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PRODUCTION OF BIODIESEL FROM PALM OIL USING COCKLE SHELL WASTE AS HETEROGENEOUS CATALYST

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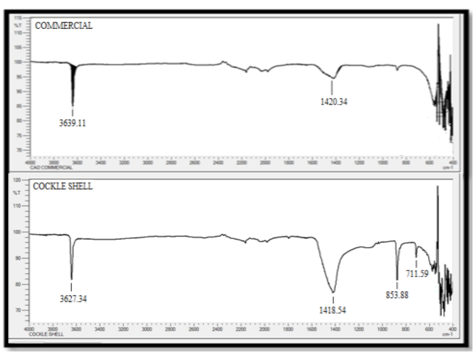
Graphical abstract



Abstract

In this study, production of biodiesel from palm oil using cockle shell wastes as catalyst was carried out using transesterification reaction. The objectives of this study are to analyze and characterize calcium oxide (CaO) from cockle shell wastes and to determine the catalytic activity of derived shell catalyst towards the percentage yield of biodiesel produced. The effect of methanol to oil ratio, reaction time and reaction temperature were investigated. The types of esters content in biodiesel and the functional group presence in catalyst were determined using FTIR and GC-MS analysis. The results showed that the optimum condition for cockle shell wastes achieved maximum yield of biodiesel (78.05%) is at reaction temperature 50°C within 1 hour with 9:1 methanol to oil ratio. Meanwhile for commercial CaO, the maximum yield is 73.95% at 60°C within 3 hours for 3:1 methanol to oil ratio. From the result obtained, this indicated that cockle shell wastes have potential to substitute commercial CaO as catalyst in transesterification reaction.

Keywords: Biodiesel, cockle shell wastes, calcium oxide, transesterification reaction, palm oil

Abstrak

Dalam kajian ini, penghasilan biodiesel daripada minyak kelapa sawit dengan menggunakan sisa kulit kerang sebagai pemangkin telah dijalankan meggunakan kaedah transesterifikasi. Objektif kajian ini dijalankan adalah untuk menganalisis dan mencirikan kalsium oksida daripada sisa kulit kerang dan untuk menentukan aktiviti sisa kulit kerang sebagai pemangkin terhadap peratusan hasil biodiesel yang dihasilkan. Kesan-kesan nisbah metanol kepada minyak, masa tindak balas dan suhu tindak balas telah dikaji. Kandungan *ester* dalam biodiesel dan kumpulan berfungsi dalam pemangkin ditentukan menggunakan FTIR dan GC-MS. Hasil kajian menunjukkan bahawa keadaan optimum yang diperolehi daripada sisa kulit kerang mencapai hasil maksimum biodiesel (78.05%) pada suhu 50°C selama satu jam dengan menggunakan 9:1 nisbah metanol kepada minyak. Sementara itu untuk komersial CaO, hasil maksimum adalah 73.95% pada suhu 60°C dalam masa 3 jam menggunakan 3:1 nisbah methanol kepada minyak. Daripada keputusan yang diperolehi, ini menunjukkan bahawa sisa kulit kerang memiliki potensi untuk menggantikan komersial CaO sebagai pemangkin dalam tindak balas transesterifikasi.

Kata kunci: Biodiesel, sisa kulit kerang, kalsium oksida, tindak balas transesterifikasi, minyak kelapa sawit

1.0 INTRODUCTION

Concern about the depletion of energy sources and environmental problems like global warming and pollutions, an alternative fuel was studied by many researchers due to the advantages from using biodiesel in car engine. Biodiesel is a one of the promising fuel that used as substitution to diesel engine without engine modification. As renewable energy sources, biodiesel did not give harmful to environment because the sources used in biodiesel production are environmental friendly. In instance, biodiesel is derived from vegetable oil and animal fats which are contain free fatty acid and triglycerides molecules [1].

