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ARTICLE

Biodiesel production from catfish *(Pangasius)* fat via ultrasound- assisted method

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ABSTRACT

This paper reports studies in ultrasound-assisted heterogeneous solid catalyzed (CaO) synthesis of biodiesel from catfish *(Pangasius)* fat. Ultrasonication provides a faster chemical reaction, and the rate enhancements, refereed by cavitation that causes the building- up of pressures and temperatures, as well as increased catalytic surface areas and improve mass transfer. This novel method offers significant advantages such as shorter reaction time and less energy consumption than the conventional method, efficient molar ratio of methanol to triglycerides and provides the mechanical energy for mixing. The required activation energy for initiating the transesterification reaction and so, it gives a higher yield by transesterification of oils into biodiesel. The optimized reaction conditions were as follows: methanol to oil molar ratio of 15:1; catalyst (B-CaO), 9 wt. %; reaction temperature, 65 ± 2 °C; reaction time, 1 h at a working frequency of 42 kHz and the power supply of 100W. Highest conversion of 96.4 wt. % was achieved.

1. Introduction

Biodiesel has become an important part of the world for production of fuels. Biodiesel is a biofuel that substitute for diesel, it becomes forefront for this ideology due to its advantages for environments, and the worlds not only face to the environment crisis but also face to devaluation of fossil fuels sources. This statement is supported by the statistics of biodiesel production in European Union is 22 million tons per year and 3.7 million tons per year in United States in 2011(Nurfitri et al., 2013). Malaysia is in the developing progress of using biodiesel. Malaysia has started its initiations by introducing National. Biofuel Policy in 2006 and implementing biodiesel B5 in 2011. The utilization of waste/used edible oils and animal fat as raw materials is a significant idea, and there are many advantages for using waste feedstock for biodiesel production such as abundant supply, available in low price, and environmental benefits. Yahyaee et al. (2013) suggested that introducing biodiesel from the fish oil can perfectly replace about 5% of total diesel fuel consumption in the first step in transportation sector. There is no doubt for the need of more extensive research work to study the other economic issues related to biodiesel production from waste fish oil.

The catalyst that is synthesized with the waste shells gives opportunity for renewable catalyst and at the same time recycles the waste created (Boro et al., 2012). The barnacle

could be a potential source of CaO since they consist of >90% of $CaCO_3$ and increasing the heating treatment will be transforming them into CaO. Several methods are used to produce biodiesel. Among them are dilution, direct use and blending, transesterification, pyrolysis, and micro emulsion. Among these major routes, transesterification is considered as the best for reducing engine complications and viscosity. Common conditions to carry out transesterification are batch process, ultrasonic methods, microwave methods and supercritical processes (Xie and Zhao, 2014). Biodiesel can be produced by the ultrasound method and conventional method. The use of ultrasound in transesterification reaction was also found to enhance the yield of methyl esters produced. Stavarche et al. (2005) concluded that low frequency ultrasound is an efficient, time saving and economically functional method that offers a lot of advantages over the classical procedure. The induced asymmetric cavitational bubbles collapse at the oil/alcohol boundary and enhance mass transfer between the phases thus accelerating the reaction.

The transesterification of triglycerides by ultrasonic irradiation provides a possibility for producing cheap alternative fuels, which could reduce pollution and protect the environment. Ultrasound is a sound wave with a frequency higher than the upper audible limit of the human audibility range. Ultrasound frequencies range from ~20 kHz to l0 MHz, with supplementary acoustic wavelengths in liquids of roughly 100-0.15 mm. The application of ultrasound towards chemical reactions and processes is called as sonochemistry. Ultrasound is very effective in solution as medium. The application of ultrasound, therefore, will contribute to a more homogeneous reaction mixture and facilitate dispersion of lipase through substrate media, reducing agglomeration so that the reaction rate does not decrease with the enhancement of lipase concentration (Liu et al., 2008). Nobel of converted Macauba oil into alcoholic esters using a commercial lipase as catalyst using ultrasound-assisted system had been proven while aiming the promising use of cost effective, non-edible oil, with very adequate field output, towards biodiesel production with an eco-friendly, green skill (Michelin et al., 2015). Hindryawati and Maniam (2015) also proved that Na-silica waste sponge as a source of low cost catalyst in the transesterification of waste cooking oil aided by ultrasound technique as an environmentally friendly and efficient transesterification. The aim of this research is to investigate the potential of barnacle shell as heterogeneous catalyst in transesterification of catfish fat for producing biodiesel using ultrasonic methods.

