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Materials Today: Proceedings

Analysis of Waste Cooking Oil Biodiesel (WCO) Synthesis with TiO2 Impregnated CaO from Waste Shells Nano-Catalyst

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Abstract

The development of clean and renewable energy sources has become crucial due to the rapid rise in crude oil prices, depleting fossil fuel reserves, and increase in environmental pollution caused by various industries. Due to this phenomenon, biodiesel has emerged as a renewable and eco-friendly alternative to conventional diesel fuel because it is non-toxic and biodegradable. Waste cooking oil (WCO) is one of the best resources in biodiesel production which it has high potential such as saving ecological systems, improving pollution, preventing food supplies and more economic. But this WCO cannot be used directly into diesel combustion due to their properties are not good as diesel fuel. Thus, it needs to be converted as biodiesel fuel. In biodiesel synthesis process, the catalyst for instance KOH, NaOH, HCL, H_2SO_4 etc. plays a significant role to increase their yield but also need a washing process. Currently, the synthesis of WCO biodiesel using CaO-TiO_2 nanoparticles as catalyst could be an excellent alternative because it eliminates the biodiesel's washing step and catalyst can be reused. Hence, the cost of biodiesel production will be reduced. CaO catalyst was produced by using waste cockle and sea snail shells as a cost-effective and environmentally friendly heterogeneous catalyst. In addition, TiO_2 impregnated CaO nanoparticles also have been studied through the ultrasonication process for the improvement in thermo-physical properties of catalyst reaction. It showed that, the 15:1 ratio is the ideal ratio for conversion of biodiesel production for both catalysts, which are 99.52% by using CaO catalyst and 97.63% by using CaO-TiO_2 catalyst. Moreover, the average time reaction of biodiesel production is 150 minutes, equivalent to two and half hours. So, the usage of the catalyst may be reduced efficiently.

Keywords: Biodiesel, Nano-catalyst, Waste cooking oil, CaO

1. Introduction

Energy is growing continuously with the population increasing worldwide annually. The development of clean and renewable energy sources has become crucial due to the rapid rise in crude oil prices, depleting fossil fuel reserves, and increasing in environmental pollution caused by fuel combustion from petroleum-fueled engines. In this context, biodiesel has emerged as a renewable and eco-friendly alternative to conventional diesel fuel because it is non-toxic and biodegradable. However, in the current situation of energy crisis urgency, biodiesel has yet to replace the fossil-based diesel fuel effectively as the primary energy source due to its high cost, which is synthesis by catalyst. Nowadays, waste cooking oil (WCO) is waste products in large volumes that can cause pollution in the sewerage system by solidified oil and cause blockage and odour or vermin problem [1-2]. To prevent this pollution and reduce the volume of waste products, the WCO is better to be synthesized and become valuable product to human utilization such as biodiesel due to high availability and easy to get. In biodiesel synthesis process, catalyst plays a significant role to increase the yield and reduce the cost of production. Sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium methoxide (CH_3ONa) and potassium methoxide (CH_3OK) were used as homogeneous base catalysts whereas hydrochloric acid (HCL), sulphuric acid (H_2SO_4) and p-toluene sulphonic acids were used as homogeneous acid catalysts in commercial process [3]. The main demerits associated with these catalysts are; non-reusable, and the process generates inferior quality of glycerol and huge amount of waste water which causes environment pollution [4-5]. To eliminate the demerits associated with the homogeneous catalyst, heterogeneous catalyst especially on nano-sizes are playing significant role to produce biodiesel, since it has higher catalytic activity, large specific surface area, high resistance to saponification reaction and good rigidity [6]. As an alternative, the washing process can eliminate by using heterogeneous catalyst which is very efficient, more environmental friendly and prevent from water pollution. In addition, heterogeneous catalyst also can be recycled or

reusable to avoid waste and reduce the operation cost. It also can improve catalytic activity, increase biodiesel yield production and reduce emissions in combustion performances. CaO is one of heterogeneous catalyst type that has a good catalytic activity, easy to get from waste products and abundantly available. It is can be fine from eggshells, clam shell, sea shell, mussel shells and etc.

