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Utilization of waste fat from catfish (*Pangasius*) in methyl esters preparation using CaO derived from waste marine barnacle and bivalve clam as solid catalysts

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ABSTRACT

The use of waste oils/fats, as well as catalyst from waste materials, for producing methyl esters (biodiesel) via transesterification has been research of recent interest. In the present work, the transesterification of waste catfish fat using barnacle and bivalve clam as a heterogeneous catalyst was attempted. X-ray diffraction and FTIR results show that, upon thermal activation, both shells transformed into CaO, the active ingredient that catalyzes the reaction. In addition, the results showed that the methyl esters (ME) content of reaction catalyzed by barnacle and bivalve clam were at 97.6 ± 0.03 and $92.0 \pm 0.05\%$, respectively in 3 h reaction duration at 65 °C. Optimization of reaction parameters revealed that MeOH:oi at 12:1 (molar) and catalyst at 4 wt.% as an optimal reaction conditions for both catalysts. Furthermore, the catalysts can be reused for four cycles while maintaining ME content above 90%.

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1. Introduction

The growing awareness concerning the environmental issues on energy supply and usage has recently been the topic of interest. Among the various alternative energy discovered, biodiesel is one of the promising blended fuel to substitute petroleum derived diesel which is environmentally friendly and sustainable. Commonly, biodiesel is produced from neat vegetable oil such as soybean, palm, rapeseed, and sunflower. The European Union (EU) uses rapeseed oil as a major biodiesel lipid feedstock for biodiesel production; the United State (US) utilizes oil from soybean for this purpose. Currently, the cost of biodiesel is higher than that of petrodiesel; as such the use of biodiesel in voluntary basis is not encouraging. Thus, there are few regions worldwide legislated the use of biodiesel.

On the other hand, the trend also indicates the need for large amounts of vegetable oil supply and if the major portion of the oil comes from neat edible oil then the question of food starvation arises. The concern in respect of food starvation or food for fuel already

constitutes a heated argument. With the increasing need for oil in the near future, it will definitely complicate the situation. Globally there are 925 million people undernourished; reported by the Food and Agriculture Organization of the United Nations in 2011 [1]. Hence, the exploitation of raw materials from waste source has been of recent interest. Researchers have effectively utilized waste frying oil, oil adsorbed onto clay, coconut waste and fat from solid waste as a source of feedstock biodiesel [2–5].

One of the most popular freshwater fish for human consumption in the world is catfish (*Pangasius*) [6]. Especially, in Malaysia *Pangasius sutchi* (commonly known in local as *ikan patin*) is a popular freshwater fish for consumption. The fish from pangasiidae family have shark headed features and the length of this fish is around 1.2 m [7]. Furthermore, in Malaysia, the retail value of catfish alone in 2011 was estimated at over USD 41 million [8]. As a result, the generation waste fat is abundant and at present it is discarded as waste. This scenario means that catfish fat is a potential feedstock or co-source for the preparation of methyl ester (biodiesel).

Transesterification is usually carried out under the homogeneous catalyst (sodium or potassium hydroxide). In this situation the usage of heterogeneous catalyst offers a better solution. Therefore, a new process using heterogeneous catalyst has been developed for environment-friendly, cost-effective process and present fewer

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Table 1
Quality parameters of oil.

Parameter	Catfish oil
Acid value (mg KOH/g)	3.85 ± 0.05
Density (kg/m ³)	913 ± 1.6
Water content (wt.%)	0.22 ± 0.02
Viscosity (mm ² /s)	65.5 ± 1.4

disposal problems [9,10]. Many types of heterogeneous catalysts, such as CaO from mud crab shells and cockle shells [11], mix-metal oxide [12], and metal supported in matrix (MSM) [13,14] have been studied in the literature. In present work, barnacle (B) and bivalve clam (BC) (calcined at 900 °C) have been used as heterogeneous catalysts. Barnacle with abundant and diverse populations, with about 1445 living species, their abundance can create serious and expensive fouling problems on ship bottoms, buoys and pilings [15]. On the other hand, BC is the second most important bivalve in Malaysia in term of total production. Estimated potential annual production is 20,000 metric tonnes [16]. The major compound of B and BC is CaCO₃, therefore they could be potential sources of CaO. To the best of our knowledge, no one has reported the use of B and BC in preparation of ME using waste catfish fat.

2. Experimental

2.1. Materials

The raw material used in this work is waste catfish fat which was collected from eateries in Gambang, Pahang, Malaysia. The barnacle shell was obtained from Tanjung Lumpur beach, Pahang and bivalve clam was obtained from the local market in Kuantan, Pahang, Malaysia. The chemicals purchased from Sigma–Aldrich company (Switzerland) include phenolphthalein (H_c = 8.2), 2,4-dinitroaniline (H_c = 15.0) and 4-nitroaniline (H_c = 18.4), methyl heptadecanoate as an internal standard GC grades (>99.1%). Methanol (anhydrous, ≥99.8%) and hexane (anhydrous, ≥99.8%) were purchased from Hamburg (Germany).

2.2. Preparation shells as catalysts and oil from catfish

The B and BC shells were cleaned using water to remove dirt and fibrous matters. Then the shells were dried in an oven at 105 °C, overnight (labeled as B-dried and BC-dried). The shells were then ground in a mortar and pestle to obtain the gross powder and further ground fine with a dry-mill blender and sieved through 75 μm mesh before being subjected to heat treatment in furnace at 900 °C. The catfish fat was cleaned with warm water to remove any visible non-fat solid matter, air-dried at room temperature, and slow-melted in an oven from room temperature to 80 °C, followed by filtration to obtain the oil. The oil was then transferred to an amber glass bottle and kept in a refrigerator. The oil content was calculated using the following formula:

$$\text{oil content (\%)} = \frac{M_1}{M_0} \times 100$$

where M_1 and M_0 are the masses of the oil and fat in g, respectively. The acid value and acidity of the oil were determined following EN 14104 standard. The determination was repeated three times. The moisture content in oil was analyzed using the Karl Fischer titration method (784 KFT Titrino, Metrohm).

2.3. Characterization of catalysts

The CaO was identified by X-ray diffraction (Rigaku) with Cu Kα as a source. FTIR (Perkin Elmer Spectrum 100) spectrophotometer

Table 2
Fatty acid profile of catfish fat.

