Application of K-Impregnated Staghorn Coral as Catalyst in the Transesterification of Waste Cooking Oil

(Penggunaan K-Impregnasi Batu Karang *Staghorn* sebagai Pemangkin dalam Transesterifikasi Sisa Minyak Masak)

NABILAH ATIQAH ZUL, SHANGEETHA GANESAN & M. HAZWAN HUSSIN*

ABSTRACT

This work focuses on the catalytic potential of K-impregnated staghorn coral as a catalyst in methyl esters production via methanolysis of waste cooking oil (WCO). The prepared catalyst was analyzed by Hammett indicators, XRF, Brunauer-Emmett-Teller (BET)-N2 adsorption method, ATR-FTIR, TGA, XRD and SEM to determine its physicochemical properties. ATR-FTIR and XRD results confirmed the formation of K_2O species upon KOH impregnation, thus, resulting in good catalytic activity. Reaction parameters such as methanol to oil ratio, reaction time and amount of catalyst were evaluated to find out the best conditions for the transesterification process. About 89.51 ± 4.78 % of biodiesel contents were obtained under the optimum conditions.

Keywords: Biodiesel; staghorn coral; transesterification; waste cooking oil

ABSTRAK

Kajian ini memfokuskan potensi pemangkin K-impregnasi batu karang staghorn sebagai pemangkin dalam penghasilan metil ester melalui metanolisis sisa minyak masak (WCO). Pemangkin yang telah disediakan telah dianalisis oleh penunjuk Hammette, XRF, kaedah Brunauer-Emmett-Teller (BET)-penjerapan N2, ATR-FTIR, TGA, XRD dan SEM untuk menentukan sifat fiziokimianya. Keputusan ATR-FTIR dan XRD mengesahkan pembentukan spesies K_2O apabila impregnasi KOH, sehingga menghasilkan aktiviti pemangkin yang baik. Parameter tindak balas seperti nisbah metanol kepada minyak, masa tindak balas dan jumlah pemangkin telah dinilai untuk mengetahui keadaan terbaik untuk proses transesterifikasi. Sebanyak 89.51 ± 4.78 % kandungan biodiesel telah diperoleh di bawah keadaan optimum.

Kata kunci: Batu karang staghorn; biodiesel; sisa minyak masak; transesterifikasi

INTRODUCTION

Over the last few decades, the demand for energy has increased exponentially by the sudden increase in the consumption especially in the transportation sector. Buses, boats, lorries and trucks are all fueled by biodiesel. In addition, the use of diesel machines in the industrial manufacturing process are also increasing. Approximately 80% of the world energy demand is covered by fossil fuel (Huang et al. 2012). However, the fossil fuel has some drawbacks such as high in price, non-renewable, limited supply as well as requires million years to form. Geothermal, wind, ocean thermal, tidal and hydropower are some examples of energy sources used by some countries as an effort to control the use of fossil fuel (Shereena & Thangaraj 2009). Surprisingly, biodiesel was selected as the perfect candidate to replace the fossil fuel due to its low cost and renewability. Biodiesel, also called as fatty acid methyl esters (FAME) is a yellowish liquid fuel that has a boiling point of over 475 K, a flash point of 420-450 K and a distillation range of 470-600 K. It also has low solubility in water and exhibits soapy odour (Demirbas 2009). The production of biodiesel can be done through several techniques such as direct use of vegetable oil/animal fats, thermal cracking, (pyrolysis), microemulsion and transesterification/esterification (Rajalingam et al. 2016). Among these techniques, transesterification has been chosen as the most productive and practical chemical process to produce biodiesel. Transesterification is a conversion process of triglycerides into alkyl esters with the presence of alcohol and catalyst (Attaphong et al. 2012). This process was first carried out in 1853 by Duffy, E. and Patrick, J. (Hassan & Kalam 2013).

Biodiesel is commonly produced from various types of feedstock namely; vegetable oil, waste used oil and animal fats. The utilization of vegetable oil as fuel in the diesel engine was firstly introduced by Rudolf Diesel in 1895 (Kapilan et al. 2009). Other than vegetable oil, waste cooking oil can also be used as a feedstock in the FAME production. The use of waste cooking oil as the biodiesel feedstock can potentially solve the uncontrollable production of waste cooking oil worldwide. The oil wastes from houses, restaurants and stalls are regularly poured into the sinks and drains, thus, causing a serious problem in the wastewater treatment plants as well as the drainage system. This matter can affect the human health due to contaminated water supply. According to Saxena et al. (2013), biodiesel is much better than diesel fuel attributed to numerous advantages such as high cetane number,

combustion efficiency and biodegradability. Biodiesel is also capable of replacing petrodiesel since both of them possess similar characteristics. Biodiesel is widely used in Malaysia and it is also popular in a few other countries such as Indonesia, China, United States of America, Brazil, Ireland, Italy, France, Australia, Germany, Canada, and Europe (Bajpai & Tyagi 2006; Shereena & Thangaraj 2009).

One of the important elements in the methyl esters production is the catalyst. The use of the right catalyst is vital as it can accelerate the production process, thus, reduce the reaction time. The catalyst can be divided into several categories: Acid catalyst, alkali catalyst and enzyme catalyst. Among the catalysts, enzyme catalyst is used the least as compared to acid and alkali catalysts in the methyl esters production. Acid and alkali catalysts can be classified into two types, which are homogeneous and heterogeneous catalysts. Acid catalysts are commonly utilized in the esterification of high free fatty acids (FFA) oil (Javidialesaadi & Raeissi 2013; Otadi et al. 2011). The presence of FFA could interfere the reaction process by promoting saponification. However, they are corrosive and exhibit low reaction rate (Lam et al. 2010). In this case, Ma and Hanna (1999) agreed that the alkali catalyst is more effective and practical than acid catalyst. Heterogeneous base catalysts have become more attractive as they exhibit better reaction rate than acid catalysts, environmentally beneficial and need moderate reaction conditions (Lam et al. 2010). In order to enhance the catalytic activity of the catalyst, some researchers have conducted thorough experimentations and tests where they found that the impregnation of additional basic sites onto the catalyst surface favors the catalytic activity (Kaur & Ali 2011; Kumar & Ali 2012).

