OPTIMIZATION OF BIODIESEL PRODUCTION PROCESS OVER SOLID BASE CATALYST

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by

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Dissertation submitted in partial fulfillment of
the requirements for the
Degree of Study (Hons)
(Chemical Engineering)

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CERTIFICATION OF APPROVAL

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Approved by,

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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TEE WEI HENG

ABSTRACT

Energy demand and its resources are increasingly day by day due to the rapid outgrowth of population and urbanization. Petroleum is a non-regenerate source of energy. The increasing price of petroleum and the environment concerns the search for alternative renewable fuels is gaining considerable attention. Biodiesel is among the most promising alternatives fuels to replace fossil fuel. In this work, biodiesel production is by transesterification of palm oil with methanol in the presence of heterogeneous catalyst which are modified KOH/MK-10 clay and MK-10 clay. This is an economic and environmental friendly reaction because the raw material and alcohol used are economical. The prepared catalyst is environmental friendly and economic because the catalyst is recyclable and very low cost. Besides that, reaction parameters of transesterification are optimized to have the highest biodiesel yield. The biodiesel yield is dependence on the reaction parameters such as molar ratio of palm oil to methanol, catalyst amount, reaction time, and reaction temperature. MK1-0 clay showed very low efficiency for biodiesel production that is 20.4% while modified KOH/MK-10 clay showed very high yield for biodiesel production process that is 70.5%. Both of the reactions using MK-10 clay and KOH/MK-10 clay catalysts achieved maximum biodiesel yield under the optimum reaction parameters such as palm oil/methanol molar ratio (1:15), reaction time (2 hours), reaction temperature (60°C), and catalyst weight (2wt%).

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

In the past few decades, research interest in alternative and renewable energy sources have been a hot topic due to depleting of fossil fuel resources because energy consumption by the nations has increased rapidly. After researches for few decades, biodiesel is among the most reliable biofuels that can be used to replace petroleum based diesel where it can be produced through a variety of methods.(Gerald S. Macala, 2008)

Biodiesel has also become a hot global issue since the past decade to replace the traditional fossil fuel as the storage of fossil fuel is depleting since the first day fossil fuel is being explored and is used in a very fast rate to generate energy in order to satisfy the energy consumption rate around the world. Since large consumption of energy has triggered the price of fossil fuel, biodiesel as an alternative renewable fuel can stabilize the price of fossil fuel. Biodiesel is mostly produced from straight vegetables oil, animal oil or fats through transesterification using alcohol in the presence of a catalyst and it is a renewable fuel that consists of fatty acid methyl esters (FAME).

Petroleum based diesel is a very common fuel used by the people around the world compared to the biodiesel that is new to the world. The frequency of using biodiesel by the people around the world is comparatively low because it is still new. However, the usage of biodiesel is growing in the past decade because biodiesel is environmental friendly and biodiesel is derived from environmental friendly materials. Besides that, biodiesel will not emit dangerous components that will cause pollution to the environment. Compare to biodiesel, petroleum based diesel will emit dangerous pollutants such as carbon monoxide, SO_x, greenhouse gases, and many more that will cause pollution to the environment such as acid rain, depletion of ozone layer, global warming and many more.

We can see that biodiesel is getting more and more popular in the world especially in the European countries because of their environmental policy to decrease pollution of the environment to the minimal. They realize that they are one of the residents of the Earth and they need to be responsible to take care of the mother Earth. The mother Earth is now moving towards to the edge of dying because of the pollutants created by human activities. In order to develop a nation, human need to use a lot of energy from the natural resources and thus tons and tons of pollutants are emitted and make the mother Earth sick. Developing a nation is just like a double edge sword, while developing the nation, the environment is polluted. However, human realized the cause and effect behind the development of the nation. Hence, in order to have a sustainable and clean environment, countermeasures are being developed and one of the countermeasures is biodiesel.

To replace petroleum based diesel with biodiesel immediately is not possible for the time being because efficiency of biodiesel is still low compared to petroleum based diesel. Many works need to be done in order to increase the efficiency of biodiesel. However, biodiesel will definitely replace petroleum based diesel in the future. Biodiesel is really a green and clean fuel and that is why some of the countries are implementing the policy of using biodiesel step by step and hopefully one day that biodiesel will replace petroleum based diesel completely. The meaning of implementing the use of biodiesel step by step is to blend the biodiesel with petroleum based diesel. The policy also encourage the popularity of using biodiesel, be part of the residents of the mother Earth to be responsible to protect the environment, and also to stabilize the price of petroleum based fuels.

The biodiesel materials are mono-alkyl esters of fatty acids which are derived from vegetable oils or animal fats. Biodiesel is a very suitable candidate of alternative renewable biofuel for compression–ignition diesel engines. Besides that, compare to petroleum middle distillates, biodiesel has superior cetane number and lubricity characteristics with comparable heat of combustion and kinematic viscosity values. Furthermore, biodiesel is non-flammable and thus it is safer to store and handle.

Mono-alkyl esters can be blending with gas oil for use as fuel in diesel engines especially mono-methyl esters. (Ebiura, Echizen, Ishikawa, Murai, & Baba, 2005). Malaysia government has implemented the B5 few years ago. B5 is the blending of 5% of biodiesel with 95% of petroleum diesel. In 1st November 2014, Malaysia started to implement B7 where 7% of biodiesel will be blended with 93% of petroleum diesel. Currently, Malaysians are using B7 diesel. From the effort of implementing the blending of biodiesel with petroleum based diesel, Malaysia is trying its best to promote the use of biodiesel, to increase the marketability of biodiesel, and also to reduce the reliance on petroleum based diesel.

Transesterification process can be speed up by using catalyst in converting triglycerides to biodiesel and it is a reversible reaction. (Meher et al., 2004). There are five methods to produce biodiesel which included supercritical process, ultra and high shear in line and batch reactors, ultrasonic reactor method, lipase-catalyzed method, and volatile fatty acids from anaerobic digestion of waste stream.

Compare to solid acid catalyst, solid base catalyst is not been used so frequently in the industries after an over 40 years of investigation on solid base catalyst. (Hattori, 2010). The reasons that solid acid catalyst is used more frequently than solid base catalyst are that solid base is insensitive to free fatty acid (FFA), esterification and transesterification reactions occurred simultaneously, and lastly the corrosion problems minimized even in the presence of acid species (Lee, Bennett, Manayil, & Wilson, 2014).

Compare to solid acid catalyst, solid base catalyst has faster reaction and higher activity (Boz & Kara 2009). It is because acidic catalysts became poisoned, and exhibit no activities since it interacted with heteroatoms vigorously. While basic catalysts act as an efficient catalysts because it rarely interacted with heteroatoms (Hattori, 2010).

Heteroatoms are any atom that is not carbon or hydrogen. Examples for heteroatoms are oxygen, nitrogen, sulfur, phosphorus, chlorine, bromine, and iodine. Besides that, the using of solid base catalyst during the transesterification process will lower the risk of polluted water and the chances to operate a continuous process since it eliminate the quenching step to isolate products (Watkins et al. 2004).