Palm oil have been selected and used as the best candidate in production of biodiesel due to the increasing in production of palm oil in global marketing. This is because of the climate factors that have influenced the growth of palm oil in Malaysia [2].

There are several methods used in production of biodiesel which are transesterification, direct use vegetable oil, microemulsions and thermal cracking. Vegetable oil cannot be used directly without process because it will damage the engine of vehicles. Therefore, transesterification was selected and used to produce biodiesel which converted triglyceride of vegetables oils to methyl ester, known as biodiesel [3].

Other than that, transesterification reaction is more favored instead of esterification process because of the types of catalysts used in the reaction. Acid catalyst is used in esterification process. Meanwhile in transesterification process, basic catalyst is used to increase the rate of transeterification reaction. Furthermore, basic catalyst is easy to find due to the abundance in nature and eco-catalyst.

Catalyst is used to accelerate the rate of reaction. Therefore, homogeneous and heterogeneous catalysts were used during the reaction [4]. In fact, both of homogeneous and heterogeneous catalyst either in acid or base catalyst are used to increase the rate of reaction due to the major parameter to obtain the best condition in production of biodiesel [5]. However, base catalyst is the most preferred compared to acid catalyst because of the higher catalytic efficiency and the reaction can be conducted in lower temperature and pressure [6].

Heterogeneous catalyst was chosen other than homogeneous catalyst due to the benefit contributed like easier to separate from the reaction mixture and capable to reuse for several times. Thus, heterogeneous catalyst is considered as a green process [7]. Moreover, heterogeneous catalyst is an alternative from homogeneous catalyst that easily to handle.

Calcium Oxide (CaO), is a promising catalyst in production of biodiesel. CaO can be obtained from waste shell like cockle shell and egg shell and thus would reduce the cost. Recently, most of waste shell catalyst is studied by some researchers to differentiate the performance of yield produced between CaO derived waste shell catalyst and commercial CaO catalyst. CaO derived from waste shell catalyst have higher potential as catalyst in biodiesel production due to its long catalyst life, high activity and requires only moderate reaction conditions [8].

2.0 METHODOLOGY

2.1 Materials

Palm oil was purchased from Mydin mall Kulaijaya, Johor. The cockle shell was collected as waste from several cafes in Universiti Teknologi Malaysia, Johor. The waste shell was rinsed with water to remove dust and impurities and was then dried in an oven at 105°C for 24 hours [9,10].

2.2 Catalyst Preparation

The catalyst was prepared by a calcination method. The dried waste shell was crushed and the powdered shell was sieved. The powdered shell waste was then calcined at 900°C in a furnace under static air with a heating rate 10°C/min for 2 hours. All calcined samples were kept in the close vessel to avoid the reaction with carbon dioxide (CO_2) [11] and humidity air before used.

2.3 Catalyst Characterization

The functional groups on the surface of the cockle shell waste catalyst were identified using the Fourier Transform Infrared analysis (FTIR). Sample of the cockle shell waste catalyst was grounded with KBr (spectroscopic grade) with a ratio 1:100 (sample : KBr) in a mortar before pressed into a 10 mm diameter disks under 6 tonnes of pressure prior to FTIR analysis. The analysis condition used was 16 scans at a resolution of 4cm^{-1} measured between 400 and 4000 cm^{-1}.

2.4 Transesterification of Palm Oil

The synthesis of biodiesel from palm oil and methanol was carried out in a 250 mL round bottom flask equipped with condenser and mechanical stirrer at atmospheric pressure. The effects of methanol to oil ratio (3 to 15), reaction time (1 to 5 hr) and reaction temperature (30 to 65°C) on the percentage yield of biodiesel produced were studied. 10wt% of catalyst loading was kept constant for the whole experiment.

