



## The Application of Calcium Oxide from Waste Cockle for Biodiesel Production from Used Cooking Oil via Microwave Heating System

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### ARTICLE INFO

### ABSTRACT

#### Article history:

Received 3 March 2018

Received in revised form 17 May 2018

Accepted 8 July 2018

Available online 10 September 2018

An experimental investigation was conducted to explore the heterogeneous catalytic performance of activated waste cockles derived CaO on the biodiesel production of used cooking oil via microwave heating system. The catalyst was characterized by X-ray diffraction (XRD), scanning electron microscope (SEM) and X-ray fluorescence (XRF) method. The effects of reaction parameters such as reaction time, methanol to oil molar ratio, catalyst concentration, and microwave exit power on the yield of biodiesel were investigated. It is clearly observed that the catalyst activity still sustained up to three successive cycles. The fuel properties of the biodiesel produced were compared with the ASTM D6751 and were in accordance with the standard method. More than 95% yield concentration was recorded through the microwave irradiation method which shows that it can be employed as an energy source due to its ability in accelerating the transesterification process.

#### Keywords:

Biodiesel, heterogeneous catalyst, transesterification, microwave, non-edible oil

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## 1. Introduction

Biodiesel offers a remarkable opportunity to improve the environmental issues, human health, vehicles and local economies as well. Due to the problems in climate change, rising fuel prices and instability in the Middle East, it might be a very good idea to have a biodiesel as an option in order to promote green renewable and non-toxic fuels for environment. Used cooking oil have been widely used as a biodiesel feedstock as a greener and cheaper alternatives fuel. These inexpensive feed stocks have recently attracted a great deal of attention. However, it has been reported that the high level of viscosity content in used cooking oil contributes to the engine failure especially at low temperature [1].

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The transesterification process of biodiesel is a very common process due to their simplicity and has been one of the most popular methods among the researchers worldwide. It is a process of turning one ester (glycerol esters) into another ester (methyl esters) by adding methanol to the triglyceride. Reversible process is a key feature of transesterification starting with converting the triglycerides into diglycerides and followed by converting diglycerides to monoglycerides and finally transformed into glycerol [2].

The cost of biodiesel production and the available and suitable feed stocks are some of ascending problems among biodiesel producers when it comes to commercializing biodiesel [3]. One of the possible alternatives is by performing transesterification method using heterogeneous catalysts from waste sources which allows simple product separation and purification and does not required neutralization process [4]. Even though homogeneous catalyst is said to be dominating the biodiesel industries due to their simple usage and very high yield production this method still has a few drawbacks such as generates water and soap formation which will consume more catalyst and in turns reduce the yield of biodiesel [5].

Heterogeneous catalysts are gaining attention among researchers now days as these catalysts have many advantages over homogeneous catalysts. These catalysts are known to be not corrosive, environmentally friendly and can be used multiple times. The bright side of using heterogeneous catalyst is the acid neutralization of free fatty acid (FFA) does not produce soap. It can be easily separated from the tested solution, reused for multiple testing and it has a longer catalyst lifespan. Basically, there are two types of heterogeneous catalyst that are currently used in biodiesel production; solid base and solid acid catalyst. The solid base is found to be more active compared to solid acid catalyst which required relatively shorter reaction time and lower reaction temperature. Naturally derived calcium oxide (CaO) based catalysts have been used extensively due to the lower in price and its easy availability [6]. On top of that, it is also been identified be able to withstand high temperatures and their performance are reported is comparable to homogeneous catalyst biodiesel production [7].

This work is attempted to optimize the process for biodiesel production from used cooking oil using waste cockle shells as renewable catalyst. A microwave assisted production of biodiesel was applied in this research to enhance the chemical reaction and give a high product yields in a short time. The effects of reaction time, methanol to oil molar ratio and catalyst loading were systematically investigated as well as the basic fuel characteristics of biodiesel.