Nomenclature and Abbreviation

TGA	Thermogravimetric analysis
GC-MS	Gas chromatography - mass spectrometry
FTIR	Fourier-transform infrared spectroscopy
FESEM	Field emission scanning electron microscopy
FFA	Free fatty acid
DTA	Differential thermal analysis
XPD	X-ray powder diffraction

2. Materials and methods

2.1 Materials

The waste catfish fat collected from an eatery in Gambang, Malaysia. Waste marine shells (barnacle) were collected at Pantai Gelora beach Pahang, Malaysia. Malaysia and The chemicals purchased from Sigma–Aldrich company (Switzerland) include phenolphthalein (H_ = 8.2), 2, 4-dinitroaniline (H_ = 15.0) and 4-nitroaniline (H_ = 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 Experimental

The barnacle was cleaned using water to remove dirt and fibrous matters. Then the shell was dried in an oven at 105°C, overnight (labeled as B-dried). The shell 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 75µmmesh before being subjected to heat treatment in furnace at 900 °C. As for the catfish fat, the fat was cleaned to remove any visible proteins and other fibrous matters. Then it was left to dry at room temperature before the dried fat was transferred to an oven and was heated slowly in a petri dish from room temperature to a maximum temperature of 90 °C. The resultant oil (after constant weight) was then filtered through a filter paper before being stored in an amber bottle in the refrigerator. The oil content was calculated using the following formula:

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

Where M1 and M0 are the masses of the oil and fat in g, respectively. The acid value and acidity of the oil were determined following EN14104 standard. The determination was repeated three times.

2.3 Characterization of Catalyst

The CaO was identified by X-ray diffraction (Rigaku) with Cu Kα as a source. FTIR (Perkin Elmer Spectrum 100) spectrophotometer was used to characterize the chemical structure of catalyst at 400– 4000 cm−1 range. The morphology of catalyst was observed by FESEM (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.

2.4 Experimental set up

The ultrasonic reaction was performed using Branson (USA) ultrasonic bath (42 kHz) with the power dissipation 100 W. The bath was filled with distilled water up to 1/ 3 of its volume. The temperature was controlled and maintained at desired level (±0.1 °C) by water circulating from a thermostated bath by means of a pump. A constituent of 10 ml oil with desired amount of catalyst and methanol was immersed in an ultrasound water bath. The effect of catalyst amount (1–12 wt.%), reaction duration (1–5 h) and methanol to oil ratio (6:1-8:1) on the conversion of triglycerides to biodiesel were investigated, with the temperature 65 ± 2 °C. Then, to further separate the product (ME and glycerol) and the catalyst centrifugation at 4000 rpm for 5 min was performed. The excess methanol was evaporated before the chromatographic analysis. The reaction was carried out three times in order to reflect the precision and errors of the results.

3. Results and discussion

3.1 Oil and Catalyst Characterization

The fat content in catfish is 5.6 ± 0.11 g/100 g which is similar with the found value of 6.23 g/100 g (Islam et al., 2012) and also comparable with Muhamad and Mohamad. (2012) where, 6.23g/100g and the oil recovered from waste catfish oil is 69 ± 0.78 wt.% (on a wet weight basis). The acid value of the catfish oil is found to be at 3.85 ± 0.05 mgKOH/g (equivalent to 1.75% FFA as oleic acid). The density value of catfish oil is 913 ± 1.60 kg/m-3 @ 25 °C. Meanwhile, the viscosity value for catfish oil is at 65.5 ± 1.4 cP @ 40 °C. For the moisture content, the value of catfish oil is 0.22 ± 0.02%.