Waste shells are the widely investigated as heterogeneous base catalysts including metal oxide of CaO for biodiesel production. CaO catalyst need to be prepared as nanoparticles catalyst to get optimum reaction. The active surface is one of the important characteristic of catalysts, which is increases when the catalyst size decreases. Moreover, if the catalysts have smaller particles and the surface to volume ratio are higher, it will reducing the amount of catalyst required in the reaction and more efficient. Nowadays, nanoparticles used in the transesterification gained more attention due to their high catalytic properties such as large pore size, high activity, large surface area and reactivity compared to macroscopic catalysts in biodiesel production. According to Bano et al. [7], with the advent of nanotechnology, nanocatalysts play a significant role in improving biodiesel yield and production quality, as well as reducing reaction time, reaction temperatures, catalyst weight, and alcohol to oil ratio. However, the production of biodiesel using metal/metal oxide nanoparticles-based catalyst is very limited and few reports are available. Y.Luo et al. [8] conducted non-catalyzed transesterification of soybean oil using mesoporous sulfated ZrO_2 nanoparticles as catalyst and the conversion was about 98.03%. Afsharizadeh and Mohsennia [9] reported that 76% and 79% WCO biodiesel yield was obtained by using of ZrO_2–CuO and ZrO_2–SrO_2 catalyst, respectively. Synthesis of biodiesel from waste olive oil via titanium dioxide (TiO_2) nanoparticles produced 91.2% of biodiesel yield [10]. Other research on WCO biodiesel production found that biodiesel was produced up to 98.3%by using mesoporous $TiO_2/PrSO_3H$ solid acid as nano-catalyst [11]. Wen et. al [12] claimed that mixed TiO_2-MgO catalyst had tremendous potential to produce large-scale biodiesel due to stability improvement and leading to defect on the catalyst surface. Meanwhile, Na_2O impregnated on CNT nano-catalyst was used and found that the Na_2O20%/CNT nano-catalyst yielded more than 97% of biodiesel and reusable in 3 times only [13]. Other study claimed that stability and catalytic activity of catalyst in conversion of WCO biodiesel was induced by substitutions of TiO_2 and MgO ions as nano-composite. Boro et al. [14] investigated biodiesel production from WCO using a series concentration of Ba (0.5%, 1.0% 1.5%) doped waste Turbonilla striatula shell-derived CaO catalyst. The optimum reaction conditions for achieving maximum conversion below 98% were 3 hours of reaction time, 1.0 wt.% catalyst amount, and 65°C reaction temperature. Buasri et al. [15] used cockle shells as a catalyst for transesterification of palm oil (FFA: 0.1%) at 65°C with MeOH: oil molar ratio of 9:1 within 3 hours and 10 wt.% catalyst loading under 1 atm pressure 15 in a glass reactor. The waste cockle shell-derived catalyst with a large surface area of 59.87 m^2/g produced 94.47% biodiesel. Sirisomboonchai et al. [16] studies have been successfully regenerated the CaO derived from the scallop shell. It was found that biodiesel yielded 96.68%. After 4 hours of calcination, the catalyst that contains CaCo3 was converted to CaO at temperatures of 1,000°C. The optimum conditions produced a conversion of palm oil of nearly 95% for waste shell-derived catalysts at a reaction time 4 hours and reaction temperature of 65°C, with methanol/oil molar ratio 9, catalyst loading 10 wt.% and pressure 1 atm in a glass reactor. The findings of the experiments revealed that the CaO catalyst had excellent activity during transesterification. Foroutan et al. [17] conducted a study on waste eggshells as a heterogeneous catalyst for making biodiesel. With a catalyst concentration of 4.471%, a methanol to oil ratio of 16.7:1, and a reaction temperature of 69.37°C, the best conversion yield of 98.37% was achieved in 7.08 hours. This catalyst can be reused up to three times while maintaining the biodiesel conversion yield above 90% of the original yield.