After the reaction was completed, solid base catalyst was filtered and the solution was transferred into separatory funnel until two layers form which are the top layer is biodiesel product and the bottom layer is glycerol. The biodiesel product was analyzed using Gas Chromatography Mass Spectrometry (GC-

MS). GC-MS analysis mainly identifies the quality and quantity of the produced biodiesel resembled in the methyl esters present in the product sample. Therefore, the total yield from the biodiesel was calculated according to Equation 1.

$$\text{Biodiesel Yield (\%)} = \text{FAME percentage from GC analysis} \times \left[\frac{\text{Volume of product}}{\text{Volume of oil}} \times 100\right] \quad (1)$$

3.0 RESULTS AND DISCUSSION

3.1 Characterization of Cockle Shell and CaO Catalyst

The IR spectra of the commercial CaO and derived CaO from cockle shell wastes are shown in Figure 1. The bottom spectrum represents the derived CaO from cockle shell wastes.

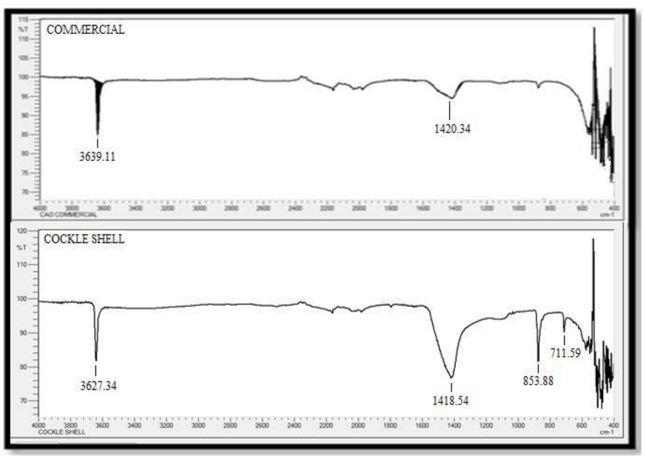


Figure 1 IR pattern of commercial CaO and derived CaO

From Figure 1, it is clearly shown that the band occurred at 1413-1436 cm^{-1} for both catalysts correspond to the bending vibration of Ca-O and the peak shown at 3639 cm^{-1} corresponds to the -OH stretching vibration of $Ca(OH)_2$ due to moisture absorption on the surface of the pellets. Meanwhile, FTIR spectrum for cockle shell catalyst shows characteristic peaks of $CaCO_3$ at peak 711 cm^{-1} and 846-871 cm^{-1} due to the stretching vibration of carbonate ions $(CO_3)^{-2}$.

Overall, both catalysts have same characteristics as shown in the IR spectra above and therefore, it can be stated that the CaO derived from cockle shell waste has a high potential as alternative to commercial CaO in biodiesel production.

3.2 Comparison Between Commercial CaO and Derived CaO

Commercial CaO and derived CaO were compared based on their reaction towards effects of methanol to oil ratio, reaction time and reaction temperature. From this data, both catalysts have different percentage yield produced and different optimum conditions.

3.3 Effect of Methanol to Oil Ratio

The biodiesel production from transesterification reaction is shown in Figure 2. By the transesterification reaction, palm oil is mixed with methanol and catalyzed using cockle shell and commercialized CaO catalyst to produce biodiesel. Transesterification reaction produced biodiesel simultaneously during the conversion of triglyceride. Meanwhile, biodiesel and glycerol as side product is produced after the reaction is completed.

The formation of calcium methoxide $Ca(CH_3O)_2$ on the surface of CaO catalyst was reported as enhancement to enhance the reaction between palm oil and methanol during transesterification reaction occur [11].

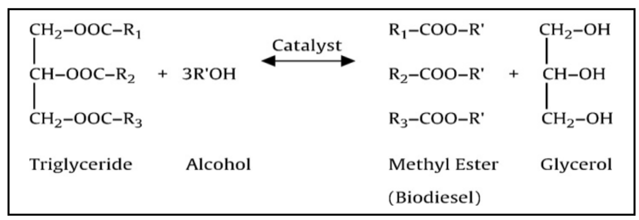


Figure 2 Transesterification reaction process

Alcohol to oil ratio is one of the important factors that affect the reaction and the yield of biodiesel as well. Hence, the study on the effect of methanol to oil ratio was done by varying the ratio from (3:1 to 15:1). The effect of methanol to oil ratio towards the percentage yield of biodiesel obtained within 3 hours reaction time at 60°C is shown in Figure 3.