Fatty acid	Composition (%)	
	Present work	Hemung et al. [17]
Saturated		
Lauric (C _{12:0})	11.5	1.05
Myristic (C _{14:0})	11.7	2.36
Pentadecanoic (C _{15:0})	1.9	0.18
Palmitic (C _{16:0})	28.1	23.59
Heptadecanoic (C _{17:0})	–	0.35
Stearic (C _{18:0})	–	6.70
Arachidic (C _{20:0})	–	0.16
Henicosanoic	–	0.45
Subtotal	53.2	34.89
Unsaturated		
Myristoleic (C _{14:1 n-5})	2.0	–
Palmitoleic (C _{16:1 n-7})	–	2.14
Oleic (C _{18:1 n-9})	26.8	37.84
Vaccenic (C _{18:1 n-7})	4.2	–
Eicosenoic (C _{20:1 n-9})	2.7	0.79
Erucic (C _{22:1 n-9})	–	0.1
Subtotal	35.7	40.87
Poly-unsaturated		
Linoleic (C _{18:2 n-6})	6.7	15.91
alpha-Linolenic (C _{18:3 n-3})	3.1	1.13
gamma-Linolenic (C _{18:3 n-6})	–	0.21
Eicosadienoic (C _{20:2 n-6})	0.8	0.83
Dihomo-gamma-linolenic (C _{20:3 n-3})	0.5	0.20
Arachidonic (C _{20:4 n-6})	–	0.50
Eicosapentaenoic (C _{20:5 n-3})	–	0.20
Adrenic (C _{22:4 n-6})	–	0.50
Docosapentaenoic (C _{22:5 n-3})	–	0.20
Docosahexaenoic (C _{22:6 n-3})	–	0.43
Subtotal	11.1	19.41
Other	–	4.88
Total	100.0	100.00

was used to characterize the chemical structure of catalyst at 400–4000 cm⁻¹ range. The morphology of catalyst was observed by FE-SEM fitted with electron dispersive X-ray (EDX) (JSM-7800F). The catalyst was examined using thermogravimetric analysis (TGA) using the Mettler Toledo TGA/DTA 851e instrument from 25 to 900 °C with 10 °C/min heating rate. Base strength of the catalyst (H_c) was determined using Hammett indicators. The following Hammett indicators were used: phenolphthalein (H_c = 8.2), 2,4-dinitroaniline (H_c = 15.0) and 4-nitroaniline (H_c = 18.4). About 25 mg of catalyst was shaken with 1 cm³ of a Hammett indicator solution diluted with methanol, and left to equilibrate for 2 h. After the equilibrium, the color change of the solution was observed.

2.4. Transesterification

The conversion of used catfish oil to biodiesel was performed in a 50 ml 2-neck round bottom flask equipped with a reflux condenser and magnetic stirrer. The transesterification reaction between oil and methanol was carried out in the liquid phase under atmospheric pressure, at 65 °C with continuous stirring. The effect of the molar ratio of methanol to oil (6:1–15:1 wt.%), catalyst/oil weight ratio (2–7 wt.%), and reaction time (2–8 h) on the conversion of triglycerides to biodiesel were investigated. After the transesterification, the reaction mixture was allowed to cool. Biodiesel was isolated by centrifuging at 4000 rpm for 5 min, to further separate the layers (methyl ester, glycerol and catalyst, and then excess amount of methanol). Excess methanol was evaporated before the chromatographic analysis. The concentration of methyl ester (ME) in the sample was quantified using GC-FID (Agilent 7890A) by following the European procedure EN 14214 with polar capillary column (DB-Wax, 30 m × 0.25 mm i.d. × 0.25 μm) using methyl heptadecanoate as an internal standard. Peaks of ME were identified by comparing them with their methyl

