

Research Article

Oyster and *Pyramidella* Shells as Heterogeneous Catalysts for the Microwave-Assisted Biodiesel Production from *Jatropha curcas* Oil

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Microwave-assisted biodiesel production via transesterification of *Jatropha curcas* oil with methanol using solid oxide catalyst derived from waste shells of oyster and *Pyramidella* was studied. The shells were calcined at 900°C for 2 h and calcium oxide (CaO) catalyst characterizations were carried out by X-ray diffraction (XRD), X-ray fluorescence (XRF), scanning electron microscope (SEM), and the Brunauer-Emmett-Teller (BET) surface area measurements. The effects of reaction variables such as reaction time, microwave power, methanol/oil molar ratio, and catalyst loading on the yield of biodiesel were investigated. Reusability of waste shell catalyst was also examined. The results indicated that the economic and environmentally friendly catalysts derived from oyster and *Pyramidella* shells showed good reusability and had high potential to be used as biodiesel production catalysts under microwave-assisted transesterification of *Jatropha curcas* oil with methanol.

1. Introduction

Many recent research programs based on energy sector are focused on the development of concepts such as renewable resources, sustainable development, green energy, and eco-friendly process [1]. Biodiesel, a renewable, biodegradable, nontoxic, carbon neutral, and environmentally benign fuel for diesel engines, has been attracting considerable interest all over the world which can significantly reduce global warming and the dependence on conventional fossil fuels [2]. It can be easily synthesized through transesterification of oil or esterification of fats using basic, acidic, enzymatic, or other kinds of catalysts with heating functions [3, 4]. Most commonly, biodiesel production utilizes an alkaline catalyst, but it is difficult to adapt this process for use with some waste oils and fats [5]. Moreover, in this conventional homogeneous method, the removal of catalysts after reaction is technically difficult and a large amount of waste-water is

produced to separate the catalyst and clean the products. Therefore, heterogeneous catalysts are very important for biodiesel synthesis as these catalysts have many advantages over homogeneous catalysts [6].

Calcium oxide (CaO) is one of the most promising heterogeneous alkali catalysts since it is cheap and abundantly available in nature, and some of the sources of this compound are renewable [7]. It closely resembled an environmentally friendly material. Generally, calcium carbonate (CaCO₃) is the raw material to produce CaO. Besides the economic advantage, the performance of CaO as catalyst for biodiesel production is also comparable to several homogeneous catalysts [8]. There are several natural calcium sources from wastes, such as eggshell, crab shell, and animal bone. Using wastes as raw materials for catalyst synthesis could eliminate the wastes and simultaneously produced the catalysts with high cost effectiveness [9]. The catalyst synthesized with the waste shells opens door for renewable catalyst and at

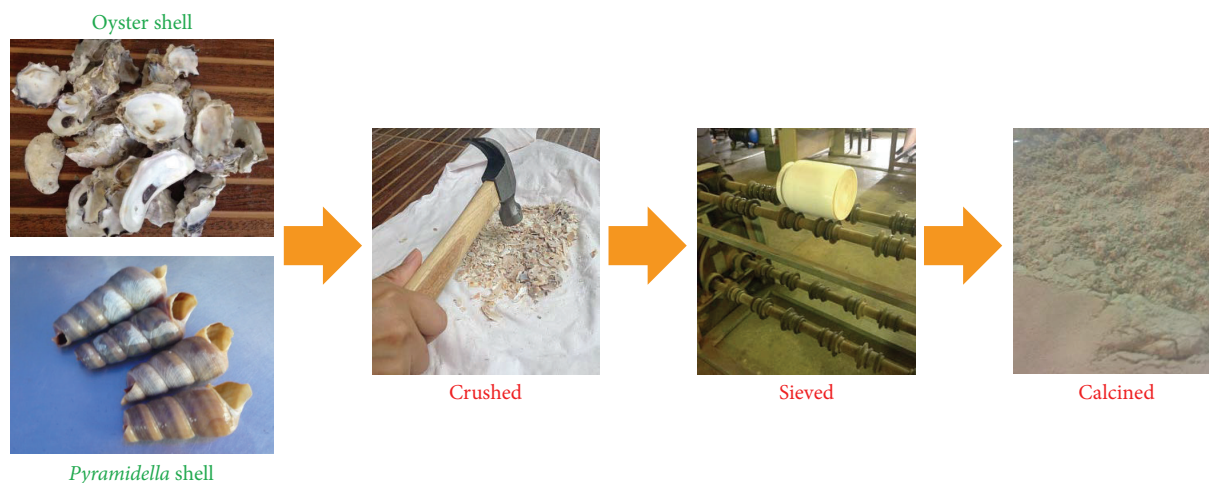


FIGURE 1: Preparation of CaO catalyst derived from oyster and *Pyramidella* shells.