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

1.2 Problem Statement

In the epoch of globalization, advanced nations are trying to become one of the greatest nations in the world while the developing nations are trying to become a more advanced nations. The result of this phenomena is that the energy consumption for the nations increased rapidly ever since, which means fossil fuels is depleting in a very fast rate. Depletion and diminishing of fossil fuel has triggered the crisis of fossil fuel price and also caused many environmental issues such as ocean acidification, global warming, oxygen depletion, extreme weather, and cryosphere.

Due to the tremendous demand of energy over the century, price of fossil fuel has fluctuated in an abnormal way and disturbed the flow of the global market because price of fossil fuel will triggered all the other prices for example price of raw materials. It is because raw materials needed to be transported to the required nations and it needs fuel to transport them. When the fuel price increased, the price of raw materials will eventually increase and this can be regarded as the domino effect. Hence, it is necessary to find an alternative energy in order to replace fossil fuel to counter the energy crisis and biofuel is one of the most promising alternative and renewable energy to replace fossil fuel.

The major drawback would be the high production cost of producing biodiesel due to expensive cost of palm oil extraction and also high expenses spent in waste water treatment as large amount of industrial water will also be produced if not using the suitable catalyst. Besides that, homogeneous catalysts are used more frequent than heterogeneous catalysts in the production of biodiesel. However, use of homogeneous catalyst will increase the overall production cost of biodiesel production because formation of soap will occurred during the reaction and hence a large amount of hot water needed to treat and wash the product. In order to overcome this weakness, heterogeneous can be used as no soap will formed during the reaction.

1.3 OBJECTIVE AND SCOPE OF STUDY

The objective of this project:

- To optimize the transesterification reaction for biodiesel production through economic and environmental friendly reaction using solid base catalyst.
- The analysis of different parameters of transesterification reaction for optimization such as molar ratio of oil to alcohol, reaction temperature, reaction time, and catalyst amount.
- To determine the highest biodiesel yield via optimized reaction condition.

The solid base catalysts used are solid clay base catalyst KOH/MK-10 clay and MK-10 clay. KOH/MK-10 clay is where potassium hydroxide is loaded with Montmorillonite K-10 clay. The use of KOH/MK-10 clay and also MK-10 clay for transesterification reaction to produce biodiesel is very rare and it is a very interesting thing to study.

The alcohol that is going to use is methanol because methanol can react quickly with triglycerides as methanol is polar and has shortest alcohol chain and it is cheap (Romero, Marinez, & Natividad, 2011). Edible palm oil is used as the source of triglycerides because Malaysia is rich in palm oil resources and it is very easy to access for the feedstock. The scope of study of this project is the study of optimization of biodiesel production process through economic and environmental reaction, and effects of molar ratio of oil to alcohol, reaction temperature, reaction time, and catalyst amount to the yield of biodiesel.

CHAPTER 2

LITERATURE REVIEW

Over these few decades, fossil fuel reserves are depleting in a fast rate due to continue usage and the rising price of crude oil have triggered the energy crisis all over the world. However, in order to overcome this problem, biomass which is derived from renewable materials has become a new alternative of fuel to replace the traditional fossil fuels. Biodiesel or fatty acid methyl ester (FAMEs) which is derived from vegetables oil or animal fats is considered one of the best biomass-fuel to replace fossil fuel. Biodiesel is a renewable energy, lack aromatic compounds, highly biodegradable, and also has low SOx emission (Nyoman Puspa Asri, 2012).

(Mustata & Bicu, 2014) reported that oil, coal, and natural gases are the source of most of the organic chemicals and fuels in the past century. However, due to the depletion of fossil resources and oil price crisis, environmentally friendly and renewable sources in order to replace mineral oil are waiting for exploration and identification. Feedstock such as vegetable oils is source for chemicals and biodiesels. Vegetables oil is environmentally friendly because it has low toxicity and it is biodegradable and it can be obtained in large quantities.

Biodiesel has gained the attention internationally as an alternative fuel since it is highly biodegradable, no toxicity, and low emission of carbon monoxide, and other harmful components. Biodiesel is a mixture of methyl alkyl. Biodiesel can be used as fuel, heating oil and it also can be used in conventional compression ignition engine almost without modification. (Al Zuhair, 2007; Vicente et al., 1998).

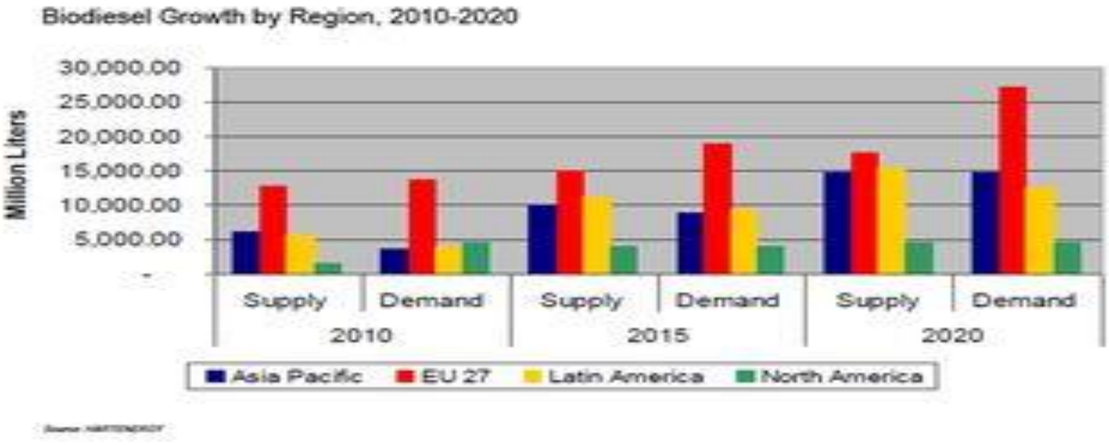


Figure 1: Biodiesel growth by region from 2010 to 2020.

From the graph above, we can see that the biodiesel growth is increasing from year to year especially in European countries because their awareness to the environment is higher compared to others. However, the data from the graph is just merely for the sake of assumption, the demand of biodiesel is just to cope with the supply of biodiesel since biodiesel still cannot replace petroleum at the moment and the price of biodiesel is expensive compared to fossil fuel petroleum.

Global warming will cause many problems such as ice melting in the North and South poles and eventually the sea level will increase and might deluge the low sea level countries. Looking at all these problems, biodiesel might be the answer to the environmental issues and the depleting fossil fuel since biodiesel is a renewable fuel and regarded as the green fuel.

One of the major advantages of biodiesel as the alternative renewable fuel is that it can act as the stabilizer of the fossil fuel price market. Countries such as Malaysia have implemented B7 in 2014 while European Union (EU) implemented B7 in 2009, Indonesia implemented B7.5 in 2012, and even Columbia implemented B8 and B10. The implementation not only can reduce the reliance on fossil fuel and stabilize the fossil fuel market, but also reduce the environmental issues.