Besides that, the additional of titanium dioxide (TiO_2) powder is used as an alternative support material for heterogeneous catalysts due to its high surface area stabilizing the catalysts in its mesoporous structure. Then, the production of biodiesel derived from WCO uses several processes like esterification and transesterification focusing on increasing biodiesel production with the addition of nano-catalysts. With the advent of nanotechnology, designing and modification of nano-catalyst gives rise to attractive properties such as increased surface area, high thermal stability, and enhanced catalytic activity. The objectives of this research study are to analyze the catalytic activity, optimum reaction of TiO_2 and CaO as nano-catalyst and yield production of WCO biodiesel synthesis. It also to determine the TiO_2 -CaO nano-particles physicochemical characterization in different types resources of CaO. On the other hand, CaO additionally had been supported on activated carbon as a catalyst. As a result, the ideal conditions for the current study are a catalyst concentration of 6 wt. %, a methanol-to-oil molar fraction of 9:1, and a reaction time of 180 min. This study also discovered that the maximum amount of biodiesel that could be produced was 87.3%. Moreover, the comprehensive results demonstrated how effective and resourceful to produce high-

quality biodiesel from waste oyster shells using a recycled waste oyster shell-derived catalyst. This high-quality green biodiesel can be used as a substitute fuel in the transportation industry, particularly in diesel engines in vehicles [18]. Buasri et al. [19] stated that waste mussel shells could be utilized as a catalyst for the transesterification of WCO. Calcination temperature for waste mussel shells is 1000°C. The perfect condition for this catalyst is around 10 wt.% of catalyst of concentration, 9:1 methanol to oil percentage, the effect of reaction time is 4 hours and reaction of temperature is about 65°C by using WCO. In addition, catalyst reusability is 1-4 times on the biodiesel conversion. The maximum yields of 97.23% were obtained in 4 hours at 65°C for mussel shells. Thereby, the acid-functionalized CaO catalyst can convert high FFA feed to biodiesel via esterification. Nurhayati et al. [20] evinced by findings with sulfonated blood clam shell catalyst (CaO treated by 3M H_2SO_4) effectively converting FFA yielded high biodiesel of 97% under reaction conditions 12:1 MeOH: oil molar ratio, at temperature 60°C for 3 h using 1 wt.% catalyst loading. Another researcher investigated the use of waste scallop shells in the production of biodiesel from WCO. Under reaction conditions of 10% catalyst load, 9:1 methanol to oil ratio, and 3 hours of reaction time, waste scallop shell resulted in 95.44% FAME yield [15]. Hangun-Balkir [21] achieved a high biodiesel yield (90–97%) from transesterification of Camelina sativa oil (FFA:1.6%) over waste lobster shells-derived catalysts. The waste shells were calcined at temperature of 900°C. The transesterification was catalyzed by 1wt/% catalyst loading with a 12:1 MeOH: oil molar ratio at 65°C for 3 hours. Buasri & Loryuenyong [22] mentioned that waste crab shells had been a good catalyst that gave a maximum yield of 94%.

The scope of work is to analyze catalytic activity, stability and reusability of TiO_2 impregnated CaO nanoparticles as nano-catalyst for the WCO biodiesel synthesis. There is a large gap analysis on stability and catalytic activity in between TiO_2 and other nanoparticles as catalyst in various types of biodiesel feedstocks. Thus, TiO_2 impregnated on CaO nanoparticles are appropriate material to use because of their outstanding catalytic property of titanium in nano-domains and its novel properties for instance chemical stability, large surface area, non-toxicity, and low production cost. Appropriate amounts of TiO_2 nanoparticles will be dispersed into methanol and this subsequent solution added into stirring WCO to break the molecules of WCO into methyl ester and glycerol.