The transesterification of canola oil into biodiesel using K_2CO_3/nano CaO catalyst has been done by impregnating various concentrations of K_2CO_3 (1-10 wt. %) into CaO in order to investigate their effects on the catalytic activity (Degirmenbasi et al. 2015). According to the experimental results, the K_2CO_3/nano CaO catalyst has higher basicity than the pure nano CaO. As the amount of K_2CO_3 increased, the basicity of the catalyst also increased, whereas the surface area decreased. The contribution toward the greater basicity is mainly associated with the K_2O phase or the presence of Ca–O–K groups which resulted from the degradation of the K loaded compounds. They then concluded that more than 3.0 wt. % of K^+ concentration was needed for the K_2CO_3/nano CaO to achieve its best activity. Two years later, Kataria et al. (2017) tested the effectiveness of nanocrystalline Zn/CaO catalyst in used frying oil transesterification by varying the amount of zinc sulphate (1.5-5.0 wt. %). The authors also tested different calcination temperature, reaction temperature and methanol to oil molar ratio to determine the optimum reaction conditions. They reported that the catalyst prepared with 5 wt. % of Zn in CaO at 700°C activation temperature (5-Zn/CaO-700) showed the best

performance during the methanolysis process yielding more than 98% of biodiesel.

In the present study, KOH impregnated staghorn coral derived CaO is utilized as a catalyst in the transesterification of waste cooking oil to biodiesel. The staghorn coral is a stony coral that belongs to the *Acropora* genus. The uniqueness of the corals relies on their antler-like branches where they can be found abundantly in shallow water but hardly seen in deep water (Kahng et al. 2010). Apart of having an important role in the reef-building, staghorn coral also acts as a habitat and shelter for various types of marine life (Pandolfi & Jackson 2006; Precht et al. 2002). Interestingly, they can be easily found at the coastal areas in Malaysia. In continuation to our previous study on the use of staghorn coral as a heterogeneous catalyst in RBD palm olein methanolysis, the current work explored the effectiveness of K-impregnated staghorn coral catalyst in the biodiesel production through methanolysis of waste cooking oil. The catalyst was firstly characterized for its physicochemical properties and then, the impacts of various reaction parameters on the catalytic activity were observed by optimizing the methanol to oil ratio, reaction time and catalyst loading.

METHODS

MATERIALS

Dead staghorn coral fragments were obtained from Beras Basah Island, Langkawi in late 2016 and waste cooking oil was acquired from a local stall. Methanol and *n*-hexane of QREC brand were used as received, while internal standard (methyl heptadecanoate) was obtained from Sigma-Aldrich (Switzerland). The determination of moisture content of the oil was performed using the Karl Fisher titrimetric method, while the acid value, FFA value, and saponification value of the oil were determined according to the methods reported by Canesin et al. (2014) and Onukwuli et al. (2017) with slight modifications (Table 1).

TABLE 1. Properties of waste cooking oil

Parameters	Waste cooking oil
Moisture content (wt. %)	0.11 ± 0.02
Acid value (mg KOH g^{-1})	1.54 ± 0.10
FFA value (%)	0.77 ± 0.05
Saponification value (mg HCl g^{-1})	222.26 ± 4.19

CATALYST PREPARATION

The coral was cleaned with tap water and oven dried at 105°C overnight. After drying, the coral was then crushed and allowed to pass through a 250 mm sieve mesh. The catalyst was prepared using wet impregnation method. The powdered staghorn coral was impregnated with 50% of potassium hydroxide (KOH). In the preparatory method, 1

g of powdered staghorn coral was suspended in 20 mL of distilled water and followed by the addition of 0.5 g of KOH pellets. Then, the mixture was stirred for 2 h at ambient temperature and oven dried overnight at the temperature of 105°C. On the next day, the dried catalyst was activated in the muffle furnace for 4 h at 900°C. The prepared catalyst is designated as K-CaO.

CATALYST CHARACTERIZATION

In this study, the K-impregnated catalyst was analyzed by Hammett indicators, X-ray Fluorescence (XRF), BET -N_2 adsorption method, Attenuated Total Reflectance-Fourier Transforms Infrared (ATR-FTIR), Thermogravimetric Analysis (TGA), X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). The determination of basic strength was accomplished using Hammett indicators. The chemical compositions of the elements in the catalyst were determined by conducting XRF test. The test was conducted by Rigaku RIX3000 using the pressed-pellet (pressure at 8.0 Pa) method. The surface area, mean pore diameter as well as pore volume of the sample were investigated on a Micromeritics ASAP 2000 surface analyzer. The surface area was calculated using BET equation and the total pore volume, V_{tot} was acquired from the N_2 adsorption data. Meanwhile, the pore size distribution was obtained through Barrett, Joyner, and Halenda (BJH) method. The functional groups that present in the catalyst were determined by using PerkinElmer System 2000 spectrophotometer. The data were collected in the scan range of 600-4000 cm^{-1} with 20 scans per sample at a resolution of 4 cm^{-1}. Besides, the sample was analyzed using Mettler Toledo TGA/DTA 851e thermo-gravimetric analyzer from 30 to 900°C with 10°C/min heating rate under nitrogen atmosphere to determine its thermal stability. XRD test was carried out to identify the crystalline phase of the catalyst, and for this purpose, X-ray Diffractometer (Siemens Diffractometer D5000) with Cu Kα as a source was employed. The sample was scanned in the range of 2 of 25-125°, with a step size of 0.05° at a scanning speed of 1° min^{-1}. Scanning electron microscope (Quanta FEI 650 instrument) was used to determine the morphology of the catalyst.