the same time recycles the waste generated. These shells may also find their utility in other base catalyzed important organic reactions which will add value to the waste generated [1, 4]. Oyster and *Pyramidella* are found in several parts of Thailand. In the production of oyster and *Pyramidella* products on very large scale, the processing also produces significant amounts of shell waste. The aim of this investigation is to examine the effect of the microwave irradiation generated from a household microwave for the transesterification of *Jatropha curcas* (physic nut) oil with methanol into biodiesel when a solid CaO catalyst derived from waste oyster and *Pyramidella* shells was employed. The effects of reaction time, microwave power, methanol/oil molar ratio, catalyst loading, and reusability of catalyst were systematically investigated.

2. Materials and Methods

2.1. Materials. *Jatropha curcas* oil was purchased from Thai Physic Nut Oil Company Limited, Thailand. The oyster and *Pyramidella* shells were collected as wastes from university cafeterias and bay in southern Thailand. The waste shells were rinsed with water to remove dust and impurities and were then dried in an oven at 80°C for 12 h. All chemicals were analytical-grade reagents (Merck, >99% purity) and were used as received.

2.2. Preparation of CaO Catalysts. The dried oyster and *Pyramidella* shells were crushed and sieved to pass 100–200 mesh screens (38–75 μm). The solid catalysts were prepared by a calcination method. The waste shells were calcined at 900°C in air atmosphere with a heating rate of 10°C/min for 2 h [3]. The products (CaO catalyst) were obtained as white powder. All calcined samples were kept in the close vessel to avoid the reaction with carbon dioxide (CO_2) and humidity in air before used [4]. Figure 1 showed the preparation process of waste shell-derived catalyst.

2.3. Characterization of CaO Catalysts. A Rigaku (MiniFlex II, England) X-ray diffraction (XRD) analyzer was used to examine the catalysts. Samples were ground at room

temperature in an alumina mortar and pestle and placed on the XRD holder. Samples were analyzed at 40 kV and 44 mA at an angle of diffraction (2θ) between 15° and 80° with a step-size of 0.04° and a scan rate of 3°/min.

The inorganic compositions of the catalysts were determined by an X-ray fluorescence spectroscopy (XRF, Oxford, ED-2000, England) under energy dispersive mode for precise measurement of both light and heavy elements.

The microstructures of the calcined waste shells were observed by a scanning electron microscope (SEM). The SEM images of the representative sample were obtained from a Camscan-MX 2000 (England) equipped with an energy dispersive spectroscope (EDS).

The surface area, mean pore diameter, and pore volume of the catalysts were determined using a Quantachrome Instrument (Autosorb-1 Model No. ASIMPVP4, USA) based on the nitrogen (N_2) adsorption-desorption method at 77 K. Prior to the analysis, all samples were degassed at 300°C for 4 h to desorb the volatiles (if any) from the surface. A residual pressure of 300 μm Hg for 24 h was performed using the degas port. The surface area was calculated using the Brunauer-Emmett-Teller (BET) equation and the mean pore diameter and pore volume were obtained by applying the Barrett-Joyner-Halenda (BJH) method on the desorption branch [10].

2.4. Transesterification of *Jatropha curcas* Oil with Methanol. The reactions were carried out in a 500 mL glass reactor equipped with condenser and mechanical stirrer at atmospheric pressure, placed inside a household microwave oven (Samsung, Korea). The fixed 100 g of *Jatropha curcas* oil and the desired amount of the derived CaO catalysts (2, 3, 4, 5, and 6 wt%) were added to the reactor, and then the methanol was introduced to the oil at various methanol/oil molar ratios of 9 : 1, 12 : 1, 15 : 1, 18 : 1, and 21 : 1. The transesterification was operated at 180–800 W with varied reaction time of 2–6 min under microwave irradiation (Figure 2), and it was instantly stopped by rapid cooling in an ice bath. In some cases, the reaction was allowed to proceed for a period of time after the microwave irradiation was stopped [3]. All experiments were



FIGURE 2: Microwave reactor for biodiesel production.

repeated 3 times and the standard deviation was never higher than 7% for any point.