The evidence shows that the FFA lies in the range of below zero to above 2.0%. With below 0.5% FFA, the oil is regarded as high quality oil, whereas any value between 0.5-2.0% and above 2.0% are the moderate and low quality oil, respectively. Accordingly, with the FFA of 1.75%, catfish oil can be classified as of moderate quality Low water content is also preferred (<0.5 wt. %) as the presence of water promotes the formation of FFA. As shown in Table 1, catfish oil contains 0.22 wt. % of water content which regulates a lower FFA. The common density range fats are between (600-1000 kg/m3) and the catfish oils falls in the range with the value of 913 kg/m3. Similarly, the viscosity is in the acceptance range (<80 cP) whereas the value (65.5 cP) falls in agreement with the literature value.

The composition for catfish oil was determining using gas chromatography- mass spectrometry (GC-MS). As tabulated in Table 1, palmitic acid was foremost with a previous report (Hemung et al., 2010). With about 53.2% of the fatty acid being of the saturated type, the remaining 35.7% of the content is accounted for unsaturated fatty acids and the rest 11.1% is for poly-unsaturated fatty acids.

The effect of the temperature drying is shown in Figure 3. The result indicated that drying at high temperature decreases the moisture content (dry basis).

Table 1. Composition of Fatty Acid in Catfish Oil

Fatty acid	**Composition (%) Present work**
Saturated	
Lauric ($C_{12:0}$)	11.5
Myristic ($C_{14:0}$)	11.7
Pentadecanoic ($C_{15:0}$)	1.9
Palmitic ($C_{16:0}$)	28.1
Subtotal	*53.2*
Unsaturated	
Myristoleic ($C_{14:1\ n\text{-}5}$)	2.0
Oleic ($C_{18:1\ n\text{-}9}$)	26.8
Vacceneic ($C_{18:1\ n\text{-}7}$)	4.2
Eicosenoic ($C_{20:1\ n\text{-}9}$)	2.7
Subtotal	*35.7*
Poly-unsaturated	
Linoleic ($C_{18:2\ n\text{-}6}$)	6.7
alpha-linolenic ($C_{18:3\ n\text{-}3}$)	3.0
Stearidonic ($C_{18:4\ n\text{-}3}$)	0.8
Eicosadienoic ($C_{20:2\ n\text{-}6}$)	0.5
Subtotal	*11*
Total	100

The uncalcined and calcined barnacle shell as catalysts was characterized by XRD (Rigaku) using Cu Kα diffractometer. The XRD pattern of Lab CaO (commercial) B-CaO at 900 °C, 700 °C, 500 °C and uncalcined catalysts are shown in Figure. 1. The patterns show, that when the calcination temperature is below 700 °C including the uncalcined catalyst, $CaCO_3$ does exist. However, with the increase in activation temperature, $CaCO_3$ completely

transforms to CaO evolving CO_2. The transformation of $CaCO_3$ to CaO occurs at 700 °C and above. Narrow and high intense peaks of the calcined catalyst define the well-crystallized structure of the catalyst. The above finding is consistent with the study by Maniam et al. (2009) and Lim et al. (2015).

The FTIR spectra of uncalcined and calcined (500, 700 and 900 °C) barnacle are compared with Lab-CaO (commercial) and shown in Figure. 2. The weak band at 3642 cm^{-1} is normally attributed to OH groups of $Ca(OH)_2$. Also, the H-O-H bending mode of lattice water appears at 1600 cm^{-1}, and this band exists in all FTIR spectra. The stretching bands at 3150, 3034 and 2880 cm−1 are attributed to the O-H groups from H2O molecules (Lin et al., 1995). Different views for uncalcined barnacle while they have major characteristic absorption peaks at 713, 875, and broad band at 1420 cm-1 is the presence of asymmetric stretch, out of plane bend and in plane bend vibration modes for CO_3^{2-} molecules. Subsequently, with the increasing calcination at 900 °C, the decreasing band at 1432 cm^{-1} is detected due to the reduced functional group attached to carbonate ions on calcination. The bands at 2511 and 2874 cm-1 correspond to the harmonic vibration of C-O bonds. The Lab-CaO chemical patterns are presented, for comparison with calcined barnacle. Legodi et al. (2001) also reported carbonate bands are present at 1802, 2511 and 2874 cm-1.