TRANSESTERIFICATION

The transesterification of triglycerides was performed with various methanol to oil molar ratio, reaction time and catalyst loading. The experiment was conducted in a 50 mL round bottom flask fitted with a condenser, mechanical stirrer and a thermometer. During the analysis, a certain amount of oil, catalyst and methanol were added into the round bottom flask. The flask was then immersed in a water bath and the reaction mixture was stirred for several hours. The temperature of the water bath was fixed at 65°C. Upon the reaction completion, the sample was let to cool and subsequently separated from the catalyst and glycerol by centrifugation for 10 min at 5000 rpm. The biodiesel was then extracted with n-hexane (3 × 3 mL) and dried using anhydrous sodium sulfate. The obtained product was then stored in a refrigerator for further use. The triplicate experiments were done.

GAS CHROMATOGRAPHY ANALYSIS

The methyl esters content was evaluated using a gas chromatography (Agilent 7890A) fitted with a flame ionization detector (FID) by following the European procedure EN 14214 with polar capillary column (Supelco-Wax, 30 m × 0.25 mm i.d. × 0.25 μm). During the analysis, both injector and detector temperatures were set at 250°C. The oven temperature was initially set at 190°C and it was then increased up to 250°C at a heating rate of 10°C min^{-1}. The sample was injected into the GC system in the split mode (1:5). Methyl heptadecanoate was employed as an internal standard for quantification. The percentage of biodiesel conversion was determined by using (1):

$$\text{Conversion } (\%) = \frac{\left(\sum{^A}\right) - {^A}\text{ISTD}}{{^A}\text{ISTD}} \times \frac{{^C}\text{ISTD} \times {^V}\text{ISTD}}{m} \times 100$$

(1)

where is the total peak area of FAME from C12:0 to C20:0; A^{ISTD} is the peak area of internal standard; C^{ISTD} is the concentration of internal standard (mg/mL); V^{ISTD} is the volume of internal standard (mL); m and is the mass of sample (mg).

RESULTS AND DISCUSSION

CATALYST CHARACTERIZATION BASIC STRENGTH

The determination of basic strength of the catalyst was accomplished using the Hammett indicator method reported by Boro et al. (2014) with some modifications. The Hammett indicators used were phenolphthalein (H_=8.2), 2,4-dinitroaniline (H_=15) and 4- nitroaniline (H_=18.4). The study showed that K-CaO catalyst altered the colour of phenolphthalein (H_= 8.2) and 2, 4-dinitroaniline (H_= 15.0) solutions from colourless to pink and yellow to mauve, respectively. However, 4-nitroaniline (H_= 18.4) solution indicator did not impart any colour change with the employment of the catalyst. Similar observation was recorded for the CaO-derived staghorn coral catalyst. Therefore, both CaO and K-CaO are regarded as strong base catalysts since their basic strengths lie in the range of 15.0 <H_< 18.4 (Boey et al. 2011). This value is higher than the basic strengths of CaO derived from palm kernel shell and MgO-KOH-20 catalyst reported by Bazargan et al. (2015) and Mutreja et al. (2011), respectively.

X-RAY FLUORESCENCE ANALYSIS

The compositions of the elements in K-CaO catalyst are shown in Table 2. The prepared K-CaO catalyst contains about 69.29% of Ca, while CaO accounts 93.86% of the overall constituent of activated staghorn coral (Supplementary material Table S1). After the KOH

impregnation, the amount of potassium increased up to 26.72%, suggesting a good dispersion of potassium ion. Other elements (Si, Fe, Ti, Al, Na) were considered as impurities due to their presence in small quantities. The high content of calcium and potassium suggest that the prepared catalyst would exhibit an excellent performance during the transesterification process.

TABLE 2. Elemental composition of K-CaO catalyst

Oxide	Composition (%)
CaO	69.29
K_2O	26.72
SiO_2	1.37
Others ($TiO_2, Al_2O_3, Fe_2O_3, MnO$, MgO, Na_2O, P_2O_5)	2.62

BET-N_2 ADSORPTION METHOD

The physical properties (surface area, pore volume and pore diameter) of K-CaO catalyst are summarized in Table 3 and the results showed that K-CaO has a surface area of 1.616 m^2g^{-1}, which is smaller than the surface area of calcined staghorn coral (Supplementary material Table S2) and calcined chicken and ostrich eggshells (Tan et al. 2015). The possible reason is that the addition of KOH has led to the plugging of CaO pores (Baroutian et al. 2010). Similar observations were also observed by Kaur and Ali (2011) and Watkins et al. (2004) when they introduced lithium into CaO. Despite that, the introduction of KOH has its own privilege as it helps to increase the number of basic sites (Buasri et al. 2012) and basic strength of

the catalyst. Interestingly, Meher et al. (2006) reported that the effectiveness of catalyst is highly dependent on basicity rather than surface area. Catalyst with high basicity and basic strength is expected to possess good catalytic activity. Apart from that, the pore volume of K-CaO also dropped to 0.002 cm^3g^{-1} after the addition of KOH, which mainly due to the pore plugging (Kaur & Ali 2011). The high pore volume of calcined staghorn coral is most likely due to the development of porosity in the catalyst (Boro et al. 2011). However, due to their trace pore volumes, both CaO and K-CaO are categorized as less-porous materials. The nitrogen adsorption-desorption isotherm of K-CaO is illustrated in Figure 1. The catalyst showed Type IV isotherm, which is consistent with mesoporous solid (Panda et al. 2010). An obvious increase in the nitrogen uptake was detected starting from the relative pressure of P/Po = 0.80 until P/Po = 0.99. These phenomena most likely occurred due to the capillary condensation inside the mesopores (Ekeoma et al. 2017). Besides, the hysteresis present in the isotherm corresponds to the existence of mesoporosity (Zielinski & Kettle 2013).