Composition of the fatty acid methyl ester (FAME) was analyzed with gas chromatograph-mass spectrometry (GC-MS QP2010 Plus, Shimadzu Corporation, Japan) equipped with a flame ionization detector (FID) and a capillary column 30 m \times 0.32 mm \times 0.25 μ m (DB-WAX, Carbowax 20M). Yield of FAME was calculated by

$$\text{Yield (\%)} = \frac{m_i A_b}{A_i m_b} \times 100, \quad (1)$$

where m_i is the mass of internal standard added to the sample, A_i is the peak area of internal standard, m_b is the mass of the biodiesel sample, and A_b is the peak area of the biodiesel sample [11]. The physical and chemical properties of FAME including kinematic viscosity, density, flash point, cloud point, pour point, acid value, and water content were analyzed according to ASTM methods [12].

3. Results and Discussions

The major component of both oyster and *Pyramidella* shells was CaCO_3 with the absence of CaO peak, as demonstrated by their clear XRD patterns. Figures 3 and 4 show the changes in the XRD pattern of the waste shells with the calcination method. The waste shells maintained their XRD patterns of CaCO_3 , while materials calcined at 900°C for 2 h exhibited those of CaO , indicating that the complete conversion of CaCO_3 to CaO by evolving the carbon dioxide (CO_2) required the calcination above 800°C [13]. Narrow and high intense peaks of the calcined catalyst define the well-crystallized structure of the CaO catalyst [7, 14]. The result reveals sharp XRD reflections with (1 1 1), (2 0 0), (2 2 0), (3 1 1), and (2 2 2) orientations, implying that the calcined material was well crystallized during the heat treatment process [4].

The major element present in the catalyst is calcium (94 wt%) in the form of oxide and is the active material

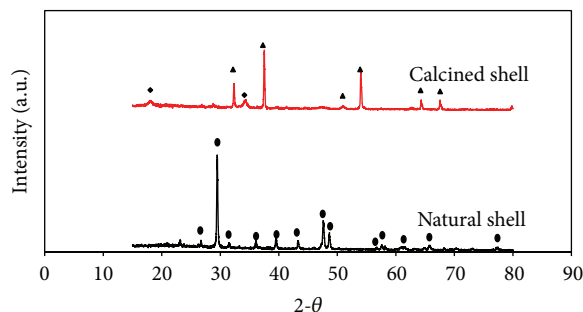
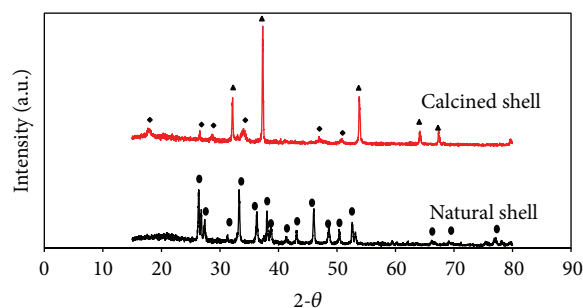
FIGURE 3: XRD patterns of natural and calcined oyster shell (symbols: ● CaCO_3 , ▲ CaO , and ◆ Ca(OH)_2).FIGURE 4: XRD patterns of natural and calcined *Pyramidella* shell (symbols: ● CaCO_3 , ▲ CaO , and ◆ Ca(OH)_2).

TABLE 1: Chemical compositions of waste shell-derived catalyst.