The overall carbon dioxide emission can be decreased since biodiesel is manufactured from plants and obtained carbon dioxide from the air during photosynthesis. Besides that, biodiesel can also reduce the emission of greenhouses gases. The overall emission of carbon dioxide has been decreased by 78% when biodiesel is used through the life cycle analysis of biodiesel compared to petroleum based diesel fuel. (Gerald S. Macala, 2008)

We can see that biodiesel has such magnificent function to decrease the overall carbon dioxide emission by 78% and this is not a small amount. If all the countries in the world are using biodiesel, the overall carbon dioxide emission can be reduced by 78% and that meant biodiesel contributed a major part of reducing the greenhouse gases that caused global warming. Hence, it will be a great milestone for the Earth when the whole world is using biodiesel. Nevertheless, environmental issues will reduced significantly since biodiesel is a green, clean, and environmental friendly fuel compared to fossil fuels.

There are many advantages of using biodiesel which included non-toxic, biodegradable, zero sulfur content, and not harmful to the environment compared to petroleum diesel. The emission of SO_x and carbon monoxide will occur due to the high sulfur content in the petroleum diesel during the combustion in engine. SO_x are one of the components that caused acid rain. The use of biodiesel during the combustion in the engine will reduce the emission of gaseous pollutants such as carbon monoxide, aromatic & polycyclic aromatic hydrocarbons (PAHs) compared to petroleum diesel. Besides that, biodiesel will help to clean and smooth the engine, safer, more stable and also it has low oil consumption in engine.

However, there are also disadvantages of using biodiesel. The disadvantage included low efficiency compared to petroleum diesel, it will block the piston as low grade of biodiesel will cause oxidation and produce precipitate in the engine because of oxygen and excess water in the low grade biodiesel.

(Ghadge & Raheman, 2006) reported that is necessity to reduce the viscosity of biodiesel in order for the vegetable oils and fats to be compatible with diesel engine by breaking down the triglyceride bonds. Transesterification, blending, microemulsion, and pyrolysis are among the four ways to convert the oils and fats into biodiesel. (Myint & M, 2008) reported that transesterification is the most used method. Transesterification process is achieved by converting triglycerides with excess alcohol in the presence of catalysts to produce fatty acid methyl ester (FAME) and glycerin. The concentration of biodiesel is written as BXX when biodiesel is blended with petroleum based diesel. “XX” is referred to the percentage volume of biodiesel. For example, B90 is referred to 90% biodiesel and 10% petroleum based diesel while B100 is referred to 100% pure biodiesel.

(Myint & M, 2008) also reported the energy content of petroleum based diesel is higher compare to the energy content of biodiesel. The factor that affecting the energy content of biodiesel is the type of feedstock used to produce biodiesel. Petroleum based diesel almost don’t have oxygen content while pure biodiesel has around 10 to 12wt% of oxygen. The combustion of biodiesel in the engine will emit less particulate matter, carbon monoxide, and also hydrocarbons because the presence of oxygen allows the biodiesel to combust completely in the engine but will increase the emission of nitrogen oxides (NO_x) because of high oxygen content. The cetane number which is the ignition quality of the diesel fuel is the major reason that biodiesel is a promising alternative fuel for petroleum based diesel. Ignition delay is the time between the start of injection and start of ignition of the fuel. When the cetane number is higher, it will provide longer time for fuel combustion process to be done as it having shorter delays.

Vegetables oil such as palm oil, and Jathropa oil or animal fat can make biodiesel (Jayed et al., 2009). Biodiesel is one of the most promising alternative fuels to substitute diesel fuels (Zubir & Chin, 2010). Palm oil is the most potential raw material to produce biodiesel in Malaysia based on few criteria. One of the criteria is that Malaysia provided a potential accessibility to palm oil since Malaysia yielded average of 3.5 to 5 tons of palm oil per hectare per year. Biodiesel is regarded as the most suitable renewable fuel to replace fossil fuels in order to solve the energy and environmental related problems. During combustion in engine compared to petroleum diesel, biodiesel emits less gaseous pollutants such as carbon monoxide, aromatics and polycyclic aromatic hydrocarbons (PAHs) (Harrington, 1986).

(Mustata & Bicu, 2014) reported that biodiesel is mostly produced through transesterification of natural fats such as vegetable oils and animal fats in the presence of homogeneous alkaline or acid catalysts using alcohols such as methanol or ethanol at reflux temperature. Esters of fatty acids are the main reaction products along with other secondary environmentally unfriendly productions from transesterification reaction. The solution to the problem of environmentally unfriendly reaction products is using solid catalysts. The advantages of using solid catalysts are it is less soluble in the reaction mixture, easier to recover by filtration and it is less corrosive. The usage of homogeneous catalysts can be replaced by some more environmentally friendly catalysts such as barium hydroxide.

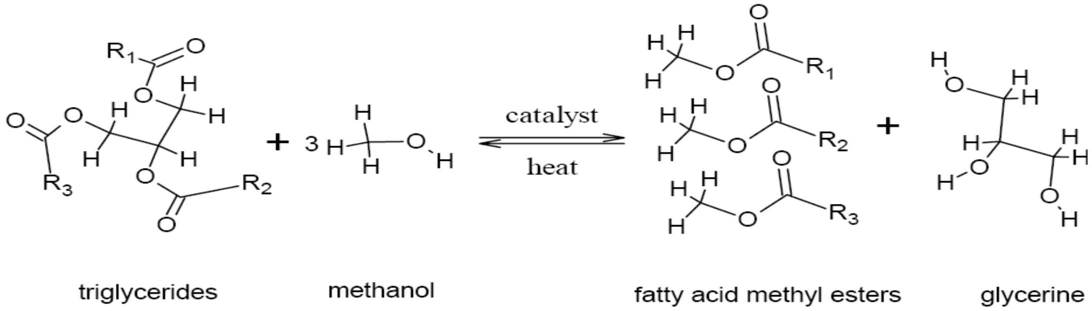


Figure 2: Transesterification reaction of triglyceride to FAME (fatty acid methyl ester)

Biodiesel is mostly produced through transesterification reaction of oil with alcohol in order to yield mono alkyl ester and glycerol in the presence of catalyst (Akgun & Iscan 2007). Homogeneous base catalyst such as potassium hydroxide and sodium hydroxide are usually used because these catalysts showed higher performance to obtain biodiesel. However, they also react with free fatty acid (FFA) to form unwanted soap by-products and expensive separation is required. Homogeneous acid-catalyzed process will corrode the equipment, toxic and need high cost to separate catalyst (Chai et al. 2007;Kiss et al. 2006). Homogeneous base catalyst such as KOH, NaOH, sodium methoxide, and potassium methoxide are traditional catalyst used in biodiesel production. However the use of these catalysts needed extra neutralization through mineral process, produced by-products, and large amount of water is required to separate and clean the catalyst and product (Nyoman Puspa Asri, 2012).

(Romero, Marinez, & Natividad, 2011) reported that by using homogeneous basic catalysts such as sodium hydroxide and potassium hydroxide that are dissolved in methanol, biodiesel can be successfully produced through transesterification using vegetables and animal fats. High activity and mild reaction condition are among the advantages of using homogeneous basic or acid catalysts. The homogeneous has high activity because the conversion can complete within one hour and has mild condition as the reaction temperature only range from 40°C to 65°C at atmospheric pressure. The disadvantages of using homogeneous catalysts are it can cause soap production, reduction of catalytic efficiency due to the catalysts are being consumed during the process, formation of gel, increase in viscosity, it is technically difficult to remove the catalyst after the reaction, and increase of overall process cost since a large amount of water is needed to separate and clean the products. Hence, the production cost of biodiesel is very expensive and cannot compare effectively to the cost of petroleum based diesel.

