Optimization of Biodiesel Production over Alkaline Modified Clay Catalyst

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The demand for energy and its resources is increasing daily due to the rapid outgrowth of population and urbanisation. Petroleum is a non-regenerate source of energy. The increasing price of petroleum and environment concerns making the search for alternative renewable fuels is gaining considerable attention. Biodiesel is among the most promising alternative fuel to replace petroleum-based diesel. In this work, biodiesel was produced via transesterification of palm oil with methanol in the presence of heterogeneous catalyst alkaline based clay KOH/MK-10. The surface and structural properties were measured via latest techniques of SEM and BET surface analysis. The characterisation of prepared catalyst showed that surface area and pore volume of modified clay decreased but the morphology of clay was observed as the same after potassium modification. The results showed that prepared KOH/MK-10 is highly active for transesterification reaction under optimized condition. The maximum conversion of triglyceride was noted 98% after 3 h of reaction at 60°C with a 15:1 molar ratio of methanol to palm oil and 3 wt % of the prepared catalyst.

Key Words
Clay, Alkaline catalyst, Biodiesel, Optimization, Montmorillonite

1. Introduction

Petroleum-based diesel is a very common fuel used by people around the world compared to biodiesel that is new to the users. The frequency of using biodiesel around the world is comparatively low because it is still new. However, the usage of biodiesel grew in the past decade because it is eco-friendly and derived from green raw materials. Besides, biodiesel will not emit dangerous components that can cause pollution to the environment. Compared to biodiesel, petroleum-based diesel emits dangerous pollutants such as carbon monoxide, SO\textsubscript{x}, and greenhouse and NO\textsubscript{x} gasses that can cause environmental pollution such as acid rain, ozone layer depletion, and global warming\textsuperscript{3}.

In the current scenario, it is not feasible to replace petroleum-based diesel with biodiesel due to its production cost and low efficiency compared to petroleum-based diesel. Further research is required to increase the efficiency of biodiesel and reduce its production cost. However, in future, biodiesel will definitely replace petroleum-based diesel\textsuperscript{2}. Biodiesel is really green and clean fuel, and this is why some countries are gradually implementing the policy of using biodiesel hoping that one day it will completely replace petroleum-based diesel. The gradual implementation of using biodiesel means that it is to be blended with petroleum-based diesel. The policy also encourages the frequent use of biodiesel by the consumers as part of the residents of mother Earth, who are responsible for protecting the environment as well as stabilising the price of petroleum-based fuels. Biodiesel is a very suitable candidate for an alternative of renewable biofuel for compression-ignition diesel engines. Besides that, compared to petroleum middle distillates, biodiesel has superior cetane number and lubricity characteristics with the comparable heat of combustion and kinematic viscosity values. Furthermore,
biodiesel is non-flammable and thus it is safer to store and handle.

Transesterification process can speed up by using a catalyst in converting triglycerides to biodiesel, which is a reversible reaction. There are six different methods to produce biodiesel, which include supercritical process, ultra and high shear in-line and batch reactors, ultrasonic reactor method, lipase-catalysed method, volatile fatty acids from anaerobic digestion of waste stream and hetrom or homogeneous catalytical conversion via acid or base catalyst. Compared to the solid acid with a base catalyst, the solid-base catalyst is not being used very frequently in the industries after over 40 years of investigation on solid-base catalyst. In fact, solid acid catalysts have greater advantages over the solid-base catalyst. Therefore, their utilisation in the industry is higher than solid-base catalysts. For biodiesel process, solid-base catalysts have a sensitivity issue with free fatty acid (FFA), esterification, and transesterification reactions that often occur simultaneously during the production of biodiesel. On the other hand, acid catalysts do not have any sensitivity issue comparatively but the capability to minimise the corrosion problems even in the presence of acid species during chemical reactions.

The solid-base catalysts also have some advantages. They have a shorter reaction time and higher activity compared to solid acid catalyst. As acidic catalysts can be easily poisoned and then they cannot perform proper activities because they may not start interaction with heteroatoms (i.e. oxygen, nitrogen, sulfur, phosphorus, chlorine, bromine, and iodine) vigorously. Meanwhile, basic catalysts act as efficient catalysts due to their rare interaction with heteroatoms. Besides that, the use of the solid-base catalyst during the transesterification process lowers the risk of polluted water and chances to operate a continuous process since it eliminates the quenching step to isolate products.

