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Economical Biodiesel Fuel Synthesis from Castor Oil using Mussel Shell-Base Catalyst (MS-BC)

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Abstract

This paper presents economical biodiesel fuel synthesis from castor oil using mussel shell-base catalyst (MS-BC). A transesterification of castor oil as non-edible feedstock to biodiesel was conducted in a flask reactor. Two catalysts were examined, where the calcined mussel shell and the impregnated calcium oxide with the potassium hydroxide were run by batch system. The catalysts and formed biodiesel were characterized and analyzed by Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD), Brunauer-Emmett-Teller (BET), Thermal Gravimetric Analysis (TGA), X-Ray Fluorescence (XRF) and Gas Chromatography (GC). The highest biodiesel yield (91.17%) was found by the catalyst loading of 2 wt/wt%, time of 3 h, temperature of 60°C and methanol oil ratio of 6:1. The impregnated catalyst provides magnificent results compared non-impregnated performance, and the reusable catalyst can be considered for beneficial biodiesel fuel synthesis.

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1. Introduction

Development of bioenergy, like biodiesel as alternative fuel, eco-friendly, biodegradable properties has been becoming interesting issues. The biodiesel can be produced from edible, non-edible oils, etc. as a replacement of diesel fossil fuel. Numerous vegetable oil such as canola oil, soybean oil, castor oil etc. can be used as biodiesel sources. The castor oil as non-edible sources has high potential to be used as raw material. The physico-chemical characteristic of castor oil, especially its elevated viscosity and polarity, are due to the presence of a high level of ricinoleic acid; such properties render the oil extremely

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valuable for the industrial production of coatings, plastics and cosmetics [1]. The castor oil contains 80-90% of hydroxyl fatty acid (a double bond and a hydroxyl group), increases the lubricity as compared to normal vegetable oils and becomes a prime candidate as additive for diesel fuel [2]. Since the content of higher unsaturated fatty acid, it can be realized in the transesterification process for biodiesel synthesis. By converting of vegetable oil into fatty acid methyl ester allows the fuel to be used in virtually all existing diesel engines [3]. Another side, the cheaper feedstock like waste oils, animal fats cannot be converted to biodiesel using conventional base mediated process, as the free fatty acid (FFA) of oils causes saponification problems. Acids can esterify FFA but the slow rates and limitation of using high cost metallurgy makes it less accepted. Heterogeneous catalysts having both acidic and basic sites have been being exploring which could esterify FFA and at the same time transesterify triglycerides to biodiesel. A biodiesel production process by homogeneous/heterogeneous catalyst has also been being testing. First the acid catalyst, both strong acid type USY, BEA and weak acid catalyst of type MCM-41 were prepared by hydrothermal synthesis procedure. Transesterification reactions were carried out at 100°C to 180°C, molar ratio of oil to methanol at 1:20, and using 5 wt. % of the catalyst. At the end of the reaction, the catalyst was separated by centrifugation, washed with water and dried overnight at 120°C. It was found that strong acid catalysts like USY, BEA were not good triglyceride conversion. Beside that, when the recovered catalyst was recycled, a sharp decrease in biodiesel yield was observed [4].

The formulation of heterogeneous catalyst as alternative catalyst such as metallic or metal oxide has wide potential to be utilized where these catalysts can be recycled easily, and does not produce soap through free fatty acid neutralization and triglyceride saponification. Beside that, its much cheaper than enzyme or other offered biochemical catalysts. Currently, the transesterification process of biodiesel using solid base heterogeneous catalyst such as calcium oxide that derived from mollusk shells has been being investigating continuously [5], [6]. The important reason is a new solid base heterogeneous should be developed due to their ability for yield improvement at lower temperature, shorter time and easy in separation process [7]. Next, the shell wastes of mussel were commonly deserted from the restaurants, food and canneries industry in Malaysia without any distinguished employment for precious products. Otherwise, the use of metal catalysts for biodiesel synthesis from edible sources like palm oil, soybean, etc. which are consumed as food creates versus fuel dilemma and expensive, thus this work aims to solve this issues by using the mussel shell-base catalyst (MS-BC) for biodiesel fuel synthesis. Biodiesel synthesis using calcium oxides base catalyst has some advantages such as higher activity, mild reaction condition and low cost [8].