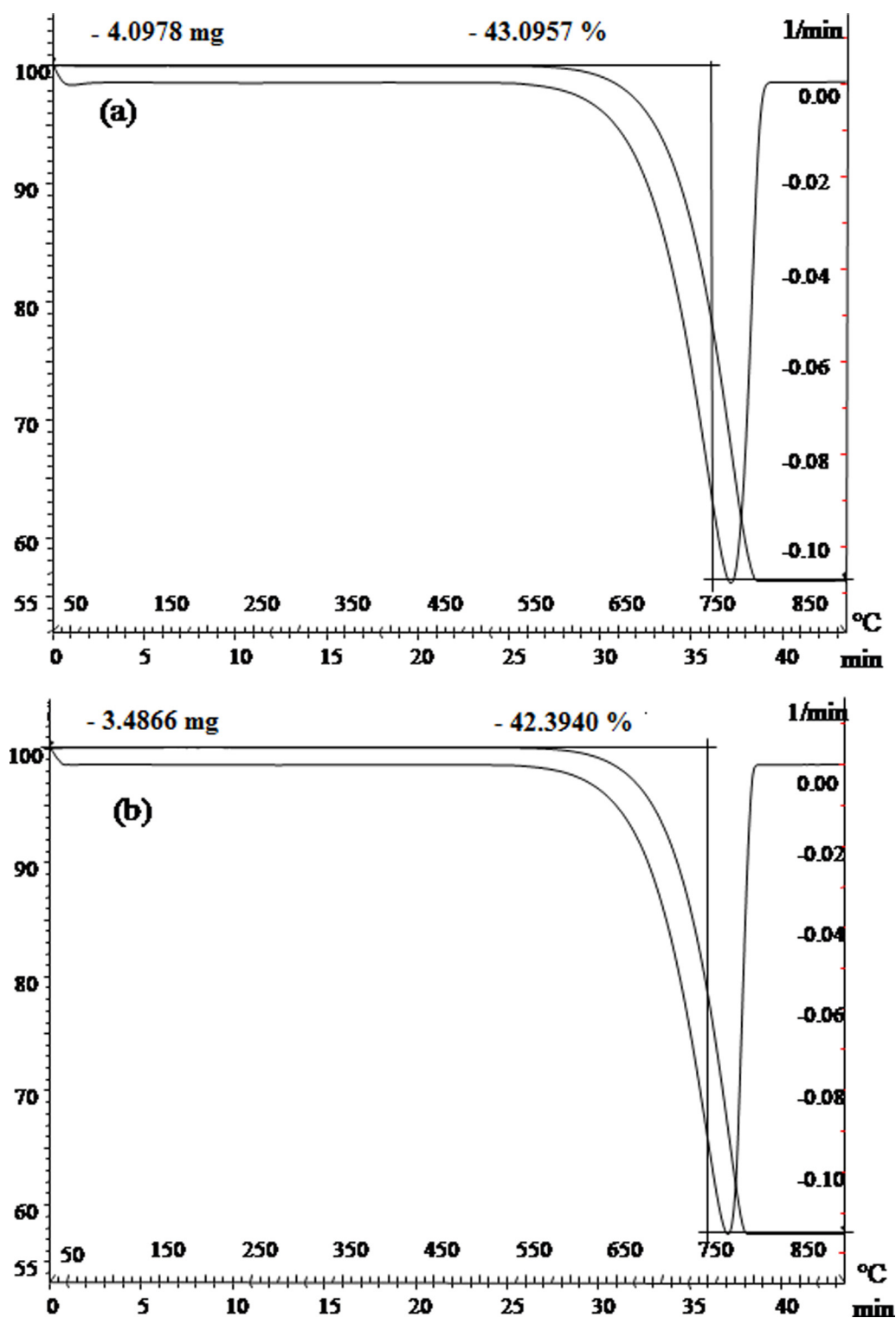


Fig. 1. DTA/TGA profile of catalyst (a) bivalve clam-900, (b) barnacle-900.

heptadecanoate standards and the content was quantified as following formula:

$$\text{content (\%)} = \frac{(\Sigma A) - A_{\text{ISTD}}}{A_{\text{ISTD}}} \times \frac{C_{\text{ISTD}} \times V_{\text{ISTD}}}{m} \times 100$$

where ΣA = total peak area of FAME from $C_{12:0}$ to $C_{18:1}$, A_{ISTD} = peak area of methyl heptadecanoate, C_{ISTD} = concentration, in mg/mL, of

the methyl heptadecanoate solution, V_{ISTD} = volume, in mL, of the methyl heptadecanoate solution, m = mass, in mg, of the sample

In order to examine the potential reutilization of the catalyst, the used catalyst was tested to assess its catalytic activity. For reuse experiments, the used solid catalyst was recovered by decanting it after a simple washing using methanol and n-hexane. The dried used catalyst was calcined at 900 °C for 2 h. The quality of the ME was tested for viscosity, acid number, free fatty acid (FFA) and density,

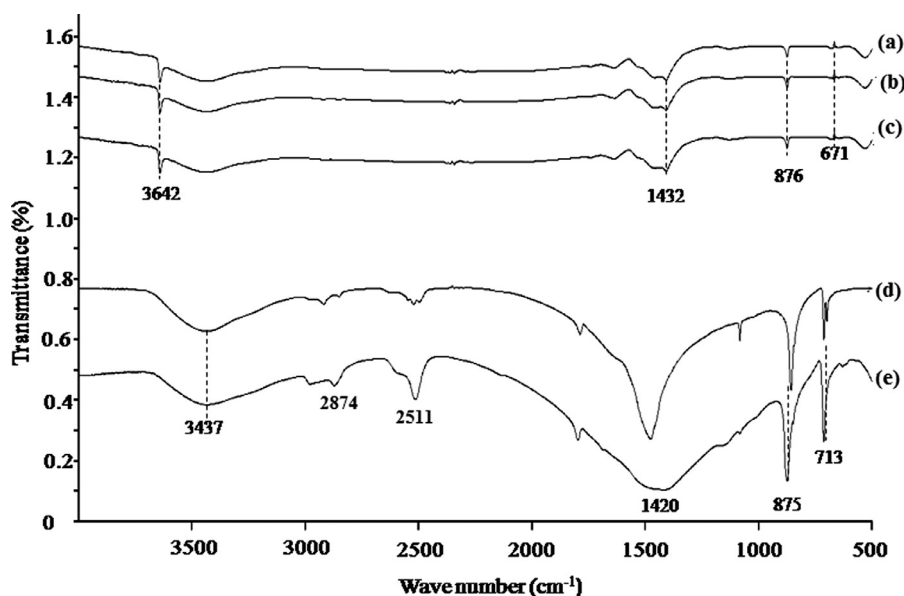


Fig. 2. FTIR spectra of calcined and dried catalysts (a) Lab-CaO, (b) barnacle-900, (c) bivalve clam-900, (d) barnacle-dried, (e) bivalve clam-dried.

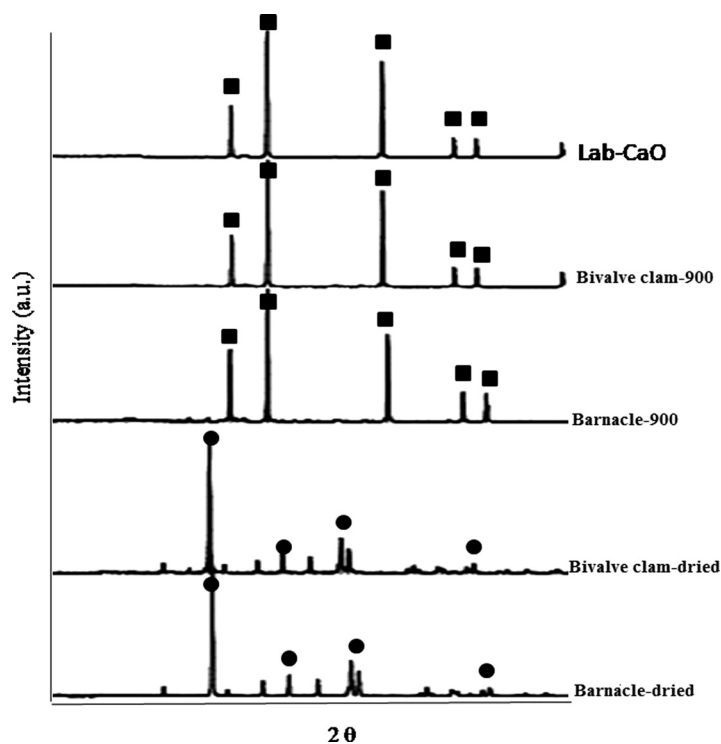


Fig. 3. Powder X-ray diffraction (XRD) patterns of the shells catalysts compared with Lab-CaO, (●: CaCO₃; ■: CaO).

water content, iodine value and flash point following the EN 14214 method.