## **2. Methodology**

### **2.1 Materials and Chemicals**

The used cooking oil with acid value of 5.25 was purchased from local restaurant in Kuala Lumpur. The physical characteristics of the used cooking oil were tested and the test result was tabulated as shown in Table 1. All tests were determined according to the ASTM D-6751, EN-14214 and AOCS method. Most of the chemicals that were used in this research were purchased from Polyscientific Chemicals, Melaka, Malaysia (methanol 99.9 % purity, KOH pellets, n-hexane HPLC grade and sulphuric acid of 95-98%) and Sigma- Aldrich (phenolphthalein). The catalyst was prepared from natural waste cockles purchased from local seafood restaurant in Melaka, Malaysia.

**Table 1**  
Properties of methyl ester of used cooking oil

Test	Unit	Method	Results
Acid value	mg KOH/g	ASTM D664	5.25
Iodine Value	g I <sub>2</sub> /100g	AOCS Id 3-92	55
Saponification Value	mg KOH/g	AOCS Cd 3-25	202.9
Water Content	%wt	EN ISO 12937	0.106
Kinematic Viscosity@ 40°C	mm <sup>2</sup> /s	ASTM D7042	44.30
Density @ 15°C	kg/L	ASTM D4052	0.9194

## 2.2 Catalyst Preparation and Characterization

The waste cockle shells were washed with tap water to remove all the impurities. Then, the cleaned samples were dried for 24 hours in the oven at 100°C for 3 to 4 hours to remove the excess water. The samples were later crushed and grounded into different particles sizes which was passed through 0.5 mm sieve mesh to obtain particles size lesser than 0.5 mm using pestle and mortar. The dried waste shells were then calcined in a furnace at 900°C with a heating rate of 10°C/min for 4 hours to convert calcium carbonate, CaCO<sub>3</sub> into calcium oxide, CaO [8]. All the produced catalyst samples were then stored in a highly sealed glass jars to prevent contamination from carbon dioxide, CO<sub>2</sub> and atmospheric water moisture. The chemical composition of the samples was observed using X-ray fluorescence in- build XRD (ARL 8660S) and scanning electron microscopy with energy dispersive X-ray detector (SEM-EDS) technique. The SEM-EDS technique was used to obtain the information of the morphology and elemental composition of the samples. The morphology of the catalysts was carried out using a HITACHI scanning electron microscope model SUI510. The element composition was analysed by using an energy dispersive X-ray detector (EDS) mounted on the microscope.

## 2.3 Apparatus and Procedure

The transesterification process of the biodiesel was carried out as a batch process inside a modified 1000 W 2450 Hz household microwave oven brand Samsung as shown in Figure 1. Two holes were drilled on top of the domestic microwave oven, one hole for placing the stirrer and the other one to adjust the thermocouple inside the microwave. The microwave was equipped with a mechanical stirrer which it was driven by a motor in order to replace the carousel. The thermocouple was connected to a USB-5104 4-channel thermocouple logger. A one-litre beaker was provided to do this experiment and a separation funnel was used to separate the biodiesel from the reaction mixture. The reaction study was performed by varying the microwave power input, catalyst loading and methanol to oil molar ratio. The sample volume (used cooking oil) was kept constant at 100 g and the desired amount of the derived catalyst were added to the reactor mixture and then the methanol was introduced to the oil at various methanol/ oil molar ratios. The transesterification was operated with varied reaction time under microwave irradiation. Composition of the FAME was analysed with gas chromatograph-mass spectrometry (GC-MS) equipped with a flame ionization detector (FID). Yield of FAME was calculated by Equation (1).

$$FAME\ Yield\% = \frac{Total\ weight\ of\ FAME}{Total\ weight\ of\ oil} \times 100 \quad (1)$$

## 2.4 Catalyst Characterization

The elemental chemical composition analysis of the calcined sample were analyzed using XRF spectroscopy. It appears from Table 2 that the major mineralogical component is CaO having concentration of CaO 93.98 wt%. These results indicated that all  $\text{CaCO}_3$  in the samples was completely transformed to CaO. Figure 2 shows the surface morphologies of the calcined heterogeneous catalyst which gave an irregular in shape and some of them bonded together as aggregate [8].