(Romero, Marinez, & Natividad, 2011) also reported in order to overcome the weaknesses of using homogeneous catalysts in biodiesel production, the development of heterogeneous catalysts can reduce the overall cost of biodiesel production using homogeneous catalysts. Besides that, soap will not produce when using heterogeneous catalysts through the free fatty acid neutralization and triglyceride saponification. Hence, the importance of efficient heterogeneous catalysts development is that it will create the chances of another pathway for biodiesel production. Variables such as oil to alcohol molar ratio, catalysts type, and reaction temperature will determine the efficiency of heterogeneous process.

Due to high activities of homogeneous base catalyst, potassium methoxide, potassium hydroxide, sodium hydroxide, and sodium methoxide are most used in the industrial process to produce biodiesel. Besides that, the advantages of homogeneous catalyzed reactions required shorter reaction time and less alcohol compared to heterogeneous catalyzed reactions (Moser, 2009). However, the vegetable oil needs to have acid value less than one and all material should be anhydrous (Kucek et al. 2007). Besides that, during the separation of homogeneous catalyst from the system during the product purification, waste water will be produced (Ma & Hanna, 1999).

Although converting triglycerides to FAME using homogeneous alkali catalyst with the advantages of producing high yield biodiesel, and required less time, but when come to separate the catalyst from the product mixture, it becomes very difficult. After transesterification, large amount of hot water is needed to neutralize or remove the catalyst and it will eventually produce large amount of industrial wastewater (Feng & Zhen 2011). Homogeneous catalysts have its own disadvantages which included they cannot be reused, complicated process of post treatment, and they produce large amount of waste water (Guo, Huang, Zheng, Li, & Huang, 2011).

Heterogeneous catalysts which are environmental friendly can replace homogeneous catalysts since homogeneous catalyst can cause many problems and increased production cost. Heterogeneous catalysts are also easier to separate and can produce pure high grade of glycerol with lower production cost (Di Serio et al. 2007). Heterogeneous catalyst is a very good alternative to produce biodiesel through transesterification because it overcomes the weaknesses of homogeneous catalysts. Reaction process using heterogeneous catalysts is expected to provide minimal effect on the environment (Nyoman Puspa Asri, 2012). In order to overcome the problems caused by homogeneous, heterogeneous catalysts have been investigated many times with respect to biodiesel production. In the end, it is suggested that use of heterogeneous catalyst can produce high yield of biodiesel (Ma, Li, Wang, Wang, & Tian, 2008).

To resolve the difficulties brought by homogeneous catalyst, a number of heterogeneous base catalysts have been developed to effectively catalyze transesterification and also can be easily removed from the reaction mixture (Liu et al., 2010). The advantages of using heterogeneous catalysts are that the catalysts are easily separated from the products. Hence neutralization steps and water washing process can be avoided. Contaminated water from the process will be reduced and eventually lower the sewage treatment fees (Feng & Zhen 2011).

Since homogeneous base catalysts such as sodium hydroxide for biodiesel production cannot be recovered or regenerated after the reaction and toxic wastewater will produced, heterogeneous solid catalyst is regarded as a substitution to homogeneous catalyst because heterogeneous solid catalysts are more environmental friendly after some studies. Heterogeneous solid catalysts are categorized into solid acid catalyst, solid acid catalyst, mesoporous silica support catalyst, and alkali support catalyst. Calcium oxide and calcined sodium silicate are a solid alkali catalyst that is used to prepare biodiesel. However, some of them are good while some of them still show lower performance compared to homogeneous catalysts in term of activity and yield of FAME. In the other hand, good catalytic activity shown in calcined sodium silicate in the first run but the catalytic activity decreased when the catalyst is used from more than five times. Besides that, CaO/mesoporous silica and sulfonated-multiwalled carbon nanotubes showed good catalytic activity for biodiesel production although they are difficult and expensive to prepare and their potential application is limited in large scale industrial operation (Soetaredjo, Ayucitra, Ismadji, & Maukar, 2011).

If the free fatty acids (FFA) content in the feedstock is more than 3 wt%, the base catalyzed transesterification reaction will not occur (Liu et al., 2010). Thus, the selection of feedstock must be very careful in determining the FFA wt% since this project is using solid base catalyst for the transesterification reaction.

High energy consumption, expensive separation of the catalyst from the reaction mixture and the purification of biodiesel fuel are among the disadvantages of homogeneous base catalyst transesterification. In order to minimize the cost of purification process, heterogeneous solid catalyst such as metal oxides, zeolites, hydroalcites, and γ-alumina have been used recently. Some of these catalysts are promising but some still have low performance compared to homogeneous catalyst in term of FAME yield and activity. The advantages of using heterogeneous are these catalysts can be separated easily from the reaction mixture and can be reuse. Most of these catalysts are alkali or alkaline oxides supported on materials with a large surface and they are more active than solid acid catalysts (Thanh, Okitsu, Boi, & Maeda, 2012).

Due to the diffusion limitations in three phases, heterogeneous transesterification rate of the reaction is lower than a homogeneous system. One of the ways is to use structure promoters or catalyst supporters to overcome this mass transfer problem. They can react with large triglyceride molecules by providing more specific surface area and pores for active species. (Zabeti et al. 2009). Different types of supports such as aluminium and zinc oxide have been used in the heterogeneous transesterification and they showed favorable support properties for alkali catalysts in biodiesel production process. The potassium hydroxide catalyst supported on palm shell activated carbon used in this work showed high performance to produce biodiesel from palm oil. (Saeid Baroutian, 2010)

The catalyst that is going to use is solid clay base catalyst which is lithium loaded with Montmorillonite K-10 clay, KOH/MK-10 clay and MK-10 clay. Potassium based catalyst formulations gave better yields than the sodium-based catalysts from the comparison at different molar ratio, concentrations, and reaction temperatures. (Singh, 2006). Potassium hydroxide is a homogeneous catalyst and it is widely used in transesterification of vegetable oils and it is a favorable catalyst in industries because of its low price and high activity. (Saeid Baroutian, 2010). However, potassium hydroxide also reacts with FFA to produce unwanted soap byproducts and it required high cost to separate (Chai et al. 2007;Kiss et al. 2006). But, by using modified MK-10 clay, the free fatty acid was effectively reduced. (Saeid Baroutian, 2010). Thus, the catalyst KOH/MK-10 clay is a good combination for transesterification of palm oil to produce biodiesel because MK-10 can reduce the FFA content to prevent KOH to react with FFA to produce unwanted soap byproducts while KOH will produce high biodiesel yield. Besides that, it also reduces the cost of production as expensive separation of catalyst is avoided.