Compound	Concentration (wt%)	
	Oyster shell	<i>Pyramidella</i> shell
CaO	93.83	94.30
SiO ₂	2.71	3.29
MgO	1.18	0.48
Al ₂ O ₃	0.78	0.43
Na ₂ O	0.50	0.34
Fe ₂ O ₃	0.24	0.27
SrO	0.23	0.37
TeO ₂	0.13	0.14
LOI	0.40	0.38

for the conversion of triglyceride (TG) into methyl ester (ME). Si, Mg, Al, Sr, Na, Fe, Te, and so forth were found in trace amounts (Table 1). The presence of calcium as the major constituent was an indication that the waste shell comprised of CaCO_3 and upon calcination they can be almost completely converted to CaO [15].

The microscopic features of oyster and *Pyramidella* shells calcined at 900°C (2 h) were examined by high resolution SEM (Figure 5). The natural waste shell displays a typical layered architecture [16]. With the calcination temperature at 900°C, the microstructures of natural shell are changed significantly from layered architecture to porous structure [17]. The calcined oyster shell showed similar particle morphology with the calcined *Pyramidella* shell. The calcined

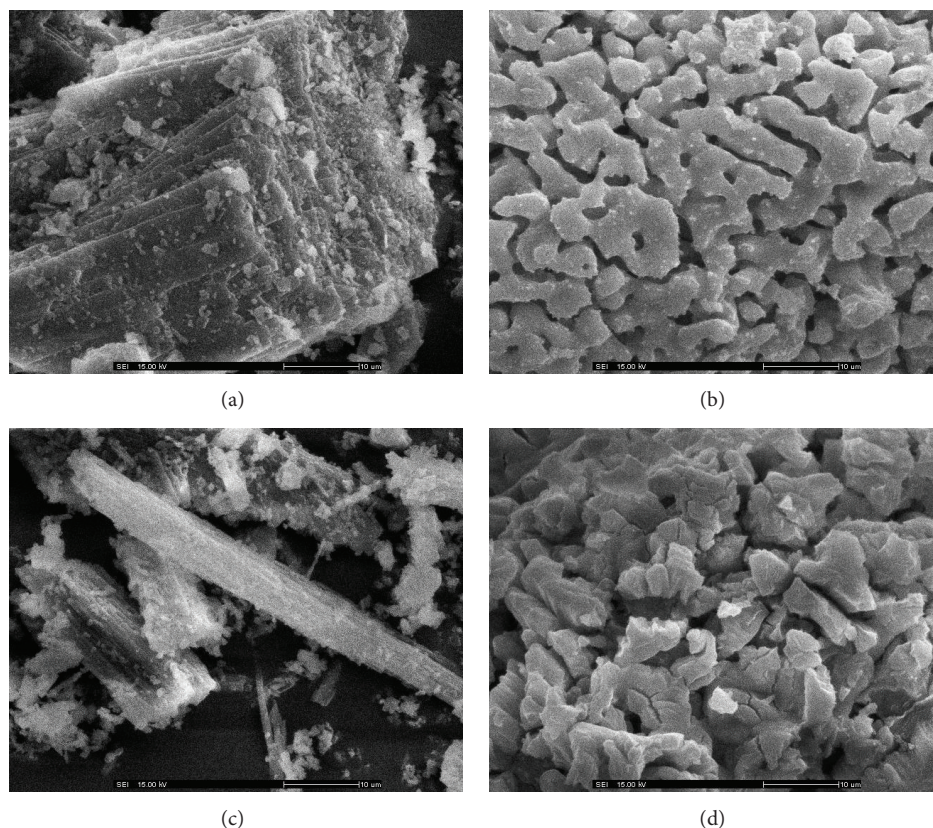


FIGURE 5: SEM images of (a) natural oyster shell, (b) calcined oyster shell, (c) natural *Pyramidella* shell, and (d) calcined *Pyramidella* shell.

TABLE 2: The physical properties of waste shell-derived catalyst.

Physical property	Derived catalyst	
	Oyster shell	<i>Pyramidella</i> shell
Surface area (m^2/g)	24	29
Pore volume (cm^3/g)	0.04	0.06
Mean pore diameter (\AA)	66.00	64.15

waste shells were irregular in shape, and some of them bonded together as aggregates. However, the smaller size of the grains and aggregates could provide higher specific surface areas. Since all samples are considered to be less-porous or even nonporous, the size of the particle should directly respond to the surface area [18].