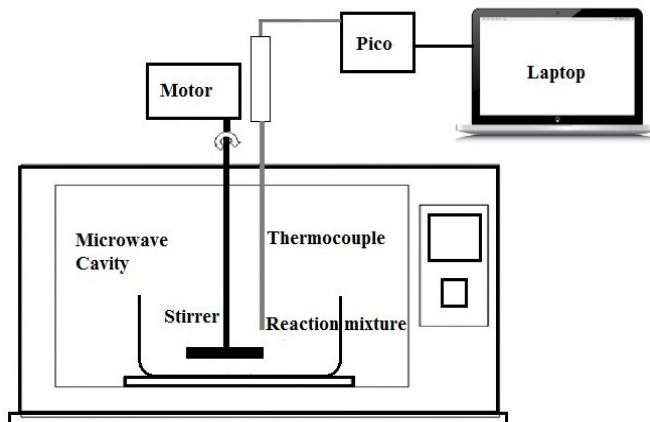


Fig. 1. Schematic diagram of the experimental setup

EDS analysis was conducted to determine the components of the surface. Typically, plenty of Calcium (Ca) and Oxygen ( $\text{O}_2$ ) were observed. Moreover the calcium contents of the catalyst are much higher indicating that the catalysts are calcium compounds. XRD pattern was used to identify the crystallographic phase of calcined cockle. After the calcination step, the diffraction lines attributed of carbonate species disappear due to its liberation in the form of  $\text{CO}_2$ , arising new diffraction lines with a lower intensity than raw cockles which suggests a decrease of the particle size for calcined cockles [9].

**Table 2**

Chemical composition of calcined cockle with XRF-XRD

Formula	CaO	Na <sub>2</sub> O	SrO	MgO	SO <sub>3</sub>	SiO <sub>2</sub>
Concentration (%)	93.98	1.34	0.21	0.16	0.12	0.04

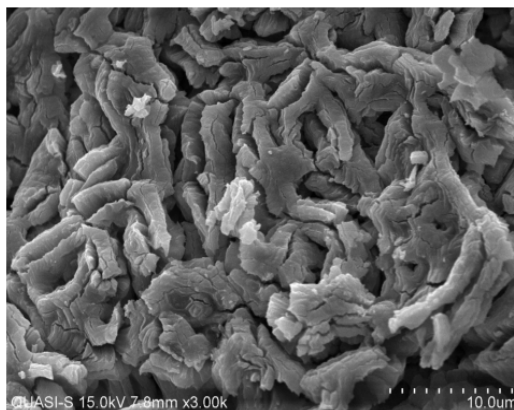


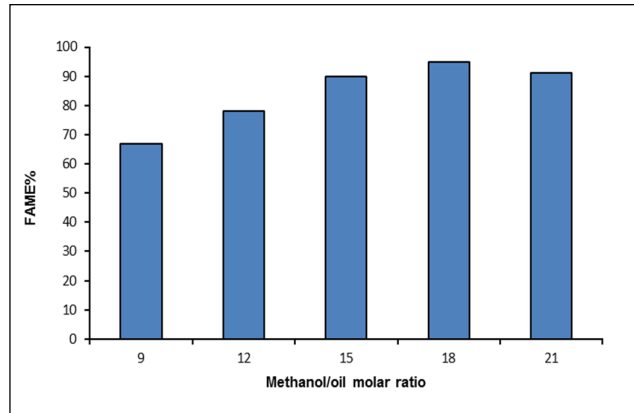
Fig. 2. SEM images of the heterogeneous cockle calcined at 900°C for 4 h