ATTENUATED TOTAL REFLECTION-FOURIER TRANSFORMS INFRARED (ATR-FTIR) ANALYSIS

The IR spectrum of K-CaO catalyst is depicted in Figure 2. From the analysis, it can be observed that the peak associated to Ca-O bond is located at 879 cm^{-1}, which is comparable with the finding of Ruiz et al. (2009). A vibrational band observed at 931 cm^{-1} is believed to have relation with the addition of KOH. This result is consistent with the work by Liu et al. (2016) when they added KBr into the calcined shell/kaolin catalyst. Meanwhile, no peak related to potassium was observed in the spectrum

TABLE 3. Physical properties of K-CaO catalyst

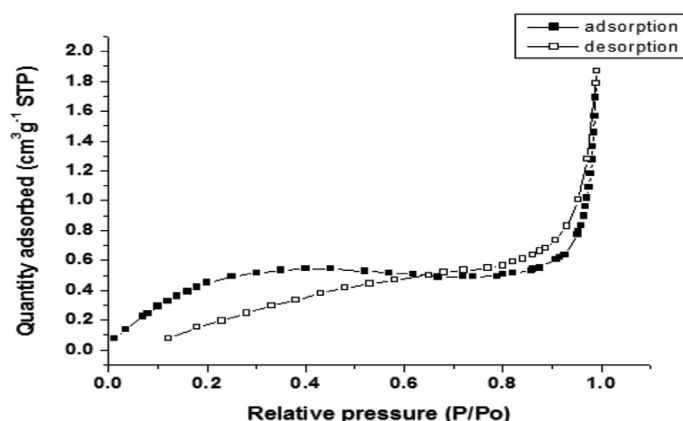| Physical properties	Value
BET surface area (m^2g^{-1})	1.616
Total pore volume (cm^3g^{-1})	0.002
Average pore diameter (A°)	55.842

FIGURE 1. Nitrogen adsorption-desorption isotherm of K-CaO catalyst

of CaO (Supplementary material Figure S1). The peaks intensities also decreased upon the KOH addition, which probably is caused by the incorporation of K$^+$ into the CaO defect sites (Boro et al. 2014). The peaks detected at 1132 and 1398 cm^{-1} prove the existence of C-O bonds of carbonate species. The stretching of hydroxyl species was detected by the presence of a peak located at 3841 cm^{-1}, which probably occurred due to the moisture adsorption by the catalyst during the analysis.
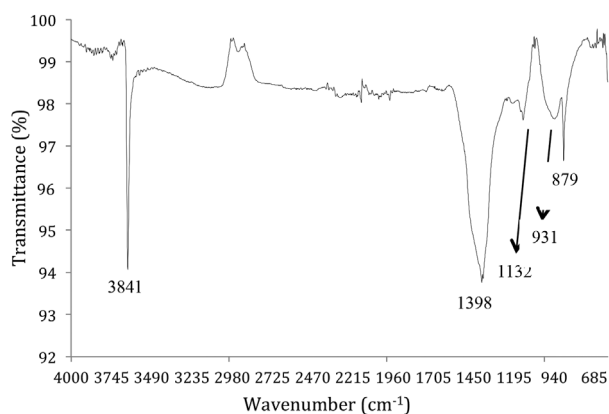

FIGURE 2. FTIR spectrum of calcined K-impregnated staghorn coral

THERMOGRAVIMETRIC ANALYSIS

The purpose of conducting the TG analysis is to determine the ideal calcination temperature of the prepared catalyst. The thermogram of uncalcined K-impregnated staghorn coral is presented in Figure 3. It was shown in the previous works that the loss of moisture usually occurred at the temperature below 250°C (Kesic et al. 2012; Xie & Li 2006; Yacob et al. 2017). However, in this current work, no weight loss was observed below 250°C as the sample was dried prior to the analysis. Between the temperature ranges of 270-430°C, a small weight loss was detected, corresponding to the removal of organic matter in the sample. A major weight loss of 23.7% occurred at the temperature range of 620-780°C with the peak temperature at 700°C. The decomposition is associated with the transformation of calcium carbonate into calcium oxide and solid-state interaction of the oxide with the support, resulting in catalytically active sites (Liu et al. 2016; Xie & Huang 2006). Above 800°C, the sample showed a constant weight, which is similar with the uncalcined staghorn coral (Supplementary material Figure S2), evidencing that the suitable activation temperature for both samples is over 800°C. This result is in agreement with the outcome of the study on chicken eggshell-derived catalyst conducted by Viriya-empikul et al. (2012). The authors proved that 800-1000°C was the best calcination temperature for a complete degradation of calcium carbonate.
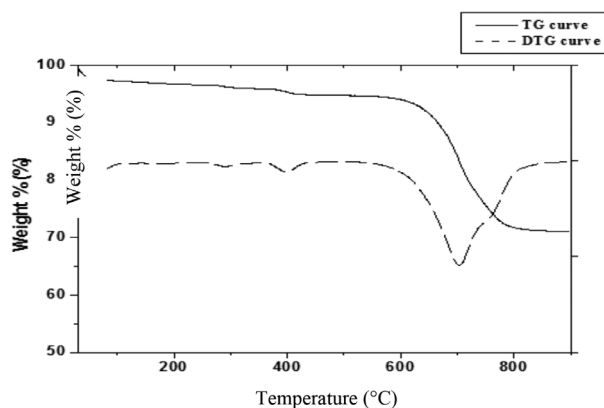