2. Materials and Methods

Biodiesel was produced from WCO using CaO catalyst derived from waste cockle and sea snail shells. Cockle and sea snail shells were washed with distilled water to expel obstruction material and dried at 103°C for 22 hours in a dry oven. Then, the cockle and sea snail shells were crushed using pestle mortar and sieved using a fine test sieve with a pore size of 75 μm. In addition, the catalyst was gained as a white powder. Calcination was completed in the muffle furnace at 900°C for 4 hours under an air atmosphere. Besides that, the samples were covered by lid and placed in a dry oven cause to prevent their reaction with CO_2 and moisture from the air. This catalyst contains $CaCO_3$ which is transformed to CaO after being calcined at 900°C for 4 hours. TiO_2 has high thermal conductivity and is likely to be an essential enhancer for improving thermal conductivity. The mixed oxide was prepared using stoichiometric of Ca and Ti at molar ratio of 1:1. For this synthesis of the mixed oxide, the calcium hydroxide was diluted in distilled water (200 ml) and then TiO_2 was added. The mixture was stirred for about 1 hour using a magnetic stirrer and the mixture was put in the sonicator at 60°C for 2 hours. After sonication, the sample was filtered out with filter paper to remove the excess water. Then, the sample dried at 105°C for 24 hours and it was then crushed using a pestle mortar followed by calcined at 750°C for 5 h in a furnace to produce $CaTiO_2$ and placed in an airtight container to avoid contact with CO_2 and H_2 O. WCOs were collected from the cafe. This oil was a dark yellow colour and has a foul odour, indicating that it had been used many times. WCO was undergoes a filtration process by using filter paper to remove medium size impurities in the oil until the oil getting clear and free from impurities.

Thus, WCO undergoes acid esterification, which reacts with lower alcohol like methanol in the presence of H_2 SO_4 as acid catalyst to reduce the acid and free fatty acid (FFA) values. The experiment was carried out using a triple neck round bottom flask set with a reflux condenser to avoid any loss of methanol. FFA conversion of WCO with methanol to oil ratio 9:1 and the esterification duration tested at 2 hours. A 1.5 g of concentrated H_2 SO_4 was poured into the beaker and mixed with 28.96 g of methanol. The solution was heated until the temperature reached 65°C. Thus, WCO were mixed into the solution at maintain temperature of 65°C, with a magnetic stirrer speed of 600 rpm and reaction time of 2 hours. The sample was placed into separation funnel to split the glycerol and treated WCO. The titration procedure was repeated to determine the amount of FFA in the triglyceride and the amount of

FFA should be less than 2%. Transesterification will be carried out after the esterification process if the percentage of FFA contained in the WCO is less than 2%. Treated WCO of 50 g was heated at 100°C and was left for 1 hour to evaporate the excess methanol and water. CaO catalyst was measured at 2.5wt% from the volume of WCO which is 1.25 g. The catalyst diluted with 14.43 g of methanol in the conical flask to form a methoxide solution. In addition, the condenser is applied to condense the vaporized methanol at a temperature of 65°C. The molar ratio of methanol to oil ratio is 9:1. The methoxide solution was mixed up using a magnetic stirrer with a speed of 450 rpm at a constant temperature of 65°C for 1 hour. After 1 hour, the WCO was poured into methoxide solution and mixed up at 1150 rpm, 65°C for 2 hours and 30 minutes. The experiment was repeated by using different molar ratios, which are 12:1 and 15:1. After the reaction time ended, the solution was poured into a separating funnel and left for 24 hours. In the separation funnel formed two layers into glycerol and biodiesel. The solution was filtered to remove the thick impurities, and the excess CaO powder.

3. Results and Discussion

The production of biodiesel was synthesized using CaO catalyst extracted from waste cockle and sea snail shells with additional nanoparticles of titanium dioxide (TiO_2) powder based on the molar ratio of alcohol to oil, catalyst loading, reaction time and reaction temperature. Several analytical techniques are employed to characterize the catalysts produced. Scanning Electron Microscopy (SEM) can be used to investigate the catalysts' surface morphology, particle sizes, and structure. On the other hand, Thermogravimetric Analysis (TGA) was used to characterize the thermal stability of the calcined CaO samples by measuring changes in their physicochemical properties, while Energy-Dispersive X-Ray Spectroscopy (EDX) was used to investigate the chemical compositions.