2. Methodology

2.1. Materials

The castor oil and potassium hydroxide were purchased by the Permula Sdn Bhd, Kuala Lumpur, Malaysia. The fatty acid methyl ester standards were obtained from from Sigma-Aldrich (Switzerland) and were chromatographic grade. Analytical grade methanol was purchased from ChemAR. Mussel shells were provided by the sea food restaurants in Kuantan, Pahang, Malaysia. Laboratory calcium oxide (assigned as lab-CaO) was ordered from R&M Chemicals (Essex, UK).

2.2. Catalyst preparation

The mussel shells were cleaned and washed thoroughly with warm water several times. The cleaned and washed mussel shells were calcined at 1000 °C with heating rate of 10 °C /min for 1 h. The solid

powder was crushed and sieved with $63\ \mu\text{m}$. This resulted solid is as known as non-impregnated catalyst. The impregnated catalyst was prepared by the impregnation process using potassium hydroxide. A typical calcium oxide was suspended in ammonia solution (5 wt%), and 50 mL aqueous potassium hydroxide was added. The solution was heated at $80\ ^\circ\text{C}$ for 2 h. The precipitate was collected, washed and calcined at $400\ ^\circ\text{C}$ for 12 h.

2.3. Castor oil transesterification

The non-impregnated and impregnated catalysts were used for biodiesel fuel synthesis. This experiment examines the ability of mussel shell-base catalyst (MS-BC) and non-MS-BC for transesterification of castor oil to biodiesel. The effects of catalyst amount (1 wt/wt%-5 wt/wt %), catalyst recyclability (1 cycle-5 cycles), time (1 h-5 h) and temperature ($40\ ^\circ\text{C}$ - $80\ ^\circ\text{C}$) on the biodiesel yield were observed. The transesterification of castor oil were carried out under batch condition over activated solid catalyst with methanol oil ratio of 6:1. The activation of calcium oxide as the first catalyst derived from mussel shell, and the second catalyst of impregnated calcium oxide was tested simultaneously. The characterization, transesterification, synthesis and analysis were conducted gradually. Analysis of castor seeds oil, catalyst and biodiesel were done by XRD, FESEM, BET, TGA, XRF and GC. The properties and performance of synthesized biodiesel were approved based on the proposed standard such as flash point, viscosity index, acid value etc. The characterization and analysis of activated and impregnated solid catalyst were compared with non-impregnated performance. The obtained castor oil biodiesel yields were interpreted based on the variation of process parameter. The synthesized biodiesels were approved by GC-MS, and its properties would be compared to the limitation of specification described by ASTM D-6751.

2.4. Gas chromatography analysis

The castor oil methyl ester was determined by GC-MS. The samples were prepared in 2 mL vial; 0.02 mL of sample was mixed with 1.98 mL of hexane (GC-grade). The analysis was conducted using GC-equipped with DB-5HT column, 30 mm x 0.25 mm, i. d. of $10\ \mu\text{m}$. The peaks of methyl ester were identified by comparing with their respective standard.

2.5. Biodiesel yield determination

The yield of biodiesel was determined by the following formula:

$$\text{Biodiesel Yield (\%)} = \frac{\text{Biodiesel mass} \times \text{Purity}}{\text{Mass of used oil}} \quad (1)$$

, where biodiesel mass (g), mass of used oil (g), and purity (%) is methyl ester composition from GC-MS analysis.

2.6. Biodiesel fuel properties test

The biodiesel fuel properties including density, flash point, cetane number, cloud point and kinematic viscosity were examined by ASTM D-941, ASTM D-93, ASTM D-613, ASTM D-2500, ASTM D-445. All of the tested results were approved by the ASTM D-6751.