3. Results and discussion

3.1. Catfish fat and catalyst characterization

The acid value of the catfish oil was found to be 3.85 mg KOH/g (equivalent to 1.75% FFA as palmitic acid), 0.22% of moisture content with 913 density (kg/m^3) and 65.5 viscosity (mm^2/s) (as in Table 1). As tabulated in Table 2, palmitic acid was the predominant fatty acid (28.1%) while 53.2% of the fatty acid being of the saturated type, 35.7% of the content accounted for unsaturated fatty acids and

the remaining 11.1% of the fatty acid being polyunsaturated. Interestingly lauric acid composition in the sample is (Table 2) higher than the previous report by Hemung et al. [17]. The difference can be attributed to the fact that different intake of food and cultured location nature. But, according to Islam et al. the lauric acid for *Pangasius pangasius* is 13.36% and *P. sutchi* is 4.26% [18]. The fat content in this sample was 5.6 ± 0.11 g/100 g and the oil recovered from waste catfish fat was 69 ± 0.78 wt.% (on wet weight basis). This data was similar with Muhamad and Mohamad (6.23 g/100 g) [7].

The basic strength of the catalyst was estimated using Hammett indicators. The basic strength of B and BC-CaO is in the range: $15 < H_L < 18.4$. Therefore, the catalyst could change the color from colorless to pink (phenolphthalein) and from yellow to mauve

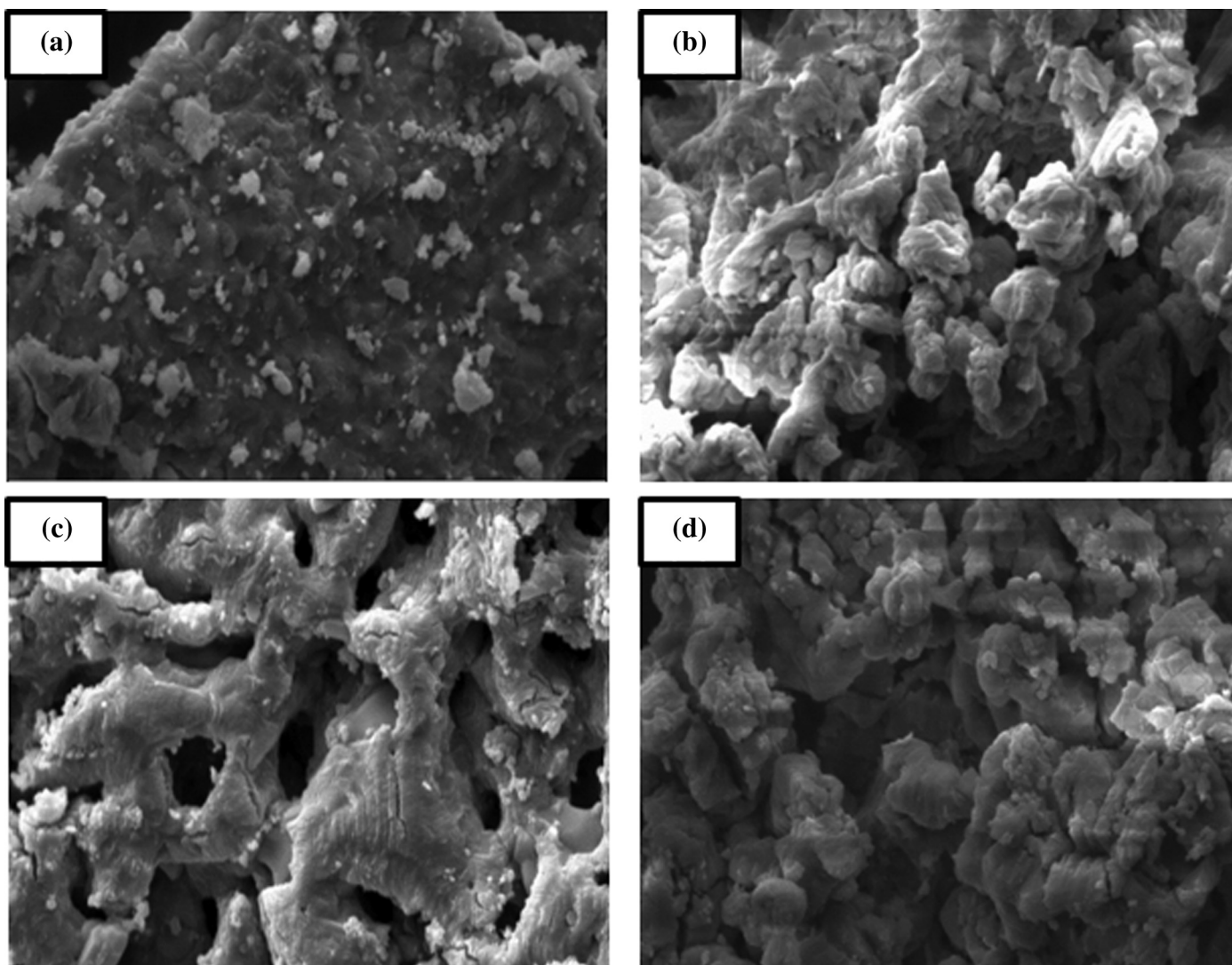


Fig. 4. Surface morphology at magnification 5.00 kx of (a) bivalve clam-dried, (b) bivalve clam -900 °C, (c) barnacle-dried, and (d) barnacle-900 °C.