The TGA/DTA result shows a major decomposition at 560-770 °C for barnacle is 42% (Figure. 3). The decomposition may be attributed to the evolvement of CO_2 and the weight loss is matched with the stoichiometrically weight loss of CO_2 to form CaO from $CaCO_3$ (Eq. 1). Upon heating calcium carbonate, it undergoes a reaction where bound CO_2 is released from the material and only calcium oxide remains after the experiment. Thermal analysis of mixed oxide in Figure 3 shows two main decomposition steps.

$$CaCO_3(s) \rightleftarrows CaO(s) + CO_2(g)$$
$$(MW=100.09) \quad (MW=56.08) \quad (MW=44.01)$$
$$\Delta H298=178 \text{ kJ/mol (Endothermic)} \ldots\ldots\ldots\ldots\ldots\ldots \text{(Eq.1)}$$

FESEM micrographs of the Uncalcined and B-CaO (900 °C, 2 h). The uncalcined barnacles demonstrate bulk morphologies without a defined shape. In contrast, calcined B-CaO form regular-shaped particles, with the small particles cohesive in the structures. Thus, increasing the surface area of the catalyst with visible pores of defined shape and size. This result is consistent with previous work on different types of shells (Empikul et al., 2010) and shows similar morphology with the calcined bivalve clam shell (Maniam et al., 2015).