Process optimization is one of the most important disciplines in a processing system. Without violating some constraints, process optimization adjusts a process to optimize some specified set of parameters. Generally, the goals are to minimise cost, increase efficiency, and maximise throughout. In this project, sets of parameters will be optimized in order to get the highest yield of biodiesel.

2. Experimental

2.1 Materials

Sodium hydroxide (99%) was purchased from BDH, UK. Montmorillonite K-10 was supplied by Sigma-Aldrich. AlCl3.6H2O was purchased from R&M Chemicals, Ltd., Malaysia. All the received chemicals were used without any further purification.

2.2 Preparation of KOH/MK-10

A 250 mL round bottom flask equipped with a reflux condenser was charged with 10 g of Montmorillonite MK-10 clay, 100 mL deionised water and an amount of KOH solution. This mixture was stirred and heated at reflux for 6 h. The slurry was then allowed to cool at room temperature. The solid was separated from the liquid by centrifugation. The liquid portion was decanted and discarded. The solids were washed by suspending again in 500 mL of deionised water and centrifuging. This sequence was repeated two more times to ensure the removal of all soluble species. The base modified clay (KOH/MTK10) was calcined in an oven at 450°C for 4 h.

2.3 Characterization

The base strengths of the catalysts (H_) were determined using Hammett indicators. About 25 mg of the catalyst sample was shaken with 5.0 mL of a solution of Hammett indicators duluted with methanol and left to equilibrate for 2 h. After the equilibration, the colour on the catalyst was noted. The following Hammett indicators were used: neutral red (H_ = 6.8), bromthymol blue (H_ = 7.2), phenolphthalein (H_ = 9.3), 2,4-dinitroaniline (H_ = 15.0), 4-chloro,2-nitroaniline (H_ = 15.0) and 4-nitroaniline (H_ = 18.4). The N2 adsorption-desorption isotherms were measured using a Belsorp II system at -196°C. The samples were degassed at 300°C for 4 h prior to analysis. The Brunauer-Emmett-Teller (BET) surface area was calculated using adsorption data in a relative pressure ranging from 0.04 to 0.20. The total pore volume was determined from the amount adsorbed at a relative pressure of about 0.99. The pore diameter was calculated from the adsorption branch by using the Barrett-Joyner-Halenda (BJH) method. Scanning electron microscopy (SEM) analysis measurements were performed using a Zeiss Supra 35VP equipment operated at 3.00 kV.

2.4 Product Analysis

A three neck bottle flask (500 mL) equipped with a reflux condenser, temperature indicator, and mechanical stirrer was used for transesterification of palm oil as shown in Fig. 1. The reactor was placed in a controlled water bath heater. The amount of catalyst to be added to the known volume of methanol was 1, 2, 3, and 5 wt %.

After that, the mixture was heated to desired temperature (20-80°C) in a controlled temperature water bath. Then, palm oil was added to the mixture under vigorous stirring of 500 rpm. The molar ratios of
palm oil to methanol used are 1:1, 1:5, 1:10, and 1:15. The transesterification reaction time was carried for 1-8 h.

The experiment was repeated using a set of general values; a reaction temperature of 60 °C, oil to methanol ratio of 1:10, and reaction time of 3 h with 3 wt% of the catalyst. For example, the experiment started by changing the reaction time from 20 to 80 °C while the other three parameters remained constant to find out the optimum temperature to produce biodiesel. After that, the experiment was continued by changing the other three parameters to find out the optimum oil to methanol molar ratio, reaction time, and catalyst amount to produce biodiesel. A number of 16 sets of experiments were completed. After the completion of the reaction, the product was taken out and the catalyst was separated using centrifugation. After that, the product was poured into a separation funnel and left for settlement. Two layers were formed, where the upper layer was observed as biodiesel and the lower layer was glycerine. The biodiesel layer was separated and weighed.