(2,4-dinitroaniline) but failed to change color of 4-nitroaniline. The DTA/TGA results shows major decomposition at 575–800 °C for B and BC was 42% and 43%, respectively (Fig. 1). The decomposition may be attributed to the evolution of CO_2 and the weight loss is matched with the stoichiometrical weight loss of CO_2 to form CaO from CaCO_3 . The FTIR spectra of dried and calcined 900 °C of barnacle and bivalve clam shells were compared with Lab-CaO as shown in Fig. 2. In the case of barnacle-dried and bivalve clam-dried they have major characteristic absorption peaks at 713, 875, and broad band at 1420 cm^{-1} which can be attributed to the present of asymmetric stretch, out-of-plane bend and in-plane bend vibration modes for CO_3^{2-} molecules. Afterwards, with the calcination at 900 °C, there is a decrease of band at 1432 cm^{-1} . This is due to the oxidation of the functional group attached to carbonate ion on calcination. The bands at 2511 and 2874 cm^{-1} correspond to the harmonic vibration of C–O bonds. A sharp peak at 3642 cm^{-1} in 900 °C shells attributed the presence of OH^- which indicates the presence of $\text{Ca}(\text{OH})_2$ which must have formed from exposure of CaO to atmospheric air. The CaO chemical patterns were presented, for comparison with waste shells calcined. The XRD profiles of the activated barnacle and bivalve clam are shown in Fig. 3. The composition of barnacle- and bivalve clam-dried consists of CaCO_3 . However, with calcination up to 900 °C, CaCO_3 has completely transformed into CaO by evolving the CO_2 . The XRD

profiles of the activated shells also closely match the profile of the Lab-CaO. In addition, the EDX results also reveal that the activated shells mainly consist of CaO. As shown in Fig. 4, SEM micrographs of the calcined (900 °C) bivalve clam (b) and barnacle (d) shells were in the form of regular-shaped particles, great amount of the small particles cohesive in the structures and similar to each other thus increasing the surface area of the catalyst. In contrast, uncalcined shells bivalve clam-dried (a) and barnacle-dried (c) exhibiting bulky substance without a define shape.

3.2. Effect of catalyst amount

The effect of catalyst amount on conversion of ME was investigated by varying the catalyst amount (2, 3, 5, 7 wt.%) with optimal conditions at 65 °C, 12:1 MeOH/oil molar ratio for 4 h. As shown in Fig. 5a, the content increased as the catalyst amount increased from 2 to 3 wt.%. This pattern occurred to both of the catalysts. A high ME content with B and BC shells of 97.3 and 96.8%, respectively, was obtained at 5 wt.% of catalyst, further increase in catalyst decreases the ME content. It is probably due to soap formation at higher catalyst loading or mass transfer limitation induces by the large amount of catalyst [19,20].

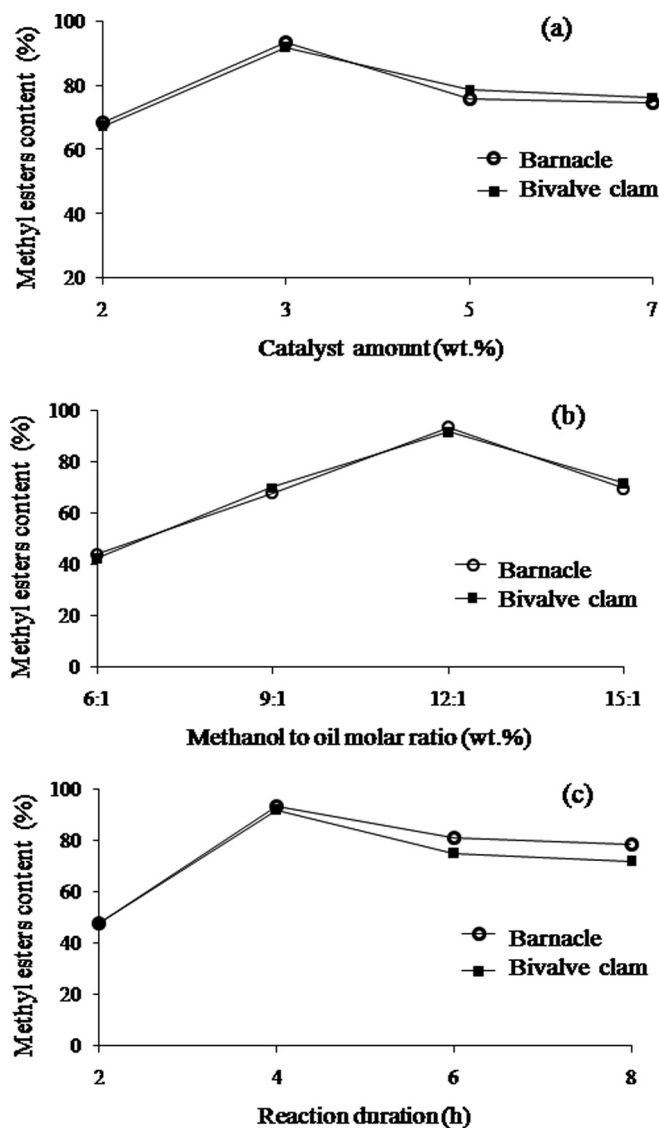


Fig. 5. Effect of (a) catalyst amount; (b) methanol/oil molar ratio and (c) reaction duration on the ME content for 2 h.

3.3. Effect of methanol to oil molar ratio

The effect of MeOH/oil molar ratio was observed at four different ratios (6:1, 9:1, 12:1 and 15:1) as presented in Fig. 5b. MeOH/oil molar ratio is one of the important factors that affect the ME content. The maximum ME content under both B and BC was achieved at 12:1 MeOH/oil molar ratio. ME content increases as the ratio was increased from 6:1 to 9:1. However, drop is observed in ME content under B and BC at higher MeOH/oil molar ratio (15:1) at 78 and 72%, respectively. At higher MeOH/oil molar ratio, it complicates the separation of ME and glycerol as well as the removal of excess MeOH. However, it is important to note that the large amount of methanol could dilute the oil, thus lowering the reaction rate and as a result, lower ME content was recorded at higher of methanol content [21].