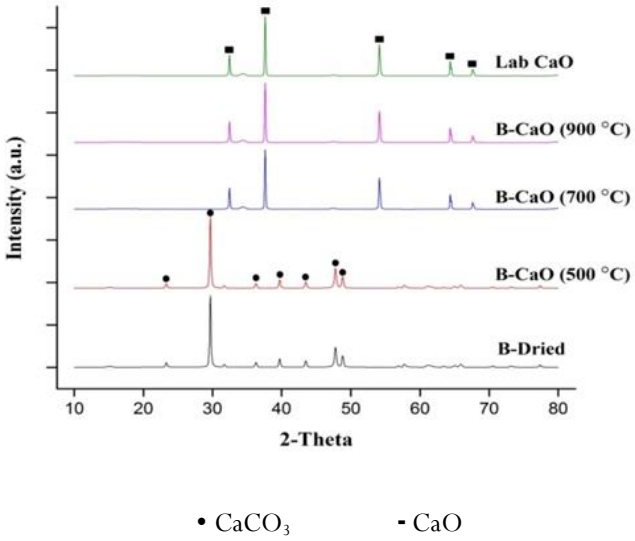

Figure 1. XRD Diffractograms of Barnacle Shell at Different Temperature

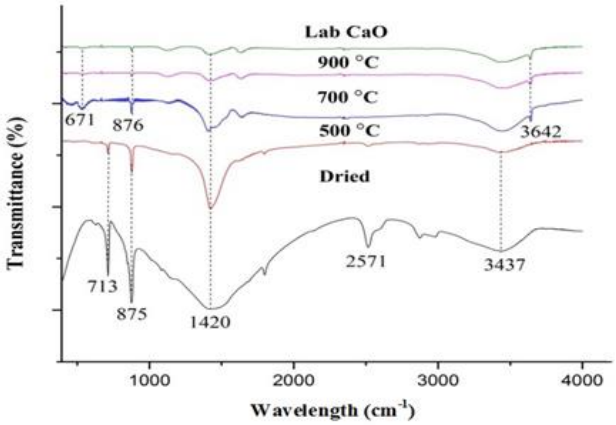

Figure 2 FTIR Spectra for Barnacle Shell at Different Temperatures

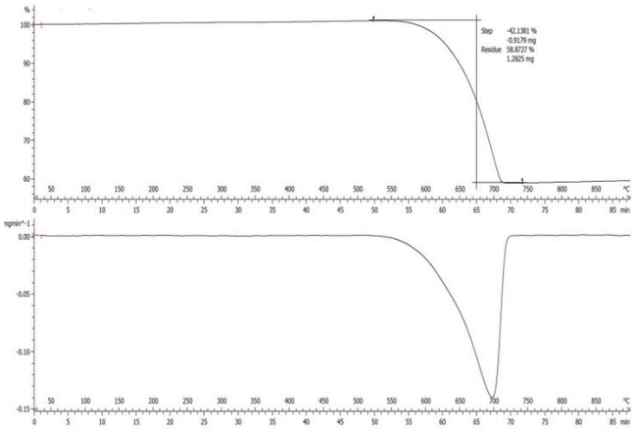

Figure 3. TGA/DTA Thermography for Uncalcined Barnacle Shell

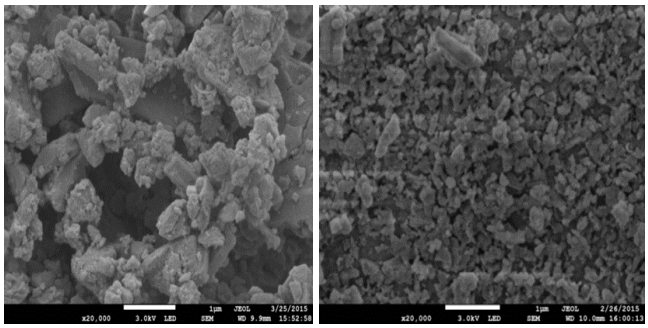

Figure 4. FESEM images for (A) Uncalcined (B) B-CaO

3.2 Effect of optimization conditions

The molar ratio of methanol to oil is one of the important variables which affect transesterification reaction. As observed, five different molar ratios of MeOH: oil was tested; 6:1, 9:1, 12:1, 15:1 and 18:1. The ME content is increased as the MeOH: oil was raised from 2:1 to 6:1. Too much methanol could dilute the oil and as a result slows the reaction rate, which in turn, lowers conversions. In additional, a higher molar ratio of alcohol to oil increases the solubility of glycerol, and as a consequence, the separation of glycerol becomes more difficult and retards the forward reaction by promoting the backward equilibrium. Ultrasound radiation causes methanol to disperse into the oil, thus increasing the contact surface between reactants, consequently accelerating the reaction. The effect of cavitation created by ultrasound supplies sufficient energy into the immiscible medium and the continuous formations and collapsing of micro bubbles accelerate the miscibility of reactants in addition to chemical and mechanical effects.

The amount of catalyst was varied in the range of 1-12 wt. %. Transesterification was dependent on the amount of catalyst used. Increasing the catalyst from 1-6 wt. % increases methyl ester from 70-88 wt. %. The ME content reaches the highest value at the catalyst amount of 9 wt. %; due to the contact opportunity between catalyst and the reactants hence propels the reaction kinetics. Based on the oil weight, the amount of catalyst used in this work seems to be higher due to several reasons; part of the catalyst could be entrapped in the clay matrix; this portion of the catalyst may not have contributed to catalytic activity. The ultrasound used in this work can affect the catalyst reactivity, positively, by enhancing the mass transfer between clay-catalyst-reactants as well as promising the presence of kinetic energy in the reaction media. Dispersion due to ultrasound increases the surface area available to the reactants. As such, the use of ultrasound promotes the efficiency of acyl conversion in a shorter time.

The effect of the reaction duration (0.5-2.5h) on the transesterification of catfish oil over barnacle shell. It is observed that with the increase in reaction time, the ME content increases progressively. It can be seen that at catalyst amount of 9 wt.%, the ME content increases steadily within the first 1 h and reached as high as 97 wt.%. Interestingly, for longer reaction duration (more than 1 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.

4. Conclusion

In this work, catfish fat and barnacle shell as catalyst was successfully utilized as a low-cost feedstock to produce ME (biodiesel) via ultrasound aided transesterification. The highest ME content of 96.4 wt. % at 65 °C. Optimization of reaction parameters revealed that MeOH to oil molar ratio, 15:1; catalyst, 9 wt. % and reaction duration 1 h as the optimal reaction conditions. The use of ultrasound undeniably assisted in achieving this significant result. Materials derived from waste sources, as used in this work, should be given a priority for a sustainable biodiesel production.

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