### 3. Results and Discussion

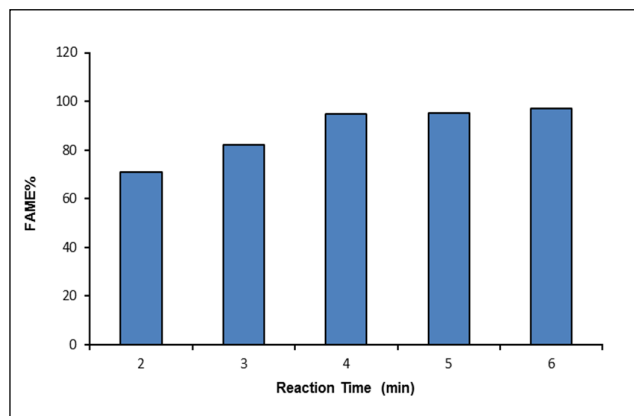
Effect of the processing variables such as reaction time, reaction temperature, alcohol/oil molar ratio, catalyst loading, microwave power input, and reusability of catalyst was investigated and all the reaction variables were associated with the type of catalysts used [10]. Therefore, the effect of reaction variables was studied in the presence of calcined cockle catalyst. Figure 3 presents the effect of methanol on the biodiesel yield performance. The yield was increased from 68.12% up to 95.88% with a methanol/oil molar ratio from 9:1 to 18:1. The rate started to diminished when increasing the rate of methanol. The transesterification reaction between used cooking oil and methanol is reversible when the reaction time is long enough. Adding more methanol/oil molar ratios, can boost up the transesterification activity [11]. By adding more methanol into the reaction, the formation of methoxy on the CaO surface will form that may lead to a shift in the equilibrium in the forward direction, and at the end enhance the rate of conversion. In the initial stages of the microwave-assisted transesterification reaction, production of biodiesel was rapid, and the rate diminished and finally reached equilibrium in about 4 minute (Figure 4) [12]. The mixing speed was set at 1000 rpm constant for all the experiments.

A similar trend was also observed for the catalyst loading effects on the yield of the biodiesel as shown in Figure 5. In the absence of catalyst, there was no FAME formed in the reaction. A maximum conversion of 95.88% was obtained with catalysts 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 triglycerides is strongly dependent on the amount of basic sites [13]. The yields biodiesel increased with increasing power. The yields were 64.56 %, 85.98 %, and 95.88 % for microwave power 100, 200 and 300 Watt respectively (Figure 6). In addition, the microwave power output must not be too high because the reaction is subjected to the highest amount of microwave energy, as it may cause damage to organic molecules (triglycerides) [14].

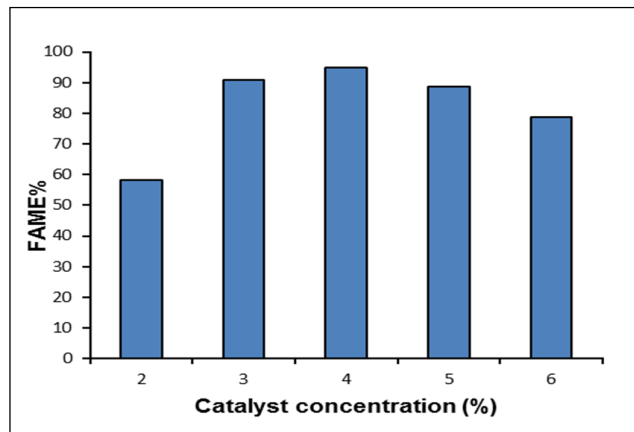
The reusability of the catalysts prepared at the optimum preparation conditions was investigated by carrying out subsequent reaction cycles (Figure 7). Following almost the same procedure of catalyst preparation, the used catalyst was once again washed with methanol to remove any adsorbed stains. After being dried at 80 °C in an oven for 12 h it 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 calcined catalyst 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)<sub>2</sub>. This may also be due to the losses of some catalyst amount during the process of washing, filtration and calcination [15].