FIGURE 3. TG/DTG curves of uncalcined K-impregnated staghorn coral

X-RAY DIFFRACTION ANALYSIS

The crystallinity of K-CaO catalyst was evaluated using X-ray diffraction analysis. The XRD profile showed that CaO is the major phase whereas K$_2$O is the minor phase (Figure 4). In the case of activated coral catalyst, most of the peaks observed were also CaO peaks but no K$_2$O detected (Supplementary material Figure S3). The sharp and clear peaks observed at 2θ= 32.20°, 37.36°, 53.90°, 64.11° and 67.36° in the K-CaO diffractogram represent CaO. These results are closely similar to the ones presented by Boro et al. (2011) and Sharma et al. (2010). Meanwhile, low intensity peaks of K$_2$O were observed at 2θ= 32.63°, 88.52°, 91.46° and 103.72°. The formation of K$_2$O is probably due to the interaction of KOH with O^{2-} species from CaO (Mutreja et al. 2011). No KOH peak is detected, showing that K$^+$ is highly dispersed in the CaO, which led to the formation of K-CaO surface (Kumar & Ali 2012). As noted by Kabo et al. (2015), the reaction between K and Ca might result in the weakening of Ca^{2+}- O^{2-} bond, which could possibly lead to an effective interaction with methanol, thus escalating its effectiveness as well as the conversion percentage.
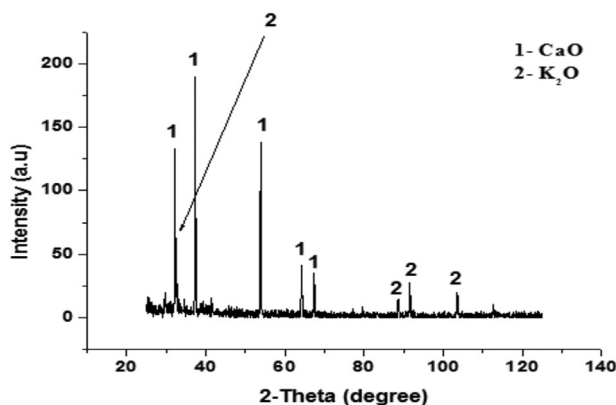

FIGURE 4. XRD pattern of K-CaO catalyst

SCANNING ELECTRON MICROSCOPY ANALYSIS

The surface morphology of the catalyst was observed using SEM at 5000× magnification. From the SEM image, it was observed that CaO comprises of smoother particles with various sizes and shapes (Supplementary material Figure S4). It also shows wave-like surface, which is similar to what Mamat and Yacob (2015) reported for calcined eggshell. As illustrated in Figure 5, the K-CaO catalyst consists of particles with various sizes and shapes. The catalyst also demonstrates an irregular surface that possibly caused by the agglomeration of the particles, which then resulted in the reduction of the catalyst's porosity (Modiba et al. 2015). This is further validated by the XRD analysis in Figure 4.
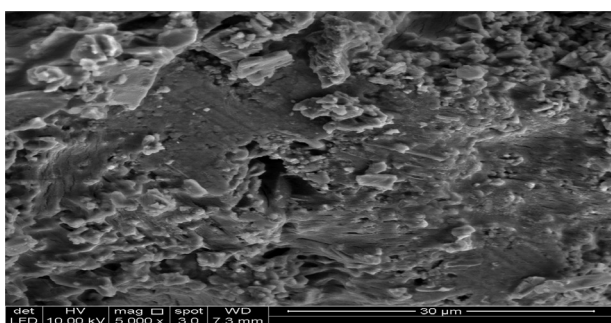

FIGURE 5. SEM image of K-CaO catalyst at magnification of 5000×

OPTIMIZATION OF TRANSESTERIFICATION OVER K-IMPREGNATED STAGHORN CORAL CATALYST

Calcium oxide derived from the staghorn coral has been characterized and applied as a catalyst in biodiesel production. However, the reaction only yielded about $62.07 \pm 4.30\%$ biodiesel under the reaction conditions of 15:1 methanol to oil molar ratio, 4 h of reaction time and 6 wt. % of catalyst loading (Supplementary material Figure S5). Therefore, catalyst modification was carried out by impregnating the staghorn coral with KOH. A series of KOH loading (40% and 50%) were incorporated into the coral, where 78.85 ± 1.59 % of biodiesel yield was recorded after the addition of 40% of KOH. Meanwhile, the reaction with 50% of KOH loading exhibited good catalytic activity with almost 90% of methyl esters conversion.

Methanol to oil molar ratio is one of the crucial parameters in biodiesel production that highly depends on the type of catalyst and the quality of oil (Roschat et al. 2012). According to Centinkaya and Karaosmanoglu (2004), 5:1 methanol/oil ratio was insufficient to give high biodiesel yield. Based on the experimental results, 15:1 has been chosen as the best ratio of methanol to oil in the CaO catalyzed transesterification reaction where CaO exhibited its best catalytic activity with more than 60% FAME content (Supplementary material Figure S5a). Nevertheless, in the case of K-CaO, less than 70% of biodiesel conversion was recorded with the use methanol: oil molar ratio of 15:1

(Figure 6(a)). The increment in the methanol to oil ratio up to 18:1 has resulted in the highest biodiesel conversion yield ($89.51 \pm 4.78\%$). The contribution towards good biodiesel yield is most likely associated with the excellent reaction between methanol and oil when the methanol/oil ratio is increased (Sirisomboonchai et al. 2015). However, when the ratio exceeded the optimum value, the reaction rate dropped significantly since too much methanol could result in the reduction of catalyst concentration and shifting the equilibrium to the reactant side (Sinha & Murugavelh 2016). In addition, the excessive amount of methanol caused the glycerol to dissolve and resulted in difficulty during the separation of biodiesel and glycerol (Moradi & Mohammadi 2014).

The effect of reaction time on the percentage of biodiesel conversion using K-CaO catalyst is shown in Figure 6(b). The biodiesel produced increased as the experimental time was prolonged from 3 to 5 h. This is probably caused by the extended contact time between reactants (Suryaputra et al. 2013). A maximum conversion of $89.51 \pm 4.78\%$ was reported after 5 h of reaction. For CaO catalyst, the reaction reached its optimum value ($62.07 \pm 4.30\%$) after 4 h of reaction time (Supplementary material Figure S5b). The reaction rate dropped drastically when reaction time was increased to 6 h since more by-products and soap were produced due the extended reaction time (Eevera et al. 2009; Freedman et al. 1984; Leung & Guo 2006; Zhang & Meng 2014). Meanwhile, other studies by Birla et al. (2012) and Boro et al. (2011) required 8 h and 6 h of reaction time in order to obtain the complete reaction, which is a much longer than the time needed in this study.