3. Results and Discussions

3.1 Mussel shell characterization and calcium oxide catalyst

The morphology of mussel shell pre-and post-activation was examined by SEM (Fig. 1a and 1b), and the non-activated shell shows a rough, layered surface with low porosity structure and compact texture compared post-calcination process. The calcined shell displays significantly changes from the layered architecture to the vesicular structure. The activated shells were fast similar to another mollusk shell, like clam shell, etc. The shells were irregular in shape, and the smaller size of the grains could provide the higher specific surface area [9]. This invention could be considered to be less-porous, the particles should directly respond to the surface area. Next, the detail chemical compositions of the catalyst are presented by the XRF analysis. The XRF indicates that a significant calcium oxide content of 97.72% with less amount of other constituents eg. Na₂O (1.09%), SrO (0.35%), SO₃ (0.16%), MgO (0.16%), P₂O₅ (0.11%), S₂O₃ (0.10%), Al₂O₃ (0.05%), Fe₂O₃ (0.03%), Cl (0.03%), K₂O (0.03%), ZrO₂ (0.01%) and CuO (0.01%). The minor components plays no so important role, but the major constituent of calcium oxide has mainly contributed for transesterification process due to its cheapness and non-toxic [10]. The calcium oxide can also be found from calcination of fish bone, etc. for biodiesel synthesis [11].

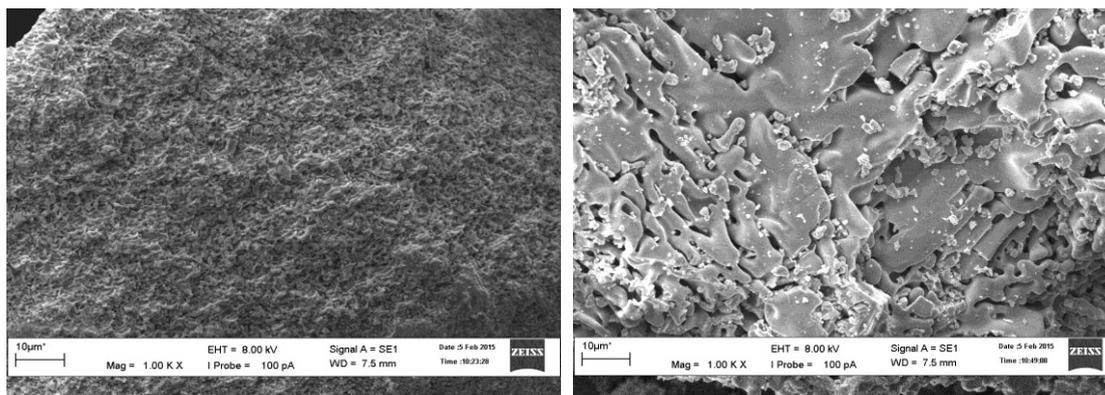


Fig.1. (a) SEM images of the non-activated mussel shell; (b) activated mussel shell

The TGA of calcined mussel shells are shown in Fig. 2. The calcium oxide reflects slightly weight loss of 0.34% from decomposition at 348.92 °C. On the other hand, at temperature is less than 150 °C (¹st stage), there is 8.901% weight loss of impregnated CaO with KOH. A significant weight loss takes place at temperature range of 350°C-450°C (²st stage). The weight losses due to the decomposition of the functional group occur at temperatures higher [12]. Then, the FTIR of mussel shell derived calcium oxide with impregnated and non-impregnated are given in Fig 3. The calcined and KOH impregnated calcium oxide identify the OH bending in these spectra. The stretching and bending vibration of OH binds to Ca, and the O-H attaches to surface of the CaO. This stretching appears as a sharp peak at 3753.72 cm⁻¹, and

the bending vibration are shown at 1462.95 cm^{-1} . Next, the O-H stretching vibration is reflected as a broad absorption band at $3100\text{ cm}^{-1} - 3800\text{ cm}^{-1}$, and the bending vibration occurs at 1401.21 cm^{-1} . The absorption peak can be seen around 1401.21 cm^{-1} , and these phenomena indicate Ca-O-Ca vibrations. It has been also approved by using catalyst nano-MgO supported on titania for biodiesel production. These absorption are attributed to surface hydroxyl species resulting from a fast reaction [13].