The physical properties (surface area, mean pore diameter, and pore volume) of the catalyst are summarized in Table 2. The calcined oyster shell had the surface area $24 \text{ m}^2/\text{g}$, pore diameter 66 \AA , and pore volume ($0.04 \text{ cm}^3/\text{g}$) and presented a uniform pore size. The calcined *Pyramidella* shell present higher values for surface area ($29 \text{ m}^2/\text{g}$) and pore volume ($0.06 \text{ cm}^3/\text{g}$) related to oyster shell. The calcined sample was well crystallized during the heat treatment process. Furthermore, the chemical composition of the calcined catalyst mainly contains a high purity of CaO with a large basic strength and a variety of basic sites. The basicity on the catalyst surface is of key importance in biodiesel

production [3]. It can be seen that the heterogeneous catalyst resulted in a strong increase in the active sites [19].

The effect of single variable on the biodiesel yield, such as reaction time, microwave power, methanol/oil molar ratio, catalyst loading, and reusability of catalyst, was examined (Figures 6–10). For the following experiments, calcined oyster and *Pyramidella* shell were used as low-cost catalyst to catalyze the microwave-assisted transesterification of *Jatropha curcas* oil and methanol.

Figure 6 depicts the reaction time dependence of FAME yield during transesterification by employing oyster and *Pyramidella* shells derived catalyst. It shows an increase in the yield with time from 2 to 5 min with a catalyst amount of 4 wt% relative to oil and a methanol/oil molar ratio of 15:1. The maximum yields of 94.81 and 95.12% were obtained in 6 min at 800 W for oyster and *Pyramidella* shell, respectively. In the initial stages of the microwave-assisted transesterification reaction, production of biodiesel was rapid, and the rate diminished and finally reached equilibrium [20] in about 5 min. This can be explained by the fact that transesterification reaction between *Jatropha curcas* oil and methanol is reversible, when the reaction time is long enough [21].

In order to determine the optimum parametric conditions for production of biodiesel assisted by microwave irradiation, the effect of power supplied by the microwave oven was studied. The %FAME result shown in Figure 7 elucidated the effect of microwave power at 150 W (26.58%),

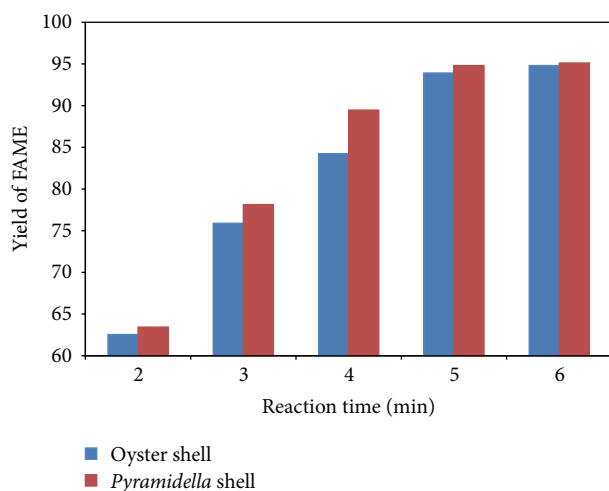


FIGURE 6: Effect of reaction time on %yield of FAME.

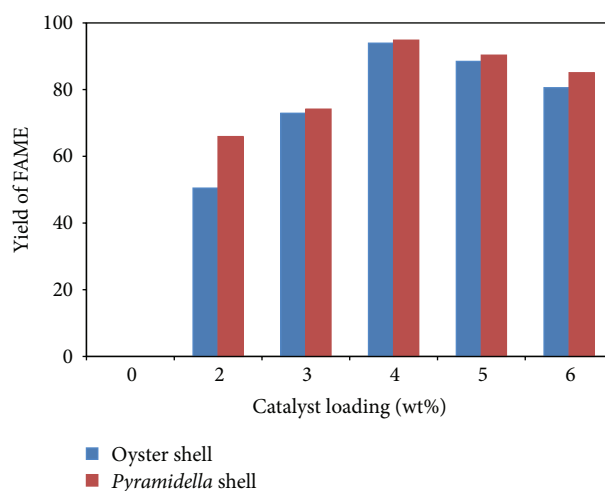


FIGURE 9: Effect of catalyst loading on %yield of FAME.