Besides methanol to oil molar ratio and reaction time, catalyst loading is also one of the important aspects in the methyl esters production. Pertaining to the optimization results, the use of 3 wt. % of catalyst loading was not enough to attain a complete transesterification reaction (Figure 6(c)). The catalytic activity increased with the employment of 4 wt. % of catalyst loading, giving the highest methyl esters conversion ($89.51 \pm 4.78\%$). The occurrence of this phenomenon is perhaps due to an increase in the proton concentration at oil and methanol interface, which in turn enhanced the reaction (Wu et al. 2013). Interestingly, this amount is much lower than the amount of catalysts (K-CaO and Li loaded eggshell) used by Boro et al. (2014) and Kumar and Ali (2012). This could be associated with the addition of KOH into CaO that helped to increase the catalytic activity of the prepared catalyst. In the present work, the loading of the catalyst by more than 4 wt. % showed an adverse effect on the methyl esters conversion, which might be due to mass transfer problem and saponification process (Moradi & Mohammadi 2014). Meanwhile, the CaO catalyzed transesterification required higher catalyst loading (6 wt. %) in order to reach its best catalytic activity (Supplementary material Figure S5c).
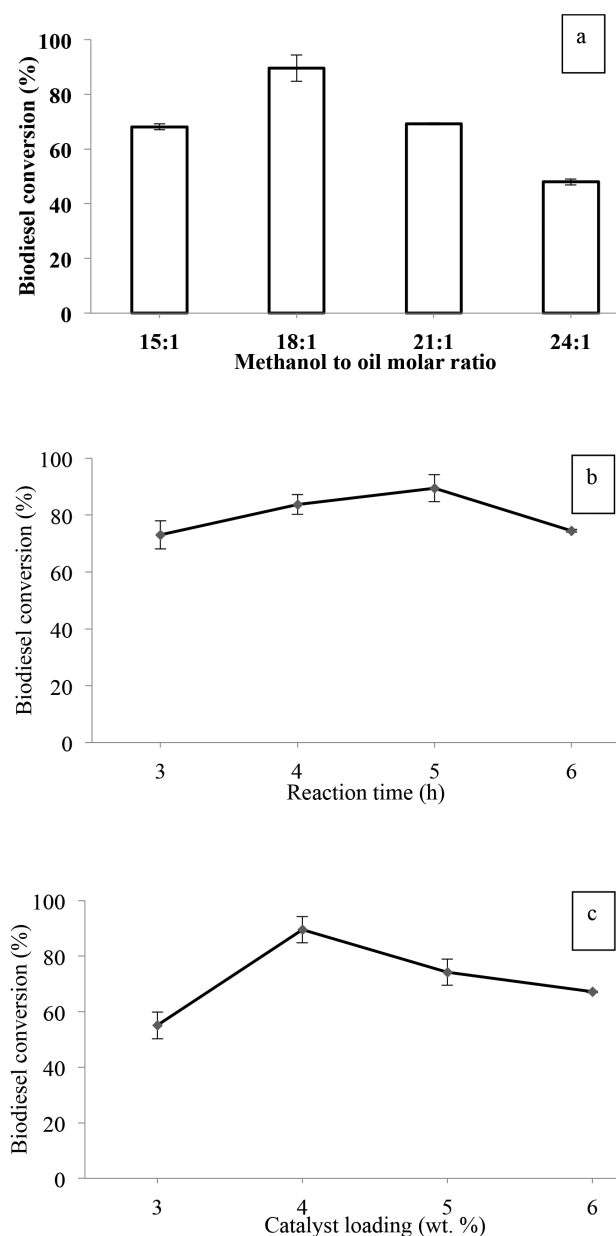
FIGURE 6. Influence of (a) methanol to oil ratio, (b) reaction time and (c) catalyst loading on biodiesel content

CONCLUSION

The present study was devoted to produce and utilize a low cost and environmental friendly catalyst in the conversion of the triglycerides into methyl esters *via* transesterification process. Firstly, the CaO catalyst was prepared by calcining the staghorn coral at 900ºC for 4 h. The catalyst showed a promising result with more than 60% of biodiesel conversion. The staghorn coral was then loaded with KOH *via* wet impregnation technique to enhance its catalytic activity. The introduction of KOH aided in the formation of the K_2O species on the catalyst's surface. The K_2O species has been proven as the main active component that helps in catalyzing the reaction. The overall results showed that a high biodiesel yield ($89.51 \pm 4.78\%$) was achieved under the optimum reaction conditions of 18:1 methanol/oil ratio, 4 wt. % of catalyst loading and 5 h reaction time. Thus, the synthesized catalyst can be considered as a promising catalyst for a large scale biodiesel production.

REFERENCES

Attaphong, C., Do, L. & Sabatini, D. 2012. Vegetable oil-based microemulsions using carboxylate-based extended surfactants and their potential as an alternative renewable biofuel. *Fuel* 94: 606-613.

Bajpai, D. & Tyagi, V.K. 2006. Biodiesel: Source, production, composition, properties and its benefits. *J. Oleo Sci.* 55: 487-502.

Baroutian, S., Aroua, M.K., Raman, A.A.A. & Sulaiman, N.M.N. 2010. Potassium hydroxide catalyst supported on palm shell activated carbon for transesterification of palm oil. *Fuel Process. Technol.* 91: 1378-1385.

Bazargan, A., Kostic, M.D., Stamenkovic, O.S., Veljkovic, V.B. & McKay, G. 2015. A calcium oxide-based catalyst derived from palm kernel shell gasification residues for biodiesel production. *Fuel* 150: 519-525.

Birla, A., Singh, B., Upadhyay, S.N. & Sharma, Y.C. 2012. Kinetics studies of synthesis of biodiesel from waste frying oil using a heterogeneous catalyst derived from snail shell. *Bioresour. Technol.* 106: 95-100.

Boey, P.L., Maniam, G.P., Hamid, S.A. & Ali, D.M.H. 2011. Crab and cockle shells as catalysts for the preparation of methyl esters from low free fatty acid chicken fat. *J. Am. Oil Chem. Soc.* 88: 283-288.