Afterward, a relatively small amount of biodiesel was tested for gas chromatography in order to determine the wt % of FAME in the biodiesel. The above process was repeated for the remaining sets of experiments. The graphs of biodiesel yield versus reaction temperature, reaction time, oil to methanol molar ratio, and the amount of catalyst were plotted to show the value of optimum parameters for the production of biodiesel. For variable parameters in all experiments, the reaction conditions were maintained as follows; methanol/oil molar ratio; 6:1 to 18:1, catalyst amount; 1 to 5 wt%, reaction time; 1 to 7 h and reaction temperature; 20 to 80 °C.

3. Results and Discussion

3.1 Morphology of clay and modified clay KOH/MK-10

The SEM images illustrate that there is no change in the morphology of both samples. However, some aggregative and massive appearances were found over MK-10 clay surface after modification with potassium. Fig. 2 shows the comparison between scanning electron micrograph images of parent MK-10 and KOH/MK-10. This figure exposed that the majority of the particles in both samples had a lamellar morphology with a composition similar to 21 phyllosilicate that corresponds with the mica phase. It can be seen that the modified sample had mostly similar morphology to the parent clay consisting mainly of flake-like particles corresponding to a layered structure of clay K-10. It is also clear that the surface texture of KOH/MK-10 was different and somewhat rougher than that of the parent clay. In conclusion, layered nature of clay MK-10 seemed to prevail.
after basic modification over it

3.2 Surface properties of clay and modified clay MK-10

The surface properties of parent and modified KOH/MK-10 were also observed and some changes were found in the surface area and pore size. In addition, the basic strength of prepared KOH/MK-10 was highly improved. Table 1 illustrates the basic strength, BET surface area, and pore volume of clay MK-10 and modified KOH/MK-10 after calcination at 450°C. As clearly noted, the basic strength of clay K-10 that is normally at 4.6 < H_+ < 7.2^10 was increased after the preparation of KOH/MK-10 to a value of 9.3 < H_+ < 15.0 after its potassium was modified.

Table 1 The surface properties of clay MK-10 and modified clay KOH/MK-10

| Properties               | MK-10   | KOH/MK-10 |
|--------------------------|---------|-----------|
| Surface Area (m²/g)      | 218     | 173       |
| Pore Volume (cm³/g)      | 0.39    | 0.32      |
| Pore Size (Å)            | 51      | 43        |
| Basic Strength (H_+)     | 4.6 < H_+ < 7.2 | 9.3 < H_+ < 15.0 |

The acidic or basic nature of montmorillonite structure mostly depends on its specific character of having combined water (structurally bound OH form or loosely bound H₂O). It was obvious that the base modification neutralises most of the acid sites within the clay and replaces them with their conjugate basic sites (O-) and impregnates the clay with cations ^11^). It is clear from this table that surface area and mesoporosity of prepared KOH/MK-10 decreased slightly after modification with potassium. A similar behaviour was noted with the pore volume and pore size of MK-10 and modified KOH/MK-10 clay catalyst. The BET surface areas of MK-10 and KOH/MK-10 were recorded as 218 and 173 m² g⁻¹, respectively. It is clear from this table that after modification with potassium both the surface area and pore diameter were found slightly decreasing. This might be due to the presence of potassium compound in the core-mesoporous area of prepared material. The same clay behaviour was also observed by the previous researcher ^12^). The modified clay was passed through different processes during its preparation. It might be possible that some portions of the layered structure of this prepared clay become block or demolish during the potassium modification treatment. Therefore, it might cause the decrease of surface area and pore volume value of prepared clay after its modification.

3.3 Influence of methanol/oil molar ratio on conversion

The transesterification reaction requires 3 moles of methanol to produce 3 moles of FAME and 1 mol of glycerol. Transesterification is a reversible reaction, thus excess methanol is required to drive the reaction towards the product. The graph of FAME yield % versus methanol/oil molar ratio over KOH/MK-10 clay catalyst is shown in Fig. 3. The yield of FAME was found to increase with the increasing molar ratio from 3:1 to 15:1. However, on further increasing ratio 18:1, the yield was found to decrease. This may happen due to the fact that an excess methanol feed is only effective to a certain extent as also reported by previous researchers ^13^). The maximum yield was observed 98% at molar ratio 1:15. It can be concluded from this figure that a very low and high methanol/oil molar ratio affects the yield of FAME while 1:15 is suitable for the high yield of FAME over prepared KOH/MK-10 clay catalyst. The reaction condition was 3 wt%, time of 3 h, and temperature of 60 °C.