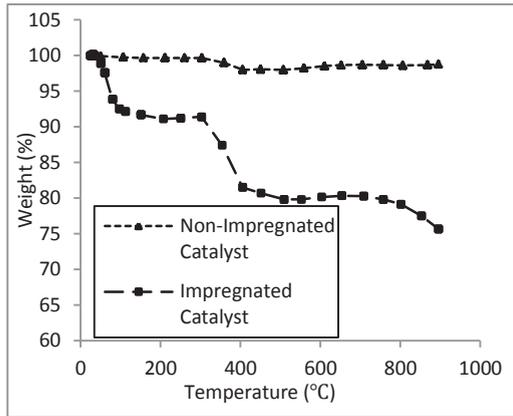


Fig. 2. TGA analysis of activated mussel shell

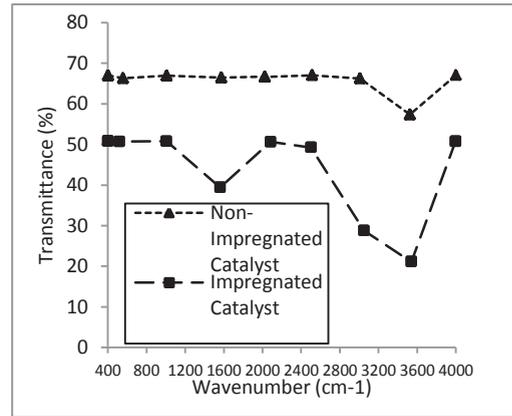


Fig. 3. FTIR spectra of activated mussel shell

Furthermore, the XRD pattern of non-calcined and activated shells are given in Fig. 4a and 4b. The XRD results reveal that the composition of calcium carbonates with the absence of calcium oxide peak. However, with the increase of the calcination temperature, the calcium carbonates completely transforms to CaO by evolving the carbon dioxide. The composition of the activated catalyst above 900°C mainly consist of the CaO. The narrow and high intense peaks of the activated catalyst define the well-cristallized structure of the calcium oxide catalyst [14].

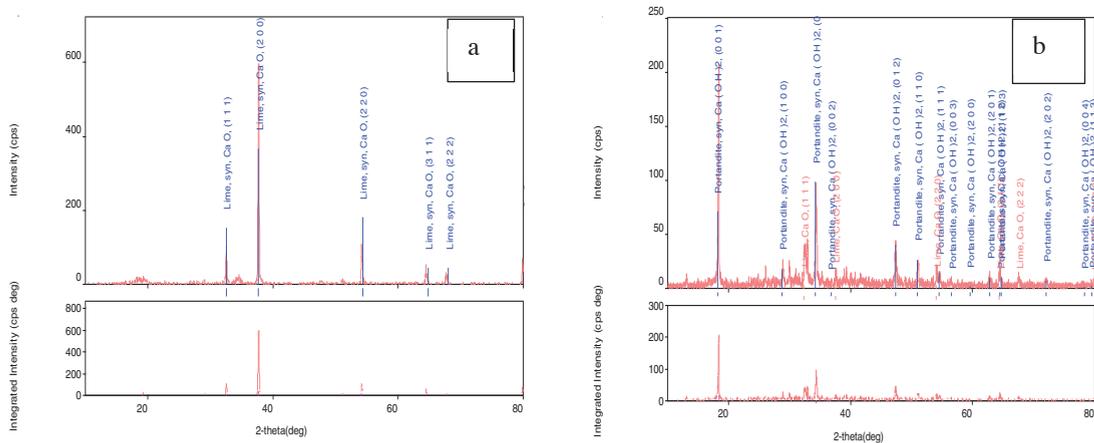


Fig. 4. (a) XRD pattern of non-impregnated mussel shell; (b) impregnated mussel shell