Montmorillonite is chemically hydrated sodium calcium aluminium magnesium silicate hydroxide, $(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$. MK-10 clay can act as an efficient catalyst because of its natural occurrence and ion exchange properties and also it has both Bronsted and Lewis acidic catalytic sites. MK-10 clay is an efficient acidic catalyst in organic chemistry in these few years. There are few advantages using MK-10 clay for a number of organic reactions which included strong acidity, non-corrosive, cheap, mild reaction conditions, high yield, selectivity, easy to setup and working up. (Kaur & Kishore, 2012).

Besides that, MK-10 clay itself is a heterogeneous catalyst where the advantages of using heterogeneous catalyst as mentioned above. Furthermore, MK-10 clay can be recovered easily and reusable. Clays are also safe to handle, cheap, reusable, can prevent waste and promote atom energy. It also can decrease the activation energy of a reaction by stabilizing the transition state. Clay also can act as general acid or base and it is environmental friendly. (Kaur & Kishore, 2012).

It is found out that the active catalyst in the transesterification of canola oil with methanol is KF/Al_2O_3 where the highest yield is 99.6% with optimum parameters of 8hr reaction at 60, methanol/oil molar ratio of 15:1 and 3 wt% of catalyst. (Boz & Kara, 2009). The biodiesel reached the highest yield of 98.03% using potassium hydroxide catalyst supported on palm shell activated carbon. The optimum conditions to reach 98.03% yield are at 64.1°C, 30.3 wt% catalyst loading, and methanol to oil molar ratio of 24:1 with catalyst leaching of 0.53ppm. (Saeid Baroutian, 2010). By using potassium hydroxide as catalyst for transesterification of Jatropha Curcas oil, it was found that the optimum biodiesel yield was achieved at molar ratio of 1:16 and catalyst concentration of 1.5%. (Cut Aisyah Z Jamil, 2012).

(Wang, Chen, Huang, Chen, & Chen, 2012) reported that using soybean oil to produce biodiesel in the presence of Li_2CO_3. The effect of amount on the biodiesel yield has been studied. The conversion of biodiesel yield has been increased from 13.5 to 85.5% when the catalyst amount is increased from 0.5 to 8%. The yield of biodiesel increased because of the increment of the active sites as the contact opportunity between the catalyst and reactant has increased and eventually affected the reaction rate and conversion. However, the reaction will reached equilibrium and the biodiesel yield will kept constant when the catalyst amount added is in the range of 8 to 10 wt%.

(Wang, Chen, Huang, Chen, & Chen, 2012) also reported use of excess alcohol will increase the yield of biodiesel because transesterification is a reversible reaction. Besides that, types of catalyst use will determine the alcohol to oil molar ratio on the biodiesel yield. For example, the molar ratio of alcohol to oil is 6:1 when using KOH as a homogeneous base catalyst. The also reported that the stoichiometric molar ratio of methanol needed to be lower than the molar ratio is required to shift the equilibrium of the transesterification of the reaction since mass transfer and reactant adsorption on the catalyst were important for homogeneous catalysts. When the molar ratio of methanol to oil is increased from 6:1 to 24:1, the biodiesel yield increased from 22.4 to 94.4%. However, the biodiesel conversion rate is slowed down when the molar ratio of methanol to oil used is more than 24:1. In conclusion, the optimal biodiesel yield is 94.4 when the molar ratio of methanol to oil used is 30.1%.

However, (Wang, Chen, Huang, Chen, & Chen, 2012) also reported that the biodiesel yield using soybean oil as feedstock in the presence of Li_2O_3 catalyst decreased to 86.1% at methanol to oil molar ratio of 30:1 when using 8% of catalyst amount. The reason behind it is the decreasing of active basic sites. The chance of contacting of catalyst and reactant is lowered when the catalyst amount used is small. Thus, the biodiesel yield is relatively low as the progress of transesterification is not enough. Another parameter to affect the biodiesel yield is the reaction time of catalyst on soybean oil. The biodiesel yield increased constantly due to close attainment of equilibrium when the reaction time ranges from 0.5 to 2 hours. The yield of biodiesel achieved the maximum conversion after 2 hours of reaction time.

(Xue, Wang, Zhang, & Tang, 2013) reported biodiesel is produced using novel solid base catalyst by surface modification CaO with ethyl bromide. The parameters that affected the biodiesel production are catalyst amount, methanol to oil ratio, reaction temperature is investigated using modified CaO with 0.2% ethyl bromide. Besides that, other parameters that affected biodiesel production are catalyst particle size, agitation speed and also water tolerance over modified CaO.

(Xue, Wang, Zhang, & Tang, 2013) in their research of biodiesel production reported the biodiesel yield increased when the methanol to oil ratio is increased in the range from 3 to 30. The maximum biodiesel yield reached when the methanol to oil ratio is 15. However, too excess of methanol only slightly increased the yield. Amount of catalyst has a major effect on the biodiesel. When the catalyst concentration is 5 wt%, the biodiesel reached its highest yield without any mixing problem due to saponification. However, further increase of catalyst will not increase the biodiesel yield because the slurry became too viscous. Besides that, another parameter which is affecting the biodiesel production is reaction temperature. Generally, exothermic reaction prefers high reaction temperature. Thus, the boiling point of methanol is chosen as the reaction temperature. At reaction temperature of 65^{o}C, the biodiesel yield exceeded 95%. The optimum reaction conditions for the biodiesel production using novel solid base catalyst by surface modification are reaction time of 3 hours, molar ratio of methanol to oil of 15:1, 5 wt% catalyst, and reaction temperature of 65^{o}C.

Another parameter that affected the biodiesel production is the effect of particle size on the rate of reactivity. The investigation of the effect of particle size of catalyst is carried out under the optimum reaction condition after 3 hours. When the particle size decreased, the yield of biodiesel increased. The highest biodiesel yield reached 96.8% when the particle size is smaller than 0.07mm. When the particle sizes range from 0.07 to 0.09mm, basically the biodiesel yield has not much difference. Besides that, the lowest yield of biodiesel is 70.1% when largest particle size is used. (Xue, Wang, Zhang, & Tang, 2013).

(Xue, Wang, Zhang, & Tang, 2013) also reported the effect of agitation speed on the yield of biodiesel under the optimum reaction conditions using alcohol in the presence of modified CaO catalyst which are 65^oC reaction temperature, 5 wt% of modified catalyst, molar ratio of methanol to oil of 15:1, and 3hours of reaction time. When the shaking speed is below 120 rpm, the yield of biodiesel will increase. However, when the shaking speed is more than 120 rpm, the biodiesel yield neither increase nor decrease meaning that the speed that below 120 rpm has less impact on the transesterification. Thus, the optimum shaking speed is 120 rpm that can effectively eliminate the effect of external diffusion.

(Guo, Huang, Zheng, Li, & Huang, 2011) in their work reported that biodiesel is produced through magnetic solid base catalysts, Na_2SiO_3/Fe_3O_4 by using cottonseed oil as the feedstock. The catalyst is prepared by using Fe_3O_4 nano particles as the magnetic core and Na_2SiO_3 as the active ingredient. The optimum reaction conditions for the transesterification of cottonseed oil using methanol in the presence of magnetic solid base catalysts are catalyst quantity of 5%, molar ratio of methanol to oil of 6:1, reaction temperature of 60^oC, 100 minutes reaction time, and 400rpm stirring speed. The maximum biodiesel conversion is 99.6% and after 7 batches under the optimum reaction conditions, the catalytic activity exceeded 90%.