The results of TGA of raw cockle and sea snail shells in the initial stage (I) at temperatures below 540°C, the weight of shell samples decreased slightly by 3.963% and 5.912% respectively. In the second stage (II), at temperatures between 540 and 724.97°C, the weights of raw cockle shells decreased rapidly. The weight possesses a slight loss of approximately 43.178% from 540°C to 724.97°C, due to the decomposition of $CaCO_3$ to CaO and CO_2 . The weights of raw sea snail shells slightly lose approximately 43.318% from 543.76°C to 732°C. Rahman et al. [23] have reported that the substantial weight reduction symbolizes that the decomposition is completed at 780°C by releasing CO_2 simultaneously. In the final stage (III), at temperatures above 724.97°C and 732°C, the weight of cockle shell and sea snail samples remained almost constant. The weight loss of the cockle shell was slightly slower than that of the sea snail shell. From the results, a temperature of 900°C is selected to calcine the raw shells to investigate their changes in elemental composition and transformation of the crystalline phases of shells. Abdelhady et al. [24] determined that the catalyst should be calcined at a temperature above 700°C to transform $CaCO_3$ in waste shells to CaO.

SEM-EDX analysis was performed on each catalyst to ensure the catalyst formation of nanoparticles in their chemical composition and surface shape. The catalyst analysis confirmed the presence of calcium (Ca) from CaO and titanium (Ti) from TiO_2 . The elemental composition of the CaO from cockle shells with TiO_2 revealed that the percentage of Ca (2.02 wt.%) and O (44.52 wt.%) were lower than from of Ti (53.46 wt.%). Thus, the elemental composition of the CaO from sea snail shells with TiO_2 revealed that the percentage of Ca (26.09 wt.%) and O (42.31 wt.%) were higher than Ti (31.60 wt.%). Ca particles are distributed on Ti. Hence, it can be concluded that the presence of TiO_2 contributed significantly to the high catalytic activity observed during the transesterification of WCO. This also revealed a significant homogeneity of CaO with TiO_2 catalyst, which was visible from the value of Ti and Ca acquired from the EDX analysis. The morphologies of nanoparticles CaO/TiO_2 powder were determined by scanning electron microscopy (GEMINI SEM500). SEM images are taken with a resolution of 20000X. The sample was sputter-coated with platinum (Pt) to enhance the conductivity for better image resolution. Fig. 2 depict the SEM image of $CaO\text{-}TiO_2$ generated from the calcination–hydration–dehydration treatment of cockle and sea snail shells with TiO_2 . Both figures showed the formation of tiny aggregates particle (interconnected) particles of a calcined sample at a temperature of 750°C. The SEM images reveal that t combustion-derived CaO with TiO_2 powder has a honeycomb-like porous surface. The surface micrograph synthesized nano-catalysts revealed rough surface and fracture. Furthermore, the observed morphological natur grain shows the spherical shape of particles similar to the structure in pure CaO [25]. The image shows high por and the material is amorphous in nature and structure. A regular shape provides an advantage of having a interconnected regular pore distribution system.

