.8% FAME yield was achieved). The main results of this study were notably observed with an increasing reaction time from 120 to 165 min, which produced a substantial increase in biodiesel yield or production, and then declined by a further increase of 10 min. The above-mentioned outcomes can be

attributed to the imperfect transesterification response of methanol and oil in a slightly reactive process, where a lengthier reaction had a higher reaction temperature, significant to glycerine, with a large higher solubility level. It was also remarkably observed that a further increase in the methanol-to-oil molar ratio from 7:1 to 9:1 produced a substantial rise in biodiesel yield, which later declined with an increase in ratio to 11:1. Therefore, a methanol-to-oil molar ratio of 9:1 would seem to be the most suitable for the production of biodiesel from waste cooking oil. There is also compelling evidence that the biodiesel production was improved by an increasing temperature from 45 to 65 °C, which then declined with a further increase in temperature to 85 °C. It can therefore be concluded that the ideal responsive environments under this study are a catalyst of 5 wt %, a fraction of 9:1 methanol-to-oil molar proportion, and a reaction period of 165 min. In addition, the overall results showed that it was effective and efficient to produce good quality biodiesel from waste cooking oil using recycled eggshell as the heterogeneous catalyst, which could be used as a substitute fuel for diesel engines.

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