Boro, J., Konwar, L.J. & Deka, D. 2014. Transesterification of non-edible feedstock with lithium incorporated eggshell derived CaO for biodiesel production. *Fuel Process. Technol.* 122: 72-78.

Boro, J., Thakur, A.J. & Deka, D. 2011. Solid oxide derived from waste shells of *Turbonilla striatula* as a renewable catalyst for biodiesel production. *Fuel Process. Technol.* 92: 2061-2067.

Buasri, A., Chaiyut, N., Loryuenyong, V., Rodklum, C., Chaikwan, T., Kumphan, N., Jadee, K., Klinklom, P. & Wittayarounayut, W. 2012. Transesterification of waste frying oil for synthesizing biodiesel by KOH supported on coconut shell activated carbon in packed bed reactor. *ScienceAsia* 38: 283-288.

Canesin, E.A., Oliveira, C.C.D., Matsushita, M., Dias, L.F., Pedrao, M.R. & Souza, N.E.D. 2014. Characterization of residual oils for biodiesel production. *Electron. J. Biotechnol.* 17: 39-45.

Cetinkaya, M. & Karaosmanoglu, F. 2004. Optimization of base-catalyzed transesterification reaction of used cooking oil. *Energy Fuels* 18: 1888-1895.

Degirmenbasi, N., Coskun, S., Boz, N. & Kalyon, D.M. 2015. Biodiesel synthesis from canola oil via heterogeneous catalysis using functionalized CaO nanoparticles. *Fuel* 153: 620-627.

Demirbas, A. 2009. Progress and recent trends in biodiesel fuels. *Energy Convers. Manage.* 50: 14-34.

Eevera, T., Rajendran, K. & Saradha, S. 2009. Biodiesel production process optimization and characterization to assess the suitability of the product for varied environmental conditions. *Renew. Energy* 34: 762-765.

Ekeoma, M.O., Okoye, P.A.C., Ajiwe, V.I.E. & Hameed, B.H. 2017. Murex turnispina shell as catalyst for bio-diesel production. *Int. Res. J. Pure Appl. Chem.* 14: 1-13.

Freedman, B., Pryde, E.H. & Mounts, T.L. 1984. Variables affecting the yields of fatty esters from transesterified vegetable oils. *J. Am. Oil Chem. Soc.* 61: 1638-1643.

Hassan, M.H. & Kalam, M.A. 2013. An overview of biofuel as a renewable energy source: Development and challenges. *Procedia Eng.* 56: 39-53.

Huang, D., Zhou, H. & Lin, L. 2012. Biodiesel: An alternative to conventional fuel. *Energy Procedia* 16: 1874-1885.

Javidialesaadi, A. & Raeissi, S. 2013. Biodiesel production from high free fatty acid-content oils: Experimental investigation of the pretreatment step. *APCBEE Procedia.* 5: 474-478.

Kabo, K.S., Yacob, A.R., Bakar, W.A.W.A., Buang, N.A., Bello, A.M. & Ruskam, A. 2015. BBD optimization of K-ZnO catalyst modification process for heterogeneous transesterification of rice bran oil to biodiesel. *Soft Soil Engineering International Conference 2015* (SEIC2015). Langkawi, Malaysia. 012063.

Kahng, S.E., Garcia-Sais, J.R., Spalding, H.L., Brokovich, E., Wagner, D., Weil, E., Hinderstein, L. & Toonen, R.J. 2010. Community ecology of mesophotic coral reef ecosystems. *Coral Reefs* 29: 255-275.

Kapilan, N., Babu, T.P.A. & Reddy, R.P. 2009. Technical aspects of biodiesel and its oxidation stability. *Int. J. ChemTech Res.* 1: 278-282.

Kataria, J., Mohapatra, S.K. & Kundu, K. 2017. Biodiesel production from frying oil using zinc-doped calcium oxide as heterogeneous catalysts. *Energ. Source Part A* 39: 861-866.

Kaur, M. & Ali, A. 2011. Lithium ion impregnated calcium oxide as nano catalyst for the bio-diesel production from karanja and jatropha oils. *Renew. Energy* 36: 2866-2871.

Kesic, Z., Lukic, I., Zdujic, M., Liu, H. & Skala, D. 2012. Mechanochemically synthesized CaO ZnO catalyst for biodiesel production. *Procedia Eng.* 42: 1169-1178.

Kumar, D. & Ali, A. 2012. Nanocrystalline K-CaO for the transesterification of a variety of feedstocks: Structure, kinetics and catalytic properties. *Biomass Bioenergy* 46: 459-468.

Lam, M.K., Lee, K.T. & Mohamed, A.R. 2010. Homogenous, heterogenous and enzymatic catalysis for transesterification of high free fatty acid oil (waste cooking oil) to biodiesel: A review. *Biotechnol. Adv.* 28: 500-518.

Leung, D.Y.C. & Guo, Y. 2006. Transesterification of neat and used frying oil: Optimization for biodiesel production. *Fuel Process. Technol.* 87: 883-890.

Liu, H., Guo, H.S., Wang, X.J., Jiang, J.Z., Lin, H., Han, S. & Pei, S.P. 2016. Mixed and ground KBr-impregnated calcined snail shell and kaolin as solid base catalysts for biodiesel production. *Renew. Energy* 93: 648-657.

Ma, F. & Hanna, M.A. 1999. Biodiesel production: A review. *Bioresour. Technol.* 70: 1-15.

Mamat, F.M. & Yacob, A.R. 2015. Kinetic study of biodiesel using egg shell for base transesterification reaction: http://eprints.utm.my/id/eprint/62086/1/ZainabRamli2015_ModifiedDesilicatedNatur alZeoliteasCatalystinKnoevenagelReaction.pdf#page=75. Accessed on 15th September 2018.

Meher, L.C., Kulkarni, M.G., Dalai, A.K. & Naik, S.N. 2006. Transesterification of karanja (*Pongamia pinnata*) oil by solid basic catalysts. *Eur. J. Lipid Sci. Technol.* 108: 389-397.