(Mustata & Bicu, 2014) reported that biodiesel is produced through transesterification reaction of corn oil using barium hydroxide as homogeneous catalyst. The corn oil esters (COE) are obtained using the response surface method and central composite design is optimized by using barium hydroxide as the catalysts and diethyl ether (DEE) as a cosolvent. The most important factors that determine the yield of COE are reaction time, catalyst concentration, and ratio of methanol to oil. The optimum conditions for maximum yield of COE which is 99.15% are reaction time of 118 minutes, methanol to oil ratio of 11.32, and 3.6 wt% of catalyst.

(Wan, Yu, Gong, Li, & Luo, 2008) using rapeseed oil as the feedstock to produce biodiesel in the presence of KF/MgO as the heterogeneous catalyst through transesterification reaction. There are a few factors affecting the biodiesel conversion which included loading amount and calcined temperature. Impregnation method is used to prepare the KF/MgO catalyst. The catalyst showed high catalytic activities for the transesterification process. The biodiesel yield achieved 79.37% when 35% KF/MgO sample is calcined at 500^oC. Besides that, the biodiesel conversion reached 79.82% with the reaction condition of 30% KF/MgO after thermal treated at 500^oC, 3% catalyst, and methanol to oil ratio of 15:1.

Besides that, (Kim et al, 2004) found out that the biodiesel production from soybean oil via transesterification using Na/NaOH/γ-Al_2O_3 can achieve the highest biodiesel conversion of 83% with the optimum reaction condition of methanol to oil loading ratio of 9:1 under the presence of n-hexane as the co-solvent. In another work, (Arzamendi et al, 2007) found out that after 24 hours of reaction at molar ratio of methanol to oil of 12:1, the biodiesel yield is 86% for the calcined catalysts. However, the biodiesel conversion can achieved 99% when using non calcined catalysts under the same reaction condition as calcined catalysts.

(Liu et al., 2010) in their work reported that biodiesel is produced through transesterification reaction using rapeseed oil as the feedstock in the presence of methanol with the solid base catalyst, calcined K_2CO_3/γ-Al_2O_3. The optimum reaction conditions for biodiesel production are catalyst amount of 4 wt%, raection temperature of 50^oC, 3 hours of reaction time, methanol to rapeseed oil molar ratio of 15:1, and 98.85 wt% of n-hexane co-solvent. Under these optimum reaction conditions, the maximum conversion of 98.62% can be achieved. The parameters that affected the converion of rapeseed oil to biodiesel being investigated in the work are calcined temperature, reaction temperature, molar ratio of methanol to rapeseed oil, amount of solvent, amount of catalyst, raection time, and the presence of water.

(Liu et al., 2010) reported the calcined temperature affected the activity of catalyst significantly. Initially, with the increased of temperature, the biodiesel conversion of rapeseed oil through transesterification reaction also increased and reached maximum conversion of 98.62% at calcination temperature of 823K. However, with the increased of calcination temperature, the conversion of biodiesel decreased and the conversion is almost negligible when the calcination temperature is increased to 1023K, 1123K, and 1223K. Hence, the optimum calcination temperature is for $K_2CO_3/\gamma\text{-}Al_2O_3$ is 823K. Besides that, the amount of catalyst also affects the conversion of rapeseed oil to biodiesel. When the amount of catalyst is increased from 2 to 4 wt%, the biodiesel conversion of rapeseed oil also increased from 93.6% to 98.62%. However, with the

further increase of catalyst amount, the conversion of rapeseed oil to biodiesel will decrease. This is due to the deterioration of mixing when the increment in amount of solid base catalyst. The maximum biodiesel conversion can be achieve by using 4 wt% of catalyst. The reaction mixture is liquid like and clear.

(Liu et al., 2010) also investigated the effect of reaction time on the conversion of rapeseed oil to biodiesel. When the reaction time is increased from 0.5 to 3 hours, the biodiesel conversion of rapeseed oil is increased from 87.64% to 98.62%. However, when the reaction time is more than 3 hours, the conversion of biodiesel from rapeseed oil will slightly decreased. The reason behind the decreased in biodiesel conversion when the reaction time is more than 3 hours is that the occurrence of side reactions. Reaction time of 3 hours is the optimum time for biodiesel conversion as the maximum conversion of 98.62% achieved. Besides that, effect of molar ratio of methanol to oil on the conversion of biodiesel from rapeseed oil is also been investigated. The biodiesel conversion from rapeseed oil can be increase by putting excess amount of methanol since transesterification is a reversible reaction as to shift the equilibrium towards the products side. When the methanol to rapeseed oil molar ratio increased from 9:1 to 15:1, the biodiesel conversion increased from 87.59% to 98.62%. However, the biodiesel conversion from rapeseed oil begins to decrease when the molar ratio is increased more than 15:1. When the molar ratio of methanol to rapeseed oil is 15:1, maximum conversion of biodiesel is achieved. Generally in the industry, excess methanol is recovered and reused after purification, but the overall cost is increased as the increment in the recycling cost. Thus, the increment of process cost due to choice of the optimal molar ratio is necessary to be taken into consideration.

Furthermore, (Liu et al., 2010) also investigated the effect of amount of solvent on the biodiesel conversion from rapeseed oil. Solvent is being introduced into the process in order to enhance the reaction rate and increase the biodiesel conversion. This is due to the rapeseed oil, methanol, and catalyst are immiscible to each other and formed a three phase reaction mixture and will limit the reaction rate. The solvent being used in this work is n-hexane and is adopted as co-solvent. In the presence of n-hexane, the conversion of biodiesel increased significantly. In the absence of n-hexane, the minimum conversion is 74.19%. In the presence of 98.85 wt% of n-hexane with respect to rapeseed oil, the maximum conversion of 98.62% is achieved. However, with the further increased of n-hexane, the biodiesel conversion is decreased. Hence, the optimum amount of n-hexane to achieve maximum biodiesel conversion is 98.85 wt%. Another parameter that is being investigated is the effect of presence of water on the conversion of biodiesel from rapeseed oil. The presence of water in the transesterification reaction system can reduce the catalytic activity of alkali catalysts significantly. The effect of water on biodiesel conversion is being studied by adding water directly into the reaction system. The biodiesel conversion decreased significantly when the water is directly added into the reaction system. This is due to water inhibited the catalytic activity of calcined $K_2CO_3/\gamma\text{-}Al_2O_3$. When water adding into the raection system increased from 1 to 4 wt% with respect to the weight of rapeseed oil, the biodeisel conversion decreased from 95.39% to 86.72%. Hydrolysis reaction occurred when water is added into the raection system caused the biodiesel conversion to decrease. Hence, before the reaction begin, the reactant must be dried and dewatered thoroughly.