3.4. Effect of reaction duration

The effect of the reaction duration (2–8 h) on the transesterification of catfish oil over barnacle (B) and bivalve clam (BC) is shown in Fig. 5c. All the shells seem to have the similar ability to be a catalyst at any specific reaction duration. It is observed that with the increase

in reaction time, the ME content increases progressively. From Fig. 5c, it can be seen that at catalyst amount of 3 wt.%, the ME content increases steadily within the first 2 h and reached as high as 47% for both B and BC. Further increase in the reaction duration the ME content increased and remained almost constant as a result of near equilibrium at 97.2 and 96.9% for B and BC, respectively. Interestingly, for longer reaction duration (more than 5 h) the ME content decreases, due to the reverse reaction of transesterification, resulting in a loss of esters as well as causing more fatty acid to form soap. Thus, from the influence of reaction duration on transesterification it is clear that, 3 wt.% catalyst, 12:1 methanol/oil molar ratio, 4 h reaction time and temperature of 65 °C are the required conditions to produce a high MEs content of 97.2 ± 0.04 and $96.6 \pm 0.03\%$ for B and BC, respectively.

3.5. Reusability and leachability of catalyst

The cost of catalyst largely influences the production cost. As such the reusability study of the catalyst is very important from the economical point of view. In order to test the reusability of the catalyst, the repeated batch experiments using the transesterification reactions under optimized conditions were applied (reaction temperature of 65 °C, methanol to oil molar ratio of 12:1, catalyst content of 5 wt.% and reaction time of 4 h). The catalyst was reused with calcination. Methanol was used to remove the glycerol whereas *n*-hexane was used to cleanse the residual oil and ME, then dried at 120 °C for 2 h, then calcined at 900 °C for 2 h. The results provided in Fig. 6a show that the catalyst can be used more than once by retaining the catalytic activity until several cycles. ME content between 97.3 and 96.8% could be obtained even after the fourth cycle. In addition, it also shows that the activity of regenerated catalyst possesses a good reproducibility.

In order to assess the leachability of the catalysts, those catalysts were stirred with methanol for 4 h (without feedstock). Then the reacted catalyst and the treated methanol were separated. The methanol-reacted solid catalysts were subjected to transesterification under the optimal conditions. Similarly, the treated methanol was also subjected to transesterification but without any catalyst. As seen in Fig. 6b, under methanol-reacted solid catalyst, a considerable ME content were achieved (95 and 94%), whereas under the treated methanol (without any catalyst), a very low ME content (2 and 2.1%) was observed for B and BC. The observation proves that there is no leaching of the CaO shells into methanol during reaction. Calcium oxide possesses relatively high basic strength and less environmental impacts due to its low solubility in methanol.

3.6. ¹³C NMR and infrared spectrum of methyl esters

The ¹³C NMR spectrum of methyl esters from catfish fat was shown in Fig. 7a. The signal at δ 174 ppm presents the carbonyl carbon of ester molecules of methyl esters and the olefinic appears at δ 127, 129 and 130 ppm. The methyl signal of the product methyl esters registered at around 51 ppm, and the glyceridic carbons of the mono-, di-, and triacylglycerols registered at 62–71 ppm. The methylene and methyl carbon of fatty acid moiety appear in the range 13–33 ppm. From the NMR data it could be verified that oils conversion into biodiesel was quite complete.

IR technique has been used as a fast and accurate method to monitor the transesterification reaction process because of the chief advantages of accuracy, reliability, operational ease, rapidity of measurement, and nondestructive nature. The FTIR spectra of catfish fat is shown in Fig. 7b. The peak goes from 1700 cm^{-1} to 1800 cm^{-1} , where biodiesel presents a prominent peak, the strong ester peaks at 1746 cm^{-1} which corresponds to the carbonyl group absorption (C=O stretching band of ester) and at 1171, 1194 and 1246 cm^{-1}

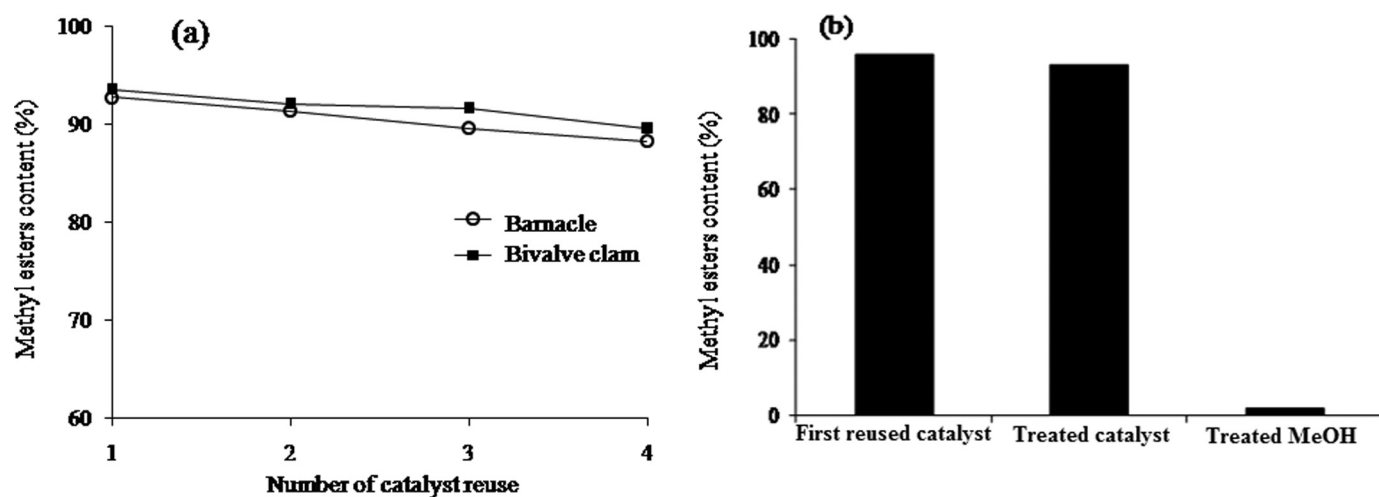


Fig. 6. (a) Methyl esters content using dried catalyst for four reuses; (b) catalyst leachability towards ME content (reaction conditions: catalyst amount 5%; methanol to oil molar ratio 12:1 at 65 °C).