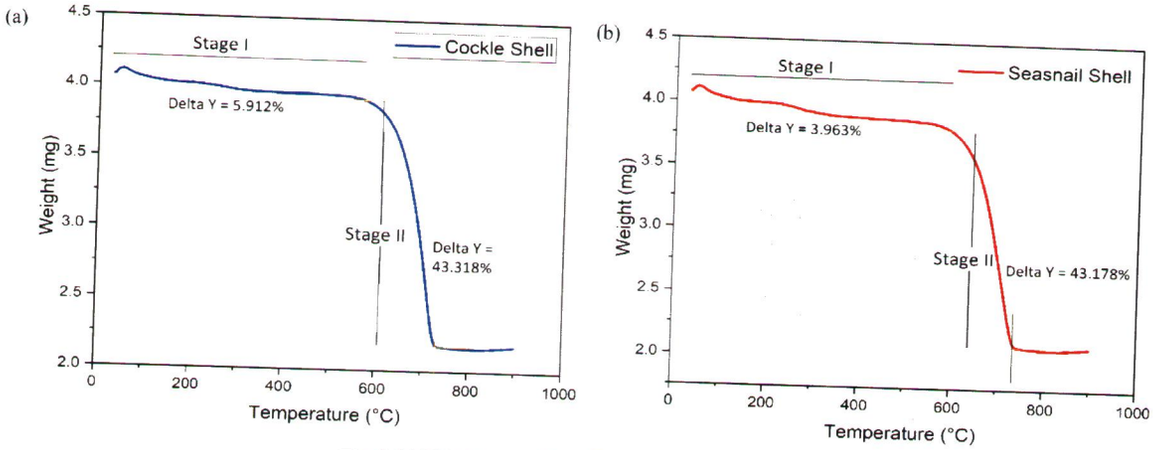

Fig. 1 (a) TGA Curve of Raw Cockle Shell (b) Sea Snail Shell

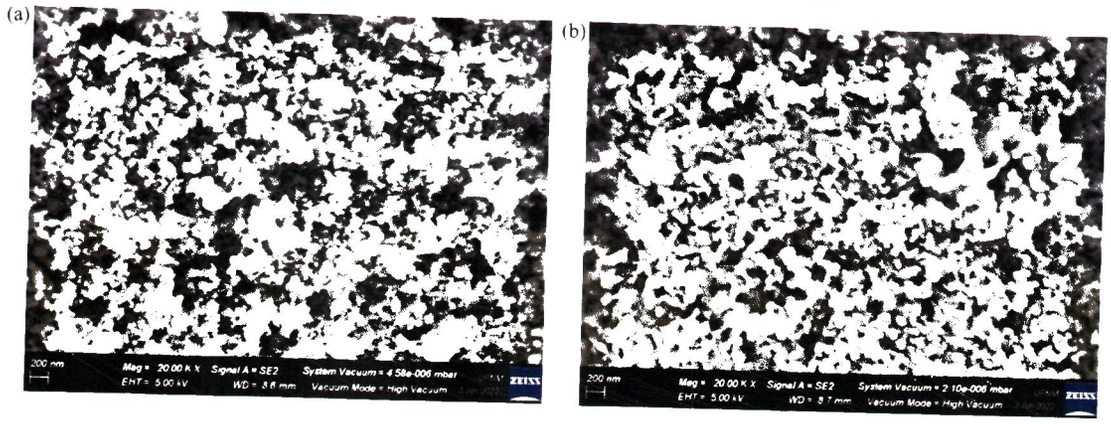

Fig. 2 (a) SEM Image of CaO Cockle Shell with TiO_2 ; (b) CaO Sea Snail Shell with TiO_2

Biodiesel yield by using heterogeneous catalyst using CaO and CaO-TiO_2 were observed on different effects including methanol to oil ratio, time of reaction and catalyst loading. Methanol to oil ratio is another factor that significantly contributes to biodiesel production's efficiency. In general, excessive methanol dosage leads the transesterification process toward biodiesel production in enhancing the efficiency of the transesterification process [17]. The effect of the methanol to oil ratio results for both catalysts are plotted in Figure 3 (a). The results showed that an increment in the methanol to oil ratio from 9:1 up to 15:1 increases the biodiesel conversion yield. It may be caused by the rate of reaction was accelerated when the amount of methanol increased [26]. Furthermore, this also can be due to the viscous nature of the fluid. Singh et al. [27] stated that by increasing the methanol to oil molar ratio, the viscosity of the reaction mixture decreases. This promotes better mixing between reactants and catalysts, which enhances the rate of mass transfer and this eventually promotes the catalytic activity during the reaction.

The reaction time experiment was varied into three parameters, which are 2 hours 30 minutes, 3 hours and 3 hours 30 minutes. The results obtained from this experiment were presented in graph reaction time against yield biodiesel in hours, as shown in Figure 3 (b). Overall, biodiesel yield increases gradually with reaction time during transesterification for both CaO and CaO-TiO_2 catalysts. At 150 minutes, the highest yields were obtained, which were 87.74% with CaO catalyst and 93.34% by CaO-TiO_2 catalyst. The reaction was slow at first, during 30–60 minutes, due to insufficient stirring time to enhance proper mixing and dispersion of the catalyst and methanol in the vegetable oil [28]. The interaction between the phases increased starting from 90 until 150 min due to adequate stirring time, which also enhanced the reaction rate. Furthermore, the transesterification reaction can remain for a longer time mainly due to the evaporation of methanol in the reaction mixture because it was carried out at maximum temperature (65°C). This phenomenon maintained the temperature without increasing dramatically by some cooling on the surface of the reaction mixture. The TiO_2 electrons migrate to the catalyst surfaces, which

induces the reduction of CaO catalyst, resulting in the increase of catalytic activity [29]. As a result, transesterification of CaO-TiO_2 catalyst produced more biodiesel. Because of the reversible reaction, it was expected that the excess reaction rate after 150 minutes would result in a slight reduction in biodiesel yields. In this study, the optimum reaction time for CaO and CaO-TiO_2 catalysts was determined to be 150 minutes. By adding TiO_2 to the surface of CaO improved the catalyst ability and increased the biodiesel yield over a longer reaction time.