(Mamilla, M.V.Mallikarjun, & Rao, 2012) in the work produce biodiesel from palm oil using transesterification method. There are 5 parameters being investigated in this work which included reaction temperature, ratio of alcohol to oil, catalyst type and concentration, mixing intensity, and purity of reactants. The reaction temperature will greatly influence the rate of reaction. When the temperature range from 60° to 80°C where alcohol to oil molar ratio is at 6:1, the maximum biodiesel conversion occurred. However, the biodiesel conversion decreased when the temperature is increased further. Excess of alcohol is needed to shift the transesterification reaction to the right since transesterification is a reversible reaction. The reaction rate is the highest when 100%

excess methanol is used. Generally, molar ratio of 6:1 is used in the industrial process to achieve 98% by weight of biodiesel. Compare to acidic catalyst, alkali metal alkoxides are the most effective catalyst for transesterification because alkaline catalysts are less corrosive to the industrial equipment. Thus, alkaline catalysts are mostly used for the commercial transesterification. Conversion of biodiesel from vegetable oil can range from 94% to 99% when the concentration of alkaline catalysts is range from 0.5 wt% to 1w%. However, conversion of biodiesel will not increase when catalyst concentration is further increase and it will also increase the production cost as extra cost is needed to remove the catalyst. Mixing intensity also affect the biodiesel conversion. During the slow rate of reaction, mixing effect is the most significant. However, mixing becomes insignificant when single phase is established. The purity of reactant also affected the biodiesel conversion. When using refined oil, biodiesel conversion ranges from 94% to 97%. When using crude vegetable oil, the biodiesel conversion ranges from 67% to 84%. Bothe of the experiments is under the same reaction conditions. Conversion of crude vegetable oil to biodiesel is less than refined oil because of the presence of free fatty acid (FFA) interfere the catalyst added into the crude vegetable oil. However, high temperature and pressure can solve the problem of low biodiesel conversion by crude vegetable oil.

There is one study found which is most similar to this project where it used homogeneous catalyst which is KOH/bentonite where bentonite itself is a clay material for biodiesel production via transesterification of palm oil. The best performance for biodiesel production was determined when catalyst is synthesized with 25% KOH loading. The optimum condition to produce the highest yield of biodiesel was 60°C reaction temperature, 3 hours reaction time, 3wt% catalyst, and methanol to oil ratio of 6 to produce the highest yield of biodiesel. (Soetaredjo, Ayucitra, Ismadji, & Maukar, 2011).

The biodiesel yield is affected by a few parameters which included KOH/bentonite loading, reaction time, catalyst amount, and catalyst stability. The KOH/bentonite loading will affect the yield of fatty acid methyl ester. The standard condition used for the experiment are 3wt% of catalyst based on weight of palm oil, methanol to oil ratio of 6:1, 3 hours of reaction time, 60^{o}C of reaction temperature. The yield of biodiesel increased when the loading amount of KOH increased from 5% to 25%. The yield of biodiesel decreased significantly when the loading amount of KOH increased from 25% to 50%. When the loading of KOH loading is at 25%, the highest yield of biodiesel is obtained at 90.7%. When the KOH loading is increased from 5% to 25%, it will increase the number of K_2O active sites in the catalyst and eventually increased the biodiesel yield. However, when the KOH loading is more than 25%, it will decrease the biodiesel yield because it will increased the concentration of the Al-O-K which lower the catalytic activity of the catalyst and eventually decrease the yield of biodiesel (Soetaredjo, Ayucitra, Ismadji, & Maukar, 2011).

Besides that, the reaction time also affected the yield of biodiesel. The highest yield of biodiesel is achieved when the reaction time is 3 hours. The yield production keeps increasing during the first three hours of reaction. However, the biodiesel yield was almost constant because the reaction reached equilibrium conversion after three hours. The amount of catalyst also affects the yield of biodiesel. The range of amount of catalyst used in the experiment is from 1wt% to 9wt%. At 1wt% of catalyst, the yield of biodiesel is 52.7% and increased to 90.7% when the amount of catalyst is 3wt%. When the catalyst amount is between 3wt% to 9wt%, there is a little further changes. The increase of active basic site (K_2O) leads to increase of biodiesel yield. Transesterification reaction is a reversible reaction. Thus, Le Chatelier's principle is used to alter the reaction into right hand side to produce fatty acid methyl ester. When the biodiesel yield is not affected with further increased of catalyst, it meant that the amount of catalyst already provided enough basic sites and equilibrium condition of the reaction is reached. The last parameter to affect the biodiesel yield is catalyst. The important criteria for industrial application of KOH/bentonite for biodiesel production are reusability and stability. Three reaction cycles are carried out to examine the stability and reusability of the catalyst. The maximum conversion of 90.7% is achieved at KOH/bentonite of 1:4. The catalyst is reused after washed with methanol at least 4 times and recalcined at 300^oC for 5 hours. The maximum biodiesel yield is less than 85% when the catalyst is used for second and third times because the basic site deactivation has occurred as some of the basic sites are possibly poisoned during the transesterification reaction. (Soetaredjo, Ayucitra, Ismadji, & Maukar, 2011).

(Taufiq-Yap, Abdullah, & Basri, 2011) It is found out that among all the synthesized catalysts, the optimum catalysts to give the best catalytic activity is the catalyst with 50 wt% of sodium hydroxide loaded on alumina and calcined in air for 3 hours. The optimum reaction condition of biodiesel production via transesterification of palm oil using $NaOH/Al_2O_3$ catalyst to achieve highest biodiesel yield of 99% is 60^oC of reaction temperature, molar ratio of methanol to oil of 15:1, reaction time of 3 hours, and catalyst amount of 3 wt%.

The transesterification reaction parameters which included molar ratio of palm oil to methanol, catalyst amount, reaction time, and reaction temperature will affect the yield of biodiesel. Transesterification is a reversible reaction, thus excess methanol is required to drive the reaction towards the product. However, excess methanol feed is only effective to certain extent only. The conversion of biodiesel can be increase by increasing the amount of catalyst. However, the biodiesel conversion decreased with further increase of catalyst amount because the mixture of catalyst and reactants became too slurry. It gives rise to mixing problem and higher power consumption demand for adequate stirring. (Taufiq-Yap, Abdullah, & Basri, 2011).

The biodiesel yield can be increase with the increase of reaction time; however, the biodiesel conversion will be almost constant after 3 hours because the equilibrium conversion had been reached. Besides that, biodiesel yield can be increase also with the increase of reaction temperature because the increase of temperature of reaction will increase the rate of reaction of reaction of transesterification and hence increase the yield of biodiesel but only up to certain extent. The conversion percentage of biodiesel will decrease after the temperature is elevated to more than 60^oC. This is because when the temperature reached the boiling point of methanol which is 64.7^oC, methanol's bubbles will form and hence prevent the mass transfer on the phase interface and decreased the biodiesel yield. (Taufiq-Yap, Abdullah, & Basri, 2011).

In conclusion, heterogeneous solid clay base catalyst, KOH/MK-10 clay and MK-10 clay are used for transesterification process because of its advantages of heterogeneous solid base catalyst as mentioned above. The use of KOH/MK-10 clay and MK-10 clay also fulfilled the objective of the project because it is an economic and environmental friendly catalyst. Palm oil is a very suitable raw material to be used in the transesterification reaction to produce biodiesel since palm oil can be easily access in Malaysia.