The BET analysis of mussel shell derived calcium oxide with impregnated treatment has a surface area ($4.68 \text{ m}^2/\text{g}$) and pore volume ($0.02 \text{ cm}^3/\text{g}$) present a uniform pore sizes. These results show higher than calcined cockle shell ($1.56 \text{ m}^2/\text{g}$) [15]. It can be seen that the activated solid catalyst results a strong increase in the active site. It has been also reported by using KOH supported on coconut shell activated carbon for transesterification of waste frying oil [16]. This hypothesis is reflected by the SEM images for the pre- and post-treatment of the used catalysts. The treated catalyst gave molecules bonded together as aggregates. The aggregates could provide higher specific surface area, which enable the catalyst to fully contact the reactant mixture [17].

3.2 Influence of reaction variables

The biodiesel yield was influenced by the reaction variables, e.g. reaction time, temperature, catalyst loading and reusability. The catalyst types and loading affected the transesterification reaction of castor oil to biodiesel. For the following investigation, the activated catalyst (non-impregnated) and impregnated catalyst of mussel shell were examined. The influence of reaction time on the biodiesel yield was observed. Fig.5 shows the obtained biodiesel yield of non-impregnated and impregnated catalyst (59.10% and 65.12 %) respectively at 60°C and 1 h of reaction time. From the reaction time of 2 h to 3 h, the yield of biodiesel improves dramatically up to achieved equilibrium condition (91.17%). After 3 h, the increase of the biodiesel yield is very slightly or disregarded. These results can be understood due to the transesterification reaction. If the reaction time is long enough, the transesterification reaction between methanol and castor oil is reversible. Next, the influence of temperature on promoting transesterification can be related with the endothermic reaction. The highest biodiesel yield was found at the operation temperature of 60°C . At the higher temperature, the reaction rate of castor oil in methanol is faster as compared to at low temperature. Thus the increased rate affects the improvement of biodiesel yield at the higher temperature (Fig. 6). It shows the role of both used catalysts, and it gives the same performance by various temperatures. As the temperature increases above 60°C , the biodiesel yield decreases. These tendencies can be estimated due to nearly boiling point of methanol, and the methanol vaporizes vigorously and form bigger number of bubbles, which can cause the reaction on the two-phase interface [18].

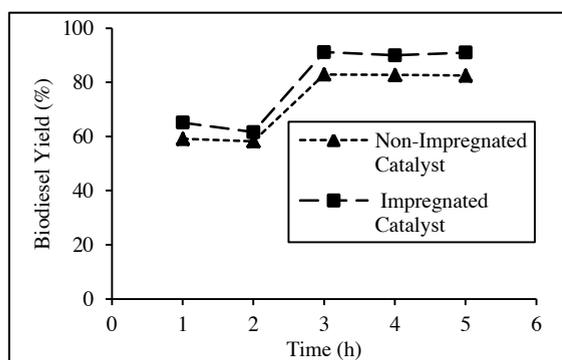


Fig. 5. Biodiesel yield vs reaction time

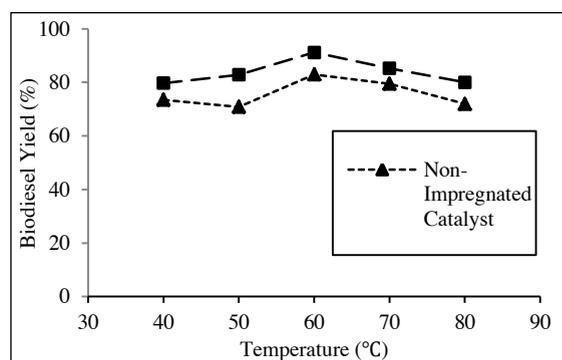


Fig. 6. Biodiesel yield vs temperature.