![Fig. 3 Influence of methanol/oil molar ratio on yield of FAME %](image-url)
3.4 Influence of catalyst amount on conversion

The yield of biodiesel was increased with the increase of catalyst amount from 1 to 5 wt% as shown in the Fig. 4. The amounts of catalyst was used as 1, 2, 3, 4, and 5 wt%. The other reaction conditions were maintained as mentioned in experimental section.

The highest yield was noted 98% when catalyst amount was added 3 wt%. However, the biodiesel conversion was decreased with further increase of catalyst amount. This is most probably due to the formation of slurry that is a mixture of catalyst and reactants. It was due to mixing problem and higher power consumption demand for adequate stirring that was also highlighted by previous researchers. Hence, it can be concluded that suitable amount of KOH/MK-10 clay catalyst for optimum yield of FAME in this reactor during biodiesel production.

3.5 Influence of reaction time on conversion

The graph of FAME yield percentage for biodiesel versus reaction time is shown in Fig. 5. It is clear from this figure that the conversion increased for the first 3 h and then slightly decreased on further increasing reaction time after 3 h. The reaction times for yield were recorded for 1, 3, 5, and 7 h. The other reaction conditions were maintained as; methanol/oil ratio of 15:1, catalyst amount of 3 wt%, and a reaction temperature of 60 °C. The highest conversion was observed 98% at the reaction time of 3 h. The biodiesel yield was found to be decreasing slightly after 3 h. This decreasing trend might be due some side reaction that occurred after this time period of reaction.

It can be concluded that the feasible reaction time for transesterification over KOH/MK-10 clay catalyst is 3 h because further increasing reaction time may not affect any drastic changes in the yield of FAME for biodiesel production. However, slight reduction in conversion was noted at 5 h and after 5 h that might belong to some of side reactions. Therefore, 3 h of reaction time was considered as a suitable time for transesterification over KOH/MK-10 clay.

3.6 Influence of reaction temperature on conversion

Fig. 6 shows the graph of FAME yield % versus reaction temperature over KOH/MK-10 clay catalyst. The range of reaction temperature of catalyst used was 30 to 80 °C, while other reaction conditions were maintained as...
Fig. 6  Influence of reaction temperature on yield of FAME %. Reaction conditions: molar ratio 1:15; catalyst amount 3 wt%; reaction time 3 h

mentioned in the experimental conditions. It is clear from this graph that the reaction for biodiesel production started at above 30 °C and then the FAME yield continuously increased until 60 °C.

At this point, the FAME yield was observed at maximum 100% and this stability in yield was found up to 70 °C. While the temperature was increased further from 70 to 80 °C, a decrease in FAME yield was noted. The elevation of temperature of reaction increased the rate of transesterification reaction and hence increased the yield of biodiesel up to a certain extent.

The yield of FAME percentage decreased after the temperature was increased to more than 70 °C that might be due to temperatures higher than boiling point of methanol. According to Zabeti and his research group, when the temperature reached the boiling point of methanol, bubbles were formed which prevented the mass transfer on the phase interface and decreased the yield percentage of biodiesel [15]. Hence, the feasible reaction temperature for transesterification reaction over KOH/MK-10 clay catalyst is 60 °C because further increasing reaction temperature may affect mass transfer on the phase interface and cause a decrease in the yield of FAME.

4. Conclusion

The alkaline based KOH/MK-10 clay was used as a catalyst for the production of FAME using palm oil via transesterification process. The morphology of this prepared clay catalyst was observed as the same after potassium modification. However, the surface area and pore volume were found to be decreased. It was noted that KOH/MK-10 clay is an active catalyst for this process. The maximum FAME yield observed was 98 wt % at 60 °C with methanol/oil ratio of 15:1, the catalyst of 3 wt%, and reaction time of 3 h.

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