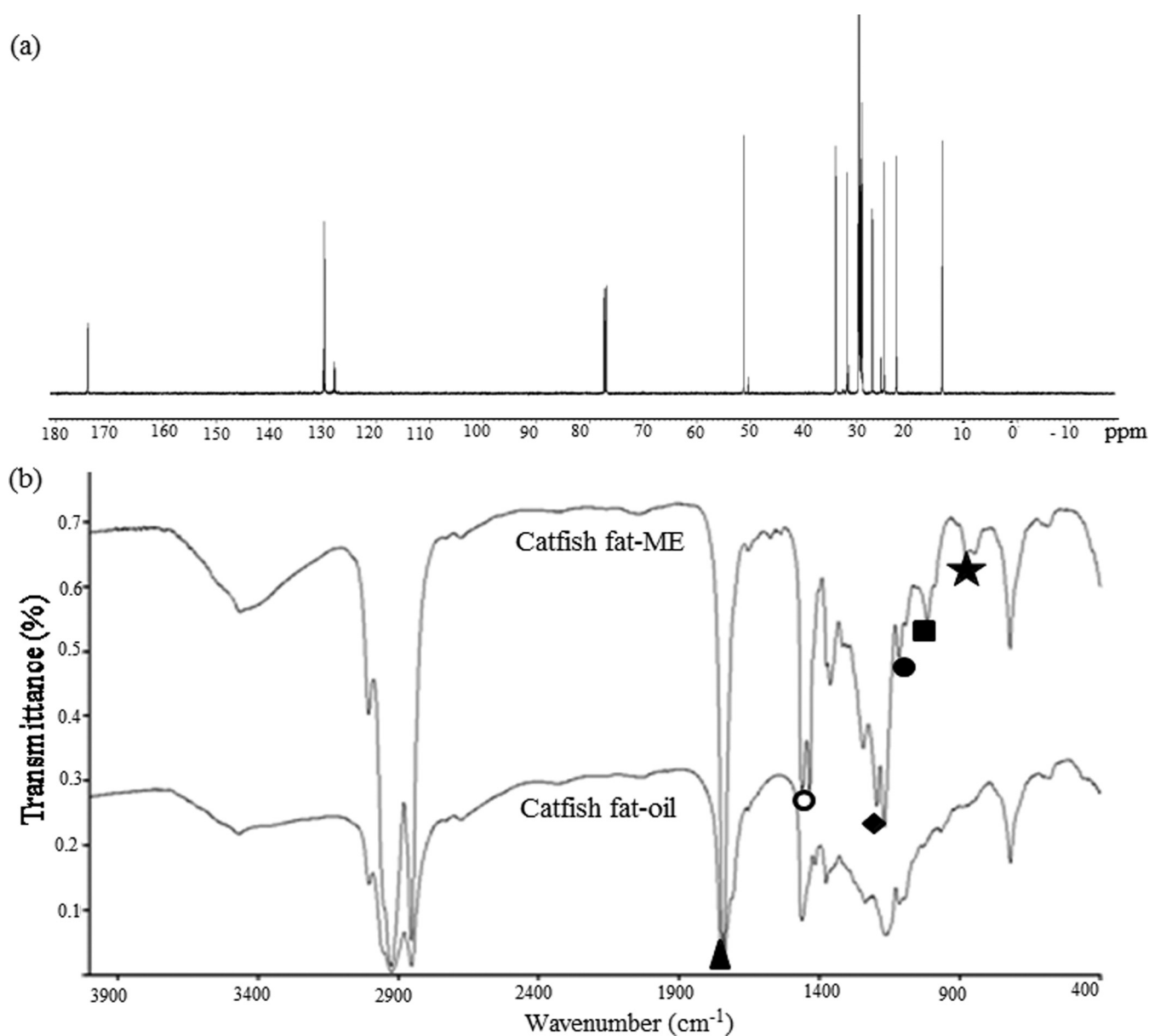


Fig. 7. (a) ¹³C NMR spectrum of catfish methyl esters (b) infrared spectra of catfish-fat-oil and catfish-fat-methyl ester (▲: C=O, ○: CH₃, ◆: O-CH₃, ●: C-O stretching, ◼: C-O, ★: C-H).

Table 3
Properties of biodiesel from waste cooking oil.

Parameters	Unit	Catalysts		Biodiesel specification EN 14214
		Barnacle (B)	Baby clam (BC)	
Ester content	wt.%	96.6 ± 0.03	98.2 ± 0.04	96.5 (min)
Density	kg/m ³	887	873	860–900
Viscosity	mm ² /s	3.4	3.2	3.5–5.0
Water content	mg/kg	300	200	500 (max)
Flash point	°C	174	168	101 (min)
Iodine value	g I ₂ /100 g	105	102	120 (max)
Acid value	mg/g KOH	0.3	0.3	0.5 (max)
High heating value	MJ/kg	37.47	37.25	35 (min)
Cloud point	°C	10	10	–
Monoglyceride	%(m/m)	0.57	0.56	0.80
Diglyceride	%(m/m)	0.20	0.18	0.20
Triglyceride	%(m/m)	0.20	0.18	0.20
Free glyceride	%(m/m)	0.008	0.006	0.02
Total glyceride	%(m/m)	0.24	0.22	0.25

(C–O stretching band of ester). This trend is in agreement with a previous report in which the researcher found that the O–CH₃ peak at 1200 cm⁻¹ increases when the percentage of methyl esters increases. The C–CH₂–O vibration at 1100 cm⁻¹ is reduced in the methyl esters but is present in triacylglycerol (TAG) [22]. Furthermore, for catfish fat-ME (Fig. 7b), C–H deformation for alkyl group is clearly present at 1036 cm⁻¹. Outside these three regions, another characteristic peak that indicates the presence of CH₃ group in the mixtures of methyl esters can be observed at 1437 cm⁻¹. Strong and sharp signals at 2858 and 2927 cm⁻¹ are due to C–H stretching. The absorbance at 3000 cm⁻¹ indicates the =C–H stretching and absorption peak at 721 cm⁻¹ suggested the CH₂ rocking. Sideways from this band, the FTIR spectra were in very good agreement with previous reports [22,23].

3.7. Methyl esters properties

In order to assess the quality of the final product, it was evaluated according to European biodiesel standard (EN) 14214 (Table 3). It was found that the final product meets all the tested parameters (ester content, density, viscosity, water content, flash point, iodine value, acid value, high heating value and cloud point) in accordance with EN 14214, for B and BC. The ester content catalyzed by B and BC (at 5 wt.%) recorded the highest value of 97.2 and 96.9%, respectively. Although many other parameters need to be analyzed in order to confirm the final product as a fuel, these nine parameters can serve as preliminary indicators for the purpose as a fuel.

