Utilization of Waste Crab Shell (*Scylla serrata*) as a Catalyst in Palm Olein Trans酯ification

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Abstract: Aquaculture activity has increased the population of crab, hence increasing the generation of related wastes, particularly the shell. In addition, the number of molting process in crabs compounds further the amount of waste shell generated. As such, in the present work, the application of the waste crab shell as a source of CaO in transesterification of palm olein to biodiesel (methyl ester) was investigated. Preliminary XRD results revealed that thermally activated crab shell contains mainly CaO. Parametric study has been investigated and optimal conditions were found to be methanol/oil mass ratio, 0.5:1; catalyst amount, 4 wt. %; and reaction temperature, 338 K. As compared to laboratory CaO, the catalyst from waste crab shell performs well, thus creating another low-cost catalyst source for producing biodiesel as well as adding value to the waste crab shell. Reusability of crab shell CaO has also been studied and the outcome confirmed that the catalyst is capable to be reutilized up to 11 times, without any major deterioration.

Key words: palm olein, transesterification, biodiesel, fatty acid methyl ester, crab shell

1 INTRODUCTION

Vegetable oils and animal fats are found to be the best candidates as alternate energy sources to cater world energy demand as well as to tackle environmental complications. Their direct use, however, is limited due to two main reasons; high viscosity and low volatility. As such, their conversion into low viscous compounds with reasonable volatility was carried out in early 1900s¹. For this purpose, vegetable oils or animal fats are transesterified with simple alcohol to produce fatty acid methyl esters (FAME) or known as biodiesel, which has similar characteristics as conventional diesel fuel. Typically, homogeneous catalysts have been used to catalyze transesterification reaction. Hydroxides of sodium and potassium are the bases classically used in homogeneous catalysts⁵. However, recent attention is shifted to heterogeneous catalysts⁶. Among the solid catalysts, calcium oxide (CaO) is a promising heterogeneous catalyst in transesterification and etherification⁴⁶. CaO has many advantages; higher activity, active in mild reaction conditions, long catalyst lifetimes, low catalyst cost, and low solubility in methanol. In biodiesel commercialization, cost is one of the main hurdles⁷; as such the search for low-cost yet highly active catalysts has been of interest. Most recently, CaO has been prepared from waste oyster shell⁸, and waste chicken egg shell⁹. Both reports stated that regardless of the source, the catalysts have high activity in transesterifying oils into biodiesel, a very similar catalytic activity with laboratory CaO.

Mud crab (*Scylla serrata*), also known as mangrove crab or black crab, are commonly found in mangrove swamps...
nearby intertidal and subtidal muddy habitat \(^{[10]}\). In Malaysia, the high price of mud crab has driven many to venture into its aquaculture activities \(^{[12]}\). The value of aquaculture production (from all aquaculture systems) has been increasing steadily from RM 654 million (1998) to RM 1.3 billion (2007), in which retail value of mud crab alone in 2007 was estimated to RM 2 million (RM 1 = USD 0.28)\(^{[12]}\). Therefore, there is abundant and increasing amount of mud crab shell, and to our best knowledge, the shell has no important uses and commonly regard as a waste material. Furthermore, each crab produces not one but many shells in its lifetime, through molting process; a regular process by crabs to shed shells in order to grow \(^{[13]}\). This further compounds the amount of waste shell, hence the abundant supply makes crab shell feasible to be used in biodiesel industry and to our best knowledge, there is no report on CaO from mud crab shell in transesterification.

In view of this situation, this paper demonstrates the use of waste crab shell as a source of CaO in transesterification of palm olein into biodiesel. The conversion trend of the catalyst has been presented versus laboratory CaO. The prepared CaO was also reutilized for several runs to evaluate its reusability performance.

2 EXPERIMENTAL

2.1 Materials and catalyst characterization

Mud crab was purchased from the local market. The shell was cleaned to remove protein and other interference substances and washed thoroughly with warm water. It was dried in an oven at 373 K, overnight. The crushed and powdered shell was then subjected to heat treatment in a furnace at 1173 K for 2 h. The prepared catalyst from mud crab shell was assigned as MC-CaO. For the purpose of comparison, laboratory calcium oxide (assigned as lab-CaO) was obtained from R&M Chemicals (Essex, UK). The basic strength of the calcined catalyst, MC-CaO (1173 K, 2 h) was tested using Hammett indicators as described in the literature\(^{4}\). The catalyst could change the colour of both phenolphthalein \((H_ = 8.2)\) from colorless to pink and of 2,4-dinitroaniline \((H_ = 15)\) from yellow to mauve but however failed to change the colour of 4-nitroaniline \((H_ = 18.4)\). Therefore the catalyst basic strength was assigned as 15 < \(H_ < 18.4\). The results of XRD, as depicted by Fig. 1, revealed that the composition of uncalcined crab shell was mainly consists of calcite-magnesia \((\text{CaCO}_3-\text{MgO})\) with absence of CaO peak. However with the increase in activation temperature, CaCO\(_3\) transforms to CaO. The composition of calcined MC-CaO was mainly consists of the active ingredient, CaO (lime) and traces of MgO, in the form of periclase. Narrow and high intense peaks of the calcined catalyst define the well crystallized structure of the catalyst. This observation demands that the catalyst has to be activated thermally before it could be used to catalyze the reaction. More detailed studies on the effect of different activation temperatures on catalyst compositions is underway.