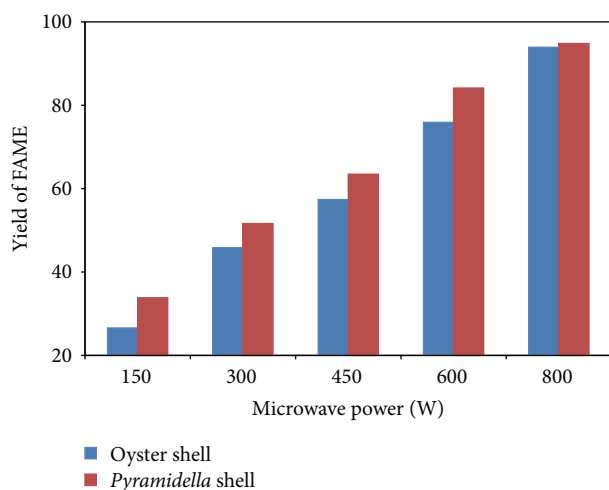


FIGURE 7: Effect of microwave power on %yield of FAME.

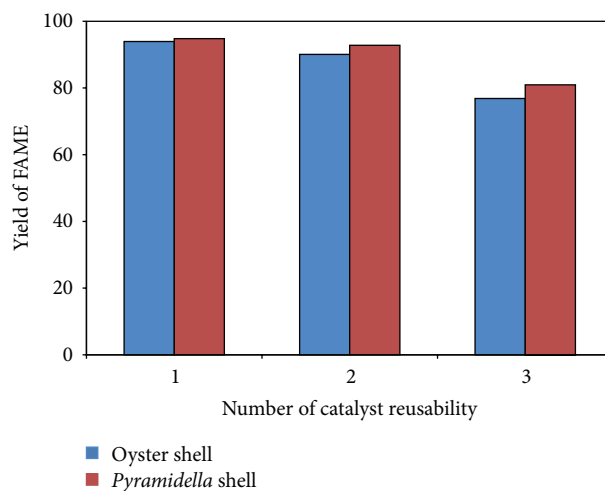


FIGURE 10: Effect of reusability of catalyst on %yield of FAME.

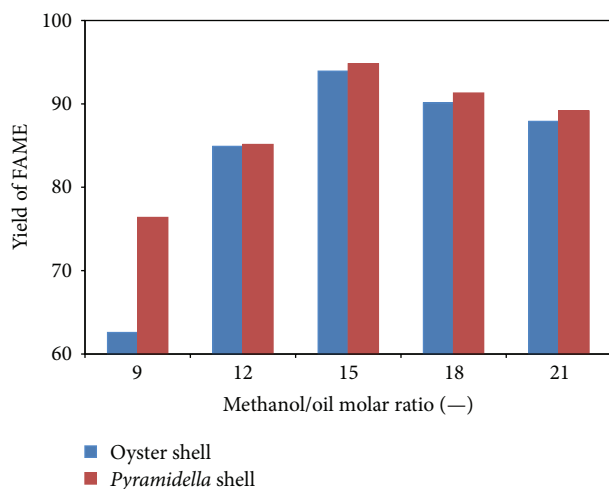


FIGURE 8: Effect of methanol/oil molar ratio on %yield of FAME.

300 W (45.84%), 450 W (57.37%), 600 W (75.90%), and 800 W (93.92%) for oyster shell. It was clear that higher microwave power gave rise to higher biodiesel yield. Thus the microwave power of 800 W would be chosen for further investigation. The microwave-assisted transesterification reaction over waste shell-derived catalysts could proceed with a rapid reaction time. It was considered that the related chemical reactions are accelerated by microwave energy, giving rise to intense localized heating and thereby accelerating the chemical reaction and giving high product yields in a short time [3].

The effect of increasing the methanol/oil molar ratio was also studied with the 4 wt% CaO catalysts. Figure 8 shows the FAME conversion over time using molar ratios of methanol to oil of 9 : 1, 12 : 1, 15 : 1, 18 : 1, and 21 : 1. The lower methanol/oil ratios resulted in poor suspension of the slurry in the reacting solution, which possibly induced mass transfer problems thus resulting in lower activity. On the other hand and in accordance with reported literature, the activity steadily

TABLE 3: The fuel properties of biodiesel.