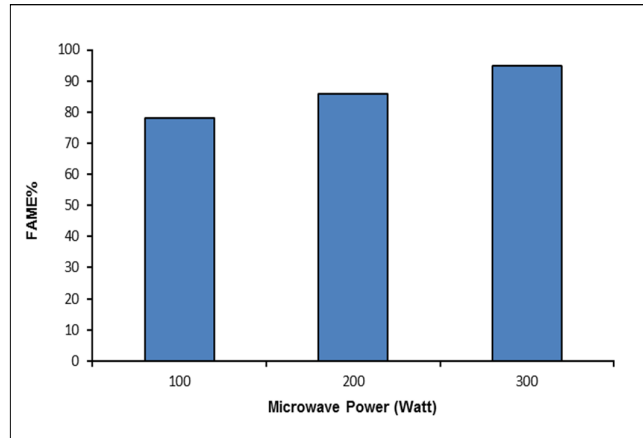
**Fig. 3.** Effect of methanol to oil molar ratio on biodiesel yield



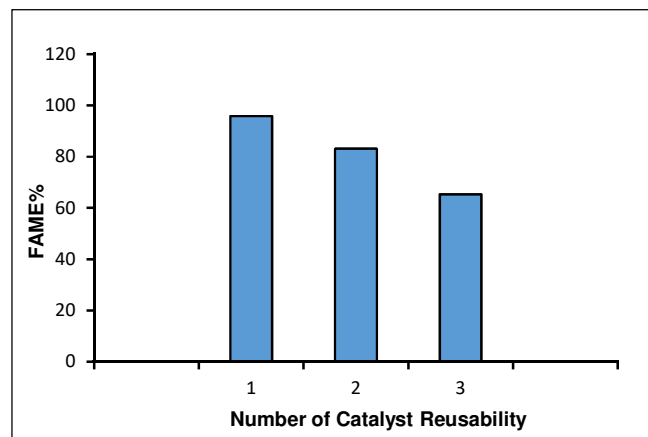
**Fig. 4.** Effect of reaction time on biodiesel yield



**Fig. 5.** Effect of catalyst concentration on biodiesel yield



**Fig. 6.** Effect of catalyst concentration on biodiesel yield



**Fig. 7.** Effect of number of catalyst reusability on biodiesel yield

### 3.1 Fuel Properties

The important fuel properties of the biodiesel produced from heterogeneous used cooking oil methyl esters are compared with biodiesel and petro diesel standards and are presented in Table 3. The heterogeneous transesterification process significantly reduced the viscosity and acid value of the oil.

**Table 3**  
 Comparison of Biodiesel Properties with ASTM Standard

Property	Unit	Prepared Biodiesel	ASTM D-6751	EN 14212
Kinematic Viscosity@40°C	mm <sup>2</sup> /s	4.73	1.9 – 6.0	3.5-5
Acid Value	mgKOH/g	0.435	< 0.5	0.5 max
Flash Point	°C	181.2	> 93	120 min
Density	25°C kg/m <sup>3</sup>	875.4	N/A	80-900
Moisture Content	%	<0.034	<0.05	<0.05

#### 4. Conclusion

Using waste cockle shells as the primary heterogeneous catalyst in this study was found having a high potential to be commercialized as a cost effective catalyst in biodiesel production due to its excellent activity and stability during reaction. The transesterification process via microwave irradiation has reduced the reaction time and at the same time have made the process more economic and environmental friendly. The highest catalytic activity from the produced biodiesel was achieved starting at reaction time 4 min with methanol to oil molar ratio 18:1 and catalyst loading 4 wt% which yielded a conversion of oil around 95%. The activated recovered catalyst was reused for successive three cycles and the gradual loss was observed due to the low adsorption rate of organic matters on the catalyst surface. The physical and chemical properties of the produced biodiesel meet all the available biodiesel standards.

#### Acknowledgements

The authors wish to acknowledge the Ministry of Higher Education Malaysia, Universiti Teknologi Malaysia for the award of UTM-Research University Grant 4F600 and Universiti Teknikal Malaysia Melaka for the financial support during the course of this study.

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