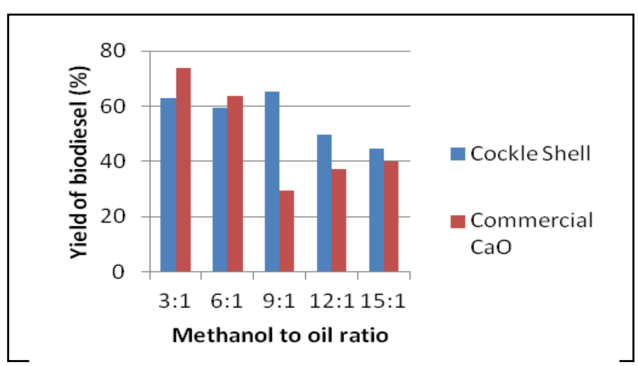


Figure 3 Effect of methanol to oil ratio on biodiesel yield

From the result obtained, for cockle shell catalyst, the percentage yield of biodiesel increased slightly with the increasing of methanol to oil ratio. However, by increasing the ratio 9:1 to 15:1, the percentage yield of biodiesel decreased after 9:1 ratio. The obtained result can be attributed to the fact that the glycerol would largely dissolve in excessive methanol and subsequently inhibited the reaction of methanol to the reactants and catalyst, resulted in a lower biodiesel yield [12]. Therefore, the maximum percentage yield of biodiesel of 65.29% was obtained with 9:1 ratio of methanol to oil.

By comparing the results, the optimum biodiesel yield for CaO obtained in this study was achieved when 9:1 methanol to oil ratio is used, which was lower than those produced from different sources such as mud clam shell (14:1 methanol to oil ratio), ostrich eggshell (12:1 methanol to oil ratio), chicken manure and waste venus clam (15:1 methanol to oil ratio) [13, 14, 15, 16]. As a remark, 9:1 methanol to oil ratio is sufficient to drive the reaction for completion and production of more methyl esters.

Meanwhile, for commercial CaO catalyst, the percentage yield of biodiesel obtained decreased gradually after 3:1 ratio of methanol to oil. For comparison, higher ratio of methanol to oil is needed in the reaction catalyzed by cockle shell wastes compared to commercial CaO catalyst in order to get the maximum yield of biodiesel. It was attributed to the presence of remaining $CaCO_3$ compound in CaO derived cockle shell catalyst, which ultimately tends to be less reactive and therefore required more methanol to enhance the contact between oil and alcohol.

3.4 Effect of Reaction Time

The reaction time is one of the parameters affect the transesterification reaction and the yield of biodiesel produced. Therefore, the sufficient time is needed for the reaction to occur [17].

The effect of reaction time was studied using 9:1 methanol to oil ratio for cockle shell catalyst and 3:1 ratio for commercial CaO catalyst at 60°C reaction temperature for both catalysts. The result was illustrated in Figure 4.

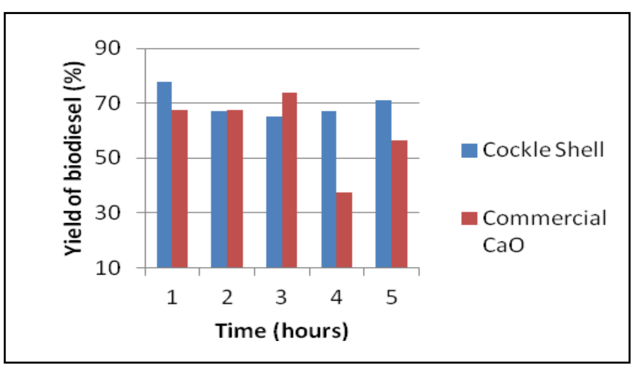


Figure 4 Effect of reaction time on biodiesel yield

From the Figure 4, it is shown that the maximum percentage yield which 77.97% was obtained in 1 hour reaction time for cockle shell catalyst compared to commercial CaO catalyst that required longer time which is 3 hours to give the maximum yield of biodiesel (73.95%). This can be explained that the biodiesel yield highly depend on the methanol to oil molar ratio, whereby the greater methanol to oil molar ratio, the shorter the reaction time for the reaching the equilibrium [18].