4. Conclusion

Activated waste shell barnacle (B) and bivalve clam (BC) have been successfully utilized as heterogeneous catalysts in the transesterification reaction of catfish fat. It was found that the different sources of CaO perform equally in the reaction. The outcome confirmed that the optimum reaction conditions of transesterification; catalyst amount of 5%; methanol to oil molar ratio of 12:1; reaction temperature at 65 °C for 4 h, with a constant stirring were able to transesterify catfish fat oil to biodiesel with the ME content 97.2 ± 0.04 and 96.9 ± 0.03% for B and BC, respectively. The catalyst was easily separated and could be reused four cycles while maintaining 96% conversion. Utilization of B and BC as catalysts and catfish fat as a feedstock makes the process of preparing biodiesel as a sustainable one. At present, the utilization of waste materials is the interest of many researchers, especially in the field of biodiesel, and the trend needs to be given priority in order to make the process more sustainable in nature. In near future, it is expected that more and more explorations of waste materials will be in place as to optimize the usage of virgin materials on the earth.

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References

- [1] Food and Agriculture Organization of the United Nations. Hunger statistic www.fao.org/hunger/en/ [accessed January 2013].
- [2] Al-Hamamre Z, Yamin J. Parametric study of the alkali catalyzed transesterification of waste frying oil for Biodiesel production. *Energy Convers Manage* 2014;79:246–54.
- [3] Boey P-L, Ganesan S, Maniam GP, Ali DMH. Ultrasound aided *in situ* transesterification of crude palm oil adsorbed on spent bleaching clay. *Energy Convers Manage* 2011;52:2081–4.
- [4] Sbihi HM, Nehdi IA, Tan CP, Al-Resayes SI. Production and characterization of biodiesel from *Camelus dromedarius* (Hachi) fat. *Energy Convers Manage* 2014;78:50–7.
- [5] Sulaiman S, Aziz RAR, Aroua MK. Reactive extraction of solid coconut waste to produce biodiesel. *J Taiwan Inst Chem Eng* 2013;44:233–8.
- [6] Abbas KA, Sapuan SM, Mokhtar AS. Shelf life assessment of Malaysian *Pangasius sutchi* during cold storage. *Sadhana* 2006;31:635–43.
- [7] Muhamad NA, Mohamad J. Fatty acids composition of selected Malaysian fishes. *Sains Malaysiana* 2012;41:81–94.
- [8] Food and Agriculture Organization of the United Nations. Fisheries and Aquaculture Department. Malaysia http://www.fao.org/fishery/culturedspecies/Pangasius_hypophthalmus/en [accessed May 2014].
- [9] Mahdavi V, Monajemi A. Optimization of operational conditions for biodiesel production from cottonseed oil on CaO–MgO/Al₂O₃ solid base catalysts. *J Taiwan Inst Eng* 2014;45:2286–92.
- [10] Shahbazi MR, Khoshandama B, Nasiri M, Ghazvini M. Biodiesel production via alkali-catalyzed transesterification of Malaysian RBD palm oil – characterization, kinetics model. *J Taiwan Inst Eng* 2012;43:504–10.
- [11] Boey P-L, Maniam GP, Hamid SA, Ali DMH. Crab and cockle shells as catalyst for the preparation of methyl esters from low free fatty acid chicken fat. *J Am Oil Chem Soc* 2011;88:283–8.
- [12] Xie W, Yang Z, Chun H. Catalytic properties of lithium-doped ZnO catalysts used for biodiesel preparations. *Ind Eng Chem Res* 2007;46:7942–9.
- [13] Xie W, Li H. Alumina-supported potassium iodide as a heterogeneous catalyst for biodiesel production from soybean oil. *J Mol Catal A: Chem* 2006;255:1–9.
- [14] Xie W, Wang H, Li H. Silica-supported tin oxides as heterogeneous acid catalysts for transesterification of soybean oil with methanol. *Ind Eng Chem Res* 2012;51:225–31.
- [15] Newman WA, Abbott DP. Cirripedia: The Barnacles, Chapter 20, pp. 504–505. <http://decapoda.nhm.org/pdfs/31753/31753.pdf> [accessed August 2013].
- [16] Sin OK, Mahmood R. Status and problems of mollusc production, sanitation and marketing in Malaysia. Fisheries and Aquaculture Department <http://www.fao.org/docrep/field/003/ab710e/AB710E17.htm> [accessed January 2014].
- [17] Hemung B-O, Visetsunthorn A, Pariwat S. Chemical properties and fatty acid profile of lipids extracted from freshwater fish species. Nutrition quality and health benefit of indigenous food, Food innovation Asia conference 2010: indigenous food research and development to global market, June 17–18, 2010, BITEC, Bangkok, Thailand, p. 668–695.

- [18] Islam R, Paul DK, Rahman A, Parvin T. Comparative characterization of lipids and nutrient contents of *Pangasius pangasius* and *Pangasius sutchi* available in Bangladesh. *J Nutr Food Sci* 2012;2:1–6.
- [19] Gao L, Xu B, Xiao G, Lv J. Transesterification of palm oil with methanol to biodiesel over a KF/Hydrotalcite solid catalyst. *Energy Fuel* 2008;22:3531–5.
- [20] Xie W, Zhao L. Production of biodiesel by transesterification of soybean oil using calcium supported tin oxides as heterogeneous catalysts. *Energy Convers Manage* 2013;76:55–62.
- [21] Veljković VB, Avramović JM, Stamenković OS. Biodiesel production by ultrasound-assisted transesterification: state of the art and the perspectives. *Renew Sustain Energy Rev* 2012;16:1193–209.
- [22] Zhang W-B. Review on analysis of biodiesel with infrared spectroscopy. *Renew Sustain Energy Rev* 2012;16:6048–58.
- [23] Santiago-Torres N, Romero-Ibarra IC, Pfeiffer H. Sodium zirconate (Na_2ZrO_3) as a catalyst in a soybean oil transesterification reaction for biodiesel production. *Fuel Process Technol* 2014;120:34–9.