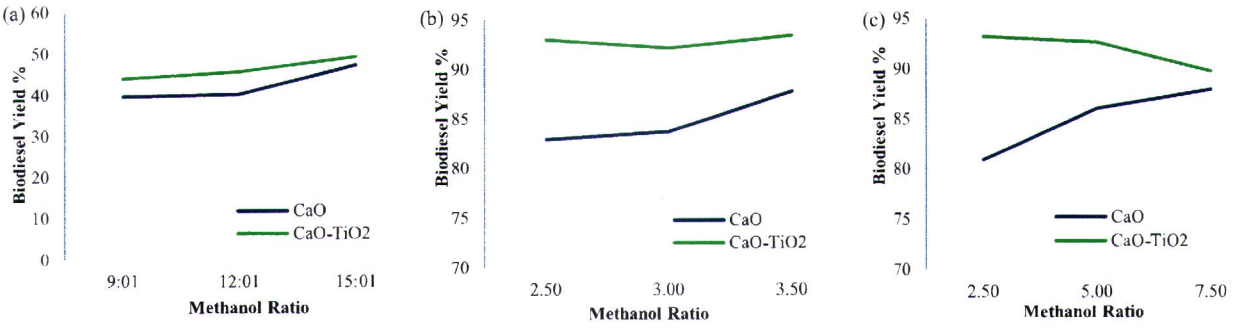

Fig. 3 (a) Methanol to Oil Ratio against Biodiesel Yield, (b) Reaction Time against Biodiesel Yield and (c) Catalyst Loading against Biodiesel Yield

The final experiment observed biodiesel yield by varying the catalyst loading by 2.5 wt.%, 5.0 wt.%, and 7.5 wt.%. The results obtained from this experiment was presented in graph catalyst loading against yield biodiesel, as shown in Figure 3(c). The yield increased with increasing catalyst loading from 2.5 to 7.5 wt.% loading for transesterification reaction with CaO catalyst. Meanwhile, the yield decreased with increasing catalyst loading for transesterification reaction with CaO-TiO_2 catalyst. According to Kouzu et al. [30], even at low catalyst concentrations, the nano CaO catalyst with high basic strength[(a)] can expedite the transesterification of oil feedstock. In general, increasing the catalyst amount increases the biodiesel yield because it increases the number of active sites available on the catalyst surface for transesterification while accelerating the reaction in the forward direction [31]. However, depending on the feedstock and reaction conditions, there is an optimum amount of the catalyst. The highest biodiesel yield with CaO catalyst and CaO-TiO_2 catalyst was 87.88% and 93.19%, respectively. It was found that the optimal catalyst loading was at 2.5%, but the decreasing yield of biodiesel was observed with a further increasing amount of catalyst by using CaO-TiO_2 .

4. Conclusion

In conclusion, the conversion of biodiesel from WCO by TiO_2 impregnated CaO as a heterogeneous catalyst that produced by waste cockle and sea snail shells. The primary objective of converting the WCO into biodiesel using a heterogeneous catalyst with the addition of TiO_2 nanoparticles by transesterification process. The methanol to oil ratio of 15:1 is the ideal ratio for conversion of biodiesel by both CaO and CaO- TiO_2 catalysts, which are 99.52% and 99.67%, respectively. Moreover, the average time reaction of biodiesel production is 150 minutes, equivalent to two and half hours. So, the usage of the heterogeneous catalyst with addition nanoparticles of TiO_2 improved the biodiesel yield efficiently.

Acknowledgements

The authors would like to thank National Defence University of Malaysia, Malaysia for providing the Short Term Research Grant (J0234 - UPNM/2020/GPJP/TK/10) for the financial support and facilities.

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