2.2 Reaction

Transesterification reactions were performed in a 25 mL 2-neck glass reactor with a condenser, immersed in water bath. In a typical reaction, 10.0 g of oil was added into a mixture of calcined catalyst and methanol. The contents were refluxed under magnetic stirring. Several reaction parameters (methanol/oil mass ratio, catalyst amount and reaction temperature) were studied to find out the optimum reaction conditions. Sample was drawn at 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 h for analysis of methyl ester content. Then the reaction mixture was allowed to cool, the resulting glycerol was separated by gravity. Centrifuge was used to further separate the layers (methyl ester and glycerol) and the residual methanol in methyl ester layer was evaporates out using rotary evaporator at 353 K to obtain the fatty acid methyl esters. Similarly, the reaction was repeated by using lab-CaO for comparison purpose.

2.3 Gas chromatography analysis

Standard materials and samples were analyzed by a gas chromatography (Perkin Elmer, Clarus 500) fitted with flame ionization detector (FID). The fatty acid methyl esters (FAME) content was determined by following the European regulation procedure EN 14103 with a polar capillary column (Supelco Wax, 30 m × 0.25 mm i.d. × 0.25 μm) using methyl heptadecanoate as an internal standard. Peaks of methyl esters were identified by comparing them with their respective standards.

3 RESULTS AND DISCUSSION

3.1 Catalyst characterization and reaction

The basic strength of the calcined catalyst, MC-CaO (1173 K, 2 h) was tested using Hammett indicators as described in the literature\(^{1}\). The catalyst could change the colour of both phenolphthalein \((H_ = 8.2)\) from colorless to pink and of 2,4-dinitroaniline \((H_ = 15)\) from yellow to mauve but however failed to change the colour of 4-nitroaniline \((H_ = 18.4)\). Therefore the catalyst basic strength was assigned as 15 < \(H_ < 18.4\). The results of XRD, as depicted by Fig. 1, revealed that the composition of uncalcined crab shell was mainly consists of calcite-magnesia \((\text{CaCO}_3-\text{MgO})\) with absence of CaO peak. However with the increase in activation temperature, CaCO\(_3\) transforms to CaO. The composition of calcined MC-CaO was mainly consists of the active ingredient, CaO (lime) and traces of MgO, in the form of periclase. Narrow and high intense peaks of the calcined catalyst define the well crystallized structure of the catalyst. This observation demands that the catalyst has to be activated thermally before it could be used to catalyze the reaction. More detailed studies on the effect of different activation temperatures on catalyst compositions is underway.
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In order to compare the catalytic activity of MC-CaO, under optimal conditions, similar experiments were conducted using lab-CaO. As shown in Fig. 2, the activity of MC-CaO was much resembled the lab-CaO, although there was a slight difference in conversion profile at the beginning of the reaction. Reaction under both catalysts approached equilibrium plateaus after 2.5 h of reaction time, indicating the source of CaO has no effect of its performance as a solid catalyst in transesterification reaction. Parametric study has been investigated and results revealed that the optimal conditions were as follow: methanol/oil mass ratio of 0.5:1 (about 12:1 molar ratio); catalyst amount, 4 wt.% (based on initial oil weight), and reaction temperature of 338 K. The mechanism of CaO catalyzed transesterification was well reported in previous studies.

3.2 Reusability of the prepared catalyst

Under the optimized conditions, the prepared catalyst was active for 11 times of reuse, as shown in Fig. 3. Before each reuse, the spent catalyst was washed with methanol to remove the adsorbed stains and calcined at 1173 K for 2 h. Catalyst deterioration was probably due to its failure to maintain the form of CaO. CaO transformation to any other form, such as Ca(OH)$_2$, will deteriorate the performance of the catalyst.$^{15,16}$ Detailed studies are needed at this point, since other researchers found that other than CaO, the contribution of calcium glyceroxide is also a factor for the reusable performance.$^{14}$

4 CONCLUSION

The prepared catalyst (MC-CaO) from waste crab shell has shown high performance in transesterification of palm olein to biodiesel. The conversion trend of the prepared catalyst was much comparable to laboratory CaO, thus confirmed that the crab shell is capable of catalyzing the reaction well, regardless of the origin. The prepared catalyst afforded to be reused successfully for several runs (up to 11 runs) without much drop in methyl ester content. This concludes that CaO from mud crab shell has potential as a solid catalyst in transesterification reaction to produce biodiesel. Utilizing this waste material not only reduces the catalyst cost, which is one of the major costs in biodiesel production, but also promoting environmental-friendly process and adding value to the waste material.
ACKNOWLEDGEMENTS

Financial support from Universiti Sains Malaysia USM-RU-PRGS Grant (1001/PIKIMIA/841005), and award of USM Fellowship are gratefully acknowledged.

References