Fig.7 reveals the influence of catalyst loading on the biodiesel yield using of non-impregnated and impregnated catalyst. By using the catalyst loading of 2 wt/wt. %, the highest biodiesel yield of 91.17 % is obtained. Decreasing the catalyst amount to 1 wt/wt. %, reduces the yield of biodiesel significantly. These

indications are caused by blocking of the catalyst activation. The catalyst blocks the contact between reactants and too many alkaline centres which can affect saponification reaction [19].

The catalyst reusability is tested by reaction cycles. It is found that the treated catalyst for non-impregnated and impregnated treatment can be used up to 5 cycles (Fig. 8), and it still give the biodiesel yield of 79.72% for 4 cycles. The yield of biodiesel drops post 5 cycles of reused catalyst.

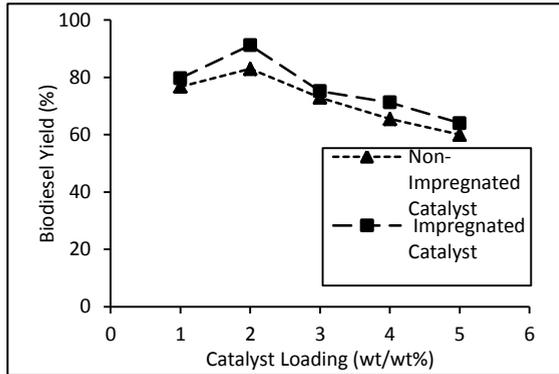


Fig. 7. Biodiesel yield vs catalyst loading.

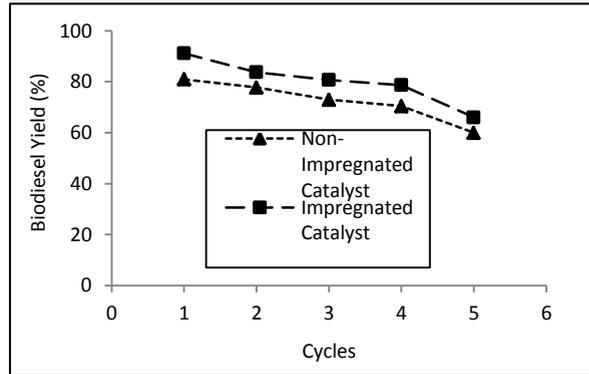


Fig. 8. Biodiesel yield vs catalyst recyclability.

3.3 Castor oil biodiesel properties

The properties of the obtained castor oil biodiesel can be summarized in Table 1. It seems the most of its properties are in the proposed range by the ASTM D-6751.

Table 1. Castor oil biodiesel fuel properties compared with ASTM

Properties	ASTM limits	KOH catalyst [20]	as H ₂ SO ₄ catalyst [21]	as Iron nano-particle as catalyst [22]	This Work: MS-BC (Impregnated catalyst)
Density (kg/m ³)	870-900	910	-	914	889
Flash point (°C)	>130	160	220	185	178.8
Cetane number	>47	-	48	-	61.05
Cloud point (°C)	-	-13	-	-6	-10
Kinematic viscosity, 40°C (mm/s)	1.9-6.0	10.75	6.2	9.8	6.3

4. Conclusion

Mussel shell derived solid catalysts with thermal activation via non-impregnated and impregnated treatment have been successfully examined in the transesterification of castor oil to biodiesel. The both used solid catalysts were able to be reused up to 5 times without debilitation in its activity, thus creating another economical catalyst source for biodiesel synthesis. As a heterogeneous catalyst, calcium oxide can minimize the cost of purification and biodiesel production. The highest biodiesel yield (91.17%) was obtained by using the mussel shell-base catalyst with impregnation (MS-BC), and the process parameters have a significant effect on the biodiesel yield. The properties of resulted biodiesel mostly fulfill the

biodiesel standards which are compatible with density, flash point, cetane number, viscosity and cloud point. The improvement of yield, biodiesel quality and advantages synthesis can be further investigated via manipulating feedstocks, purification methods and solid catalysts from other invaluable wastes.

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