Fuel property	Derived catalyst		ASTM D6751	EN14214
	Oyster shell	<i>Pyramidella</i> shell		
Kinematic viscosity (mm ² /s)	4.5	4.4	1.0–6.0	3.5–5.0
Density (g/cm ³)	0.879	0.876	NS	0.860–0.900
Flash point (°C)	163	162	130 Min	120 Min
Cloud point (°C)	11	13	NS	NS
Pour point (°C)	8	9	NS	NS
Acid value (mg KOH/g oil)	0.37	0.41	0.8 Max	0.5 Max
Water content (%)	0.01	0.02	0.050 Max	0.050 Max

NS: not specified, Min: minimum, and Max: maximum.

increased with higher methanol/oil molar ratios [22]. The FAME content increased significantly when the methanol/oil molar ratio was changed from 9 to 21. The high amount of methanol promoted the formation of methoxy species on the CaO surface, leading to a shift in the equilibrium in the forward direction, thus increasing the rate of conversion up to 93.92 and 94.81% for oyster and *Pyramidella* shell, respectively. However, further increases in the methanol/oil molar ratio did not promote the reaction. It is understood that the glycerol would largely dissolve in excessive methanol and subsequently inhibit the reaction of methanol to the reactants and catalyst, thus interfering with the separation of glycerin, which in turn lowers the conversion by shifting the equilibrium in the reverse direction [4, 23].

The effect of catalyst amount on the *Jatropha curcas* oil conversion has been evaluated by running the microwave-assisted transesterification at 800 W for 5 min with catalyst subsequently 2, 3, 4, 5, and 6 wt% with respect to the amount of oil loaded in the reactor. In the absence of catalyst, there was no FAME formed in the reaction. A maximum conversion of 94.81% was obtained with a CaO catalyst (*Pyramidella* shell) loading of 4 wt%. The lower yields at catalyst concentrations above 4 wt% were due to the formation of slurries which were too viscous for adequate mixing. This result implies that the transesterification of TG is strongly dependent on the amount of basic sites [24]. From this study, we can conclude that the suitable amount of CaO required for the transesterification of *Jatropha curcas* oil with methanol is 4 wt%.

The reusability of the CaO catalyst prepared at the optimum preparation conditions was investigated by carrying out subsequent reaction cycles. After 5 min of the reaction, the catalyst was separated from the reaction mixture by filtration followed by washing with methanol to remove any adsorbed stains. Afterwards it was dried at 80°C in an oven for 12 h and was used again for second reaction cycle under the same reaction conditions as before. The results indicated that the yield decreased with the repeated use of the waste shell-derived catalysts and it exhibited poor catalytic activity after being used for more than two times. This deactivation was probably due to the structural changes leading to the failure to maintain the form of CaO or its transformation to other form such as Ca(OH)₂. This may also be due to the losses of some catalyst amount during the process of washing, filtration, and calcination [25].

For biodiesel to be used in diesel engines, the fuel must meet various specifications stated in biodiesel standard, mainly United States biodiesel standard (ASTM D6751) and European biodiesel standard (EN14214) [26, 27]. The fuel properties of FAME obtained in this work were summarized in Table 3 along with a comparison to the recommended biodiesel international standards ASTM D6751 and EN14214. The physicochemical properties assessed include kinematic viscosity (40°C), density (80°C), flash point, cloud point, pour point, acid value, and water content. It can be seen that most of its properties are in the range of fuel properties as described in the latest standards for biodiesel [28].

4. Conclusions

Activated waste oyster and *Pyramidella* shells have been successfully utilized as heterogeneous catalysts in the microwave-assisted transesterification of *Jatropha curcas* oil. This catalyst contains CaCO₃ which is converted to CaO after calcination at temperatures 900°C for 2 h. The optimum conditions, which yielded a conversion of oil of nearly 93% for both waste shell-derived catalysts, were reaction time 5 min, microwave power 800 W, methanol/oil molar ratio 15, and catalyst loading 4 wt%. The experimental results show that CaO catalyst had excellent activity and stability during reaction. The catalyst was used for 3 cycles and apparent low activity loss was observed. The activity of spent catalyst could be restored by recalcination process. The physical and chemical properties of biodiesel produced conform to the available standards.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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