It also can be observed from Figure 4 that there was a decrease in the biodiesel yield above the optimal value for both catalysts. This decrement was due to the soap formation and the backward reaction was favored when the reaction time is getting longer [17, 19].

3.5 Effect of Reaction Temperature

The reaction and yield of biodiesel are strongly influenced by the reaction temperature used. This study was conducted at various reaction temperatures from 30 to 65°C, in order to investigate the effect of reaction temperature towards the yield of biodiesel produced. The effect of reaction temperature was studied by using reaction time 1 hour and 9:1 ratio methanol to oil for cockle shell catalyst while 3 hours reaction time and 3:1 ratio was used for commercial CaO catalyst.

Thus, the result from the effect of various temperature used on the percentage yield of biodiesel obtained is shown in Figure 5. Furthermore, transesterification reaction can occur at different range of temperature and it is also depend on the type of oil used [20].

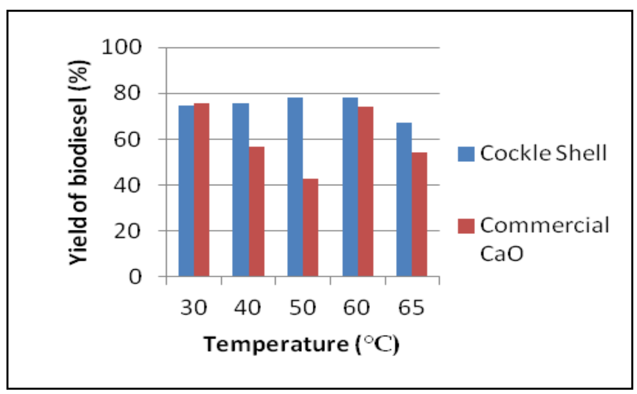


Figure 5 Effect of reaction temperature on biodiesel yield

Generally, the formation of biodiesel increases by increasing the reaction temperature. However, by increasing the reaction temperature beyond the boiling point of methanol, it will vaporized the methanol [21] and may influence the saponification reaction of triglycerides [20, 22].

From Figure 5, it can be observed that, the yield of biodiesel linearly increased by increasing the temperature from 30 to 50°C. Hence, the maximum percentage yield of biodiesel (78.05%) was obtained at reaction temperature 50°C for cockle shell catalyst and 73.95% is maximum yield at 60°C for commercial CaO catalyst. Similar work with shell derived CaO catalyst have been carried out previously and the highest biodiesel yield was found in a temperature range from 50 to 60°C [10, 13, 14].

However, the yield obtained for both catalysts decreased at 65°C due to the vaporization of methanol [20]. This is because of the temperature used is very close to the boiling point of methanol.

4.0 CONCLUSION

The study on the transesterification reaction conditions of palm oil indicated that the methanol to oil ratio, reaction time and reaction temperature are the factors that affect the yield of biodiesel production. In fact, biodiesel can be produced via transesterification of palm oil using derived CaO from cockle shell wastes as heterogeneous catalyst. Other than that, this catalyst is economically cheap, technically simple in production and its performance was equally matched with commercial CaO. In this study, CaO used to produce heterogonous catalyst was extracted from waste material, which is waste cockle shell. As can be highlighted, this study was more focused on the utilization of waste materials for synthesizing of valuable catalyst using a simple approach and therefore offers a more economical solution in managing their waste disposal problems.

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