Modiba, E., Enweremadu, C. & Rutto, H. 2015. Production of biodiesel from waste vegetable oil using impregnated diatomite as heterogeneous catalyst. *Chin. J. Chem.* 23: 281-289.

Moradi, G. & Mohammadi, F. 2014. Utilization of waste coral for biodiesel production via transesterification of soybean oil. *Int. J. Environ. Sci. Technol.* 11: 805-812.

Mutreja, V., Singh, S. & Ali, A. 2011. Biodiesel from mutton fat using KOH impregnated MgO as heterogeneous catalysts. *Renew. Energy* 36: 2253-2258.

Onukwuli, D.O., Emembolu, L.N., Ude, C.N., Aliozo, S.O. & Menkiti, M.C. 2017. Optimization of biodiesel production from refined cotton seed oil and its characterization. *Egypt. J. Petrol.* 26: 103-110.

Otadi, M., Shahraki, A., Goharrokhi, M. & Bandarchian, F. 2011. Reduction of free fatty acids of waste oil by acid-catalyzed esterification. *Procedia Eng.* 18: 168-174.

Pandolfi, J.M. & Jackson, J.B.C. 2006. Ecological persistence interrupted in Caribbean coral reefs. *Eco. Lett.* 9: 818-826.

Precht, W.F., Bruckner, A.W., Aronson, R.B. & Bruckner, R.J. 2002. Endangered acroporid corals of the Caribbean. *Coral Reefs* 21: 41-42.

Rajalingam, A., Jani, S.P., Kumar, A.S. & Khan, M.A. 2016. Production methods of biodiesel. *J. Chem. Pharm. Res.* 8: 170-173.

Roschat, W., Kacha, M., Yoosuk, B., Sudyoadsuk, T. & Promarak, V. 2012. Biodiesel production based on heterogeneous process catalyzed by solid waste coral fragment. *Fuel* 98: 194-202.

Ruiz, M.G., Hernandez, J., Banos, L., Montes, J.N. & Garcia, M.E.R. 2009. Characterization of calcium carbonate, calcium oxide, and calcium hydroxide as starting point to the improvement of lime for their use in construction. *J. Mater. Civil Eng.* 21: 694-698.

Saxena, P., Jawale, S. & Joshipura, M.H. 2013. A review on prediction of properties of biodiesel and blends of biodiesel. *Procedia Eng.* 51: 395-402.

Sharma, Y.C., Singh, B. & Korstad, J. 2010. Application of an efficient nonconventional heterogeneous catalyst for biodiesel synthesis from *Pongamia pinnata* oil. *Energy Fuels* 24: 3223-3231.

Shereena, K.M. & Thangaraj, T. 2009. Biodiesel: An alternative fuel produced from vegetable oils by transesterification. *Electron. J. Bio.* 5: 67-74.

Sinha, D. & Murugavelh, S. 2016. Biodiesel production from waste cotton seed oil using low cost catalyst: Engine performance and emission characteristics. *Perspect. Sci.* 8: 237-240.

Sirisomboonchai, S., Abuduwayiti, M., Guan, G., Samart, C., Abliz, S., Hao, X., Kusakabe, K. & Abudula, A. 2015. Biodiesel production from waste cooking oil using calcined scallop shell as catalyst. *Energy Convers. Manage.* 95: 242-247.

Suryaputra, W., Winata, I., Indraswati, N. & Ismadji, S. 2013. Waste capiz (*Amusium cristatum*) shell as a new heterogeneous catalyst for biodiesel production. *Renew. Energy* 50: 795-799.

Tan, Y.H., Abdullah, M.O., Nolasco-Hipolito, C. & Taufiq-Yap, Y.H. 2015. Waste ostrich- and chicken-egg shells as heterogeneous base catalyst for biodiesel production from used cooking oil: Catalyst characterization and biodiesel yield performance. *Appl. Energy* 160: 58-70.

Viriya-Empikul, N., Krasae, P., Nualpaeng, W., Yoosuk, B. & Faungnawakij, K. 2012. Biodiesel production over Ca-based solid catalysts derived from industrial wastes. *Fuel* 92: 239-244.

Watkins, R.S., Lee, A.F. & Wilson, K. 2004. Li-CaO catalysed tri-glyceride transesterification for biodiesel applications. *Green Chem.* 6: 335-340.

Wu, H., Zhang, J., Wei, Q., Zheng, J. & Zhang, J. 2013. Transesterification of soybean oil to biodiesel using zeolite supported CaO as strong base catalysts. *Fuel Process. Technol.* 109: 13-18.

Xie, W. & Huang, X. 2006. Synthesis of biodiesel from soybean oil using heterogeneous KF/ZnO catalyst. *Catal. Lett.* 107: 53-59.

Xie, W. & Li, H. 2006. Alumina-supported potassium iodide as a heterogeneous catalyst for biodiesel production from soybean oil. *J. Mol. Catal. A Chem.* 255: 1-9.

Yacob, A.R., Muda, N.W. & Zaki, M.A.M. 2017. Effect of one step activation KOH modified carbon in dimethyl carbonate transesterification reactions. *Malaysian J. Anal. Sci.* 21: 820-829.

Zhang, J. & Meng, Q. 2014. Preparation of KOH/CaO/C supported biodiesel catalyst and application process. *World J. Eng. Technol.* 2: 184-191.

Zielinski, J.M. & Kettle, L. 2013. *Physical Characterization: Surface Area and Porosity*. London: Intertek. p.1-5.

Nabilah Atiqah Zul, Shangeetha Ganesan &
Mohd Hazwan Hussin*
School of Chemical Sciences
Universiti Sains Malaysia
11800 Minden, Pulau Pinang
Malaysia

Nabilah Atiqah Zul & Mohd Hazwan Hussin*
Materials Technology Research Group (MaTReC)
School of Chemical Sciences
Universiti Sains Malaysia
11800 Minden, Pulau Pinang
Malaysia

*Corresponding author; email: mhh@usm.my