CHAPTER 3

METHODOLOGY

3.1 REACTION PROCEDURE

A two neck bottle flask (250mL) (APPENDIX 1) that equipped with a reflux condenser and thermometer is used for transesterification of edible palm oil. Reflux condenser is used to condense the methanol evaporated while thermometer is to measure the temperature of the mixture. The two neck bottle is immersed completely in oil bath and is heated using hot plate and the temperature is controlled by the hot plate. Magnetic bar is put into the two neck bottle for stirring purpose and the speed is controlled by the hot plate. Amount of KOH/MK-10 clay and MK-10 clay to be added to known volume of methanol are 1wt%, 2 wt%, and 3 wt%. After that, the mixture will be heated to desired temperature (40^{o}C, 50^{o}C, 60^{o}C, 70^{o}C) in a controlled temperature oil bath. Then, palm oil will be added into the mixture under vigorous stirring of 200 rpm. The molar ratios of palm oil to methanol to be used are 1:10, 1:15, and 1:20. The transesterification reaction time will be carried for 0.5hr, 1hr, and 2hr.

The experiment will be repeated using a set of general values: reaction temperature of 60^{o}C, oil to methanol ratio of 1:10, reaction time of 2 hours, and 2wt% of catalyst. For example, the experiment will start by changing the reaction time from 40^{o}C to 70^{o}C while the other three parameters remained constant to find out the optimum temperature to produce biodiesel. After that, the experiment will continue by changing the other three parameters to find out optimum oil to methanol molar ratio, reaction time, and catalyst amount to produce biodiesel. There will be 18 sets of experiments to be done.

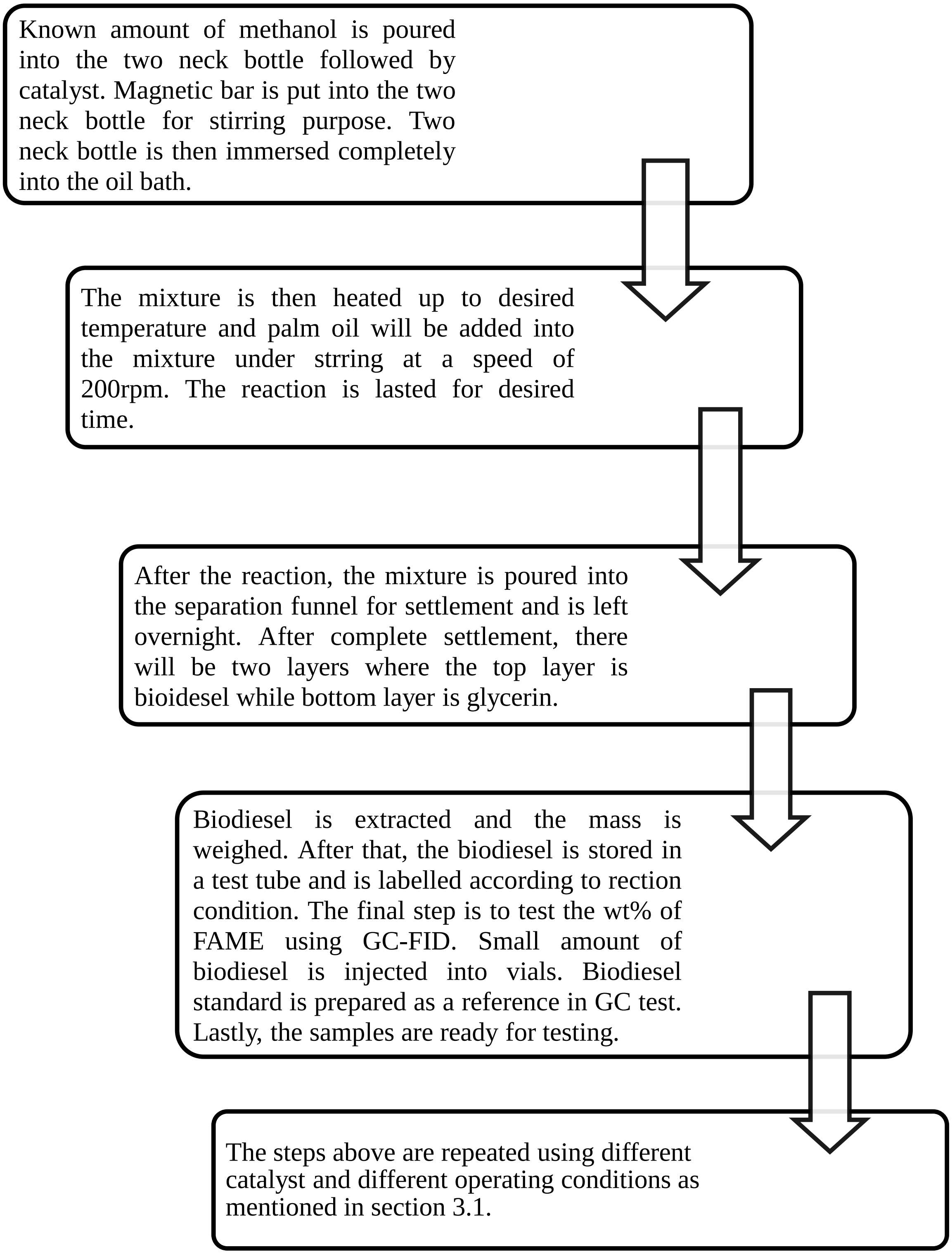
After the reaction, the reaction product is poured into a separation funnel and will be left overnight for settlement. Two layers will form where the upper layer is biodiesel and lower layer is glycerin and catalyst. The biodiesel layer will be extracted and weighed. After that, a relative small amount of biodiesel will be taken to undergo gas chromatography in order to determine the wt% of FAME in the biodiesel. The steps stated above will be repeated for the remaining sets of experiments.

The yield of biodiesel will be calculated using the formula below:

$$yield(\%) = \frac{weight\ of\ biodiesel\ \times total\ weight\ \%\ of\ FAME\ in\ sample}{weight\ of\ palm\ oil} \times 100$$

Graphs of biodiesel yield versus reaction temperature, reaction time, oil to methanol molar ratio, and amount of catalyst will be plotted to show the value of optimum parameters to produce biodiesel.

3.1.1 REACTION PROCEDURE IN BLOCK DIAGRAM



Known amount of methanol is poured into the two neck bottle followed by catalyst. Magnetic bar is put into the two neck bottle for stirring purpose. Two neck bottle is then immersed completely into the oil bath.

The mixture is then heated up to desired temperature and palm oil will be added into the mixture under strring at a speed of 200rpm. The reaction is lasted for desired time.

After the reaction, the mixture is poured into the separation funnel for settlement and is left overnight. After complete settlement, there will be two layers where the top layer is bioidesel while bottom layer is glycerin.

Biodiesel is extracted and the mass is weighed. After that, the biodiesel is stored in a test tube and is labelled according to rection condition. The final step is to test the wt% of FAME using GC-FID. Small amount of biodiesel is injected into vials. Biodiesel standard is prepared as a reference in GC test. Lastly, the samples are ready for testing.

The steps above are repeated using different catalyst and different operating conditions as mentioned in section 3.1.

3.1.2 REACTION PROCEDURE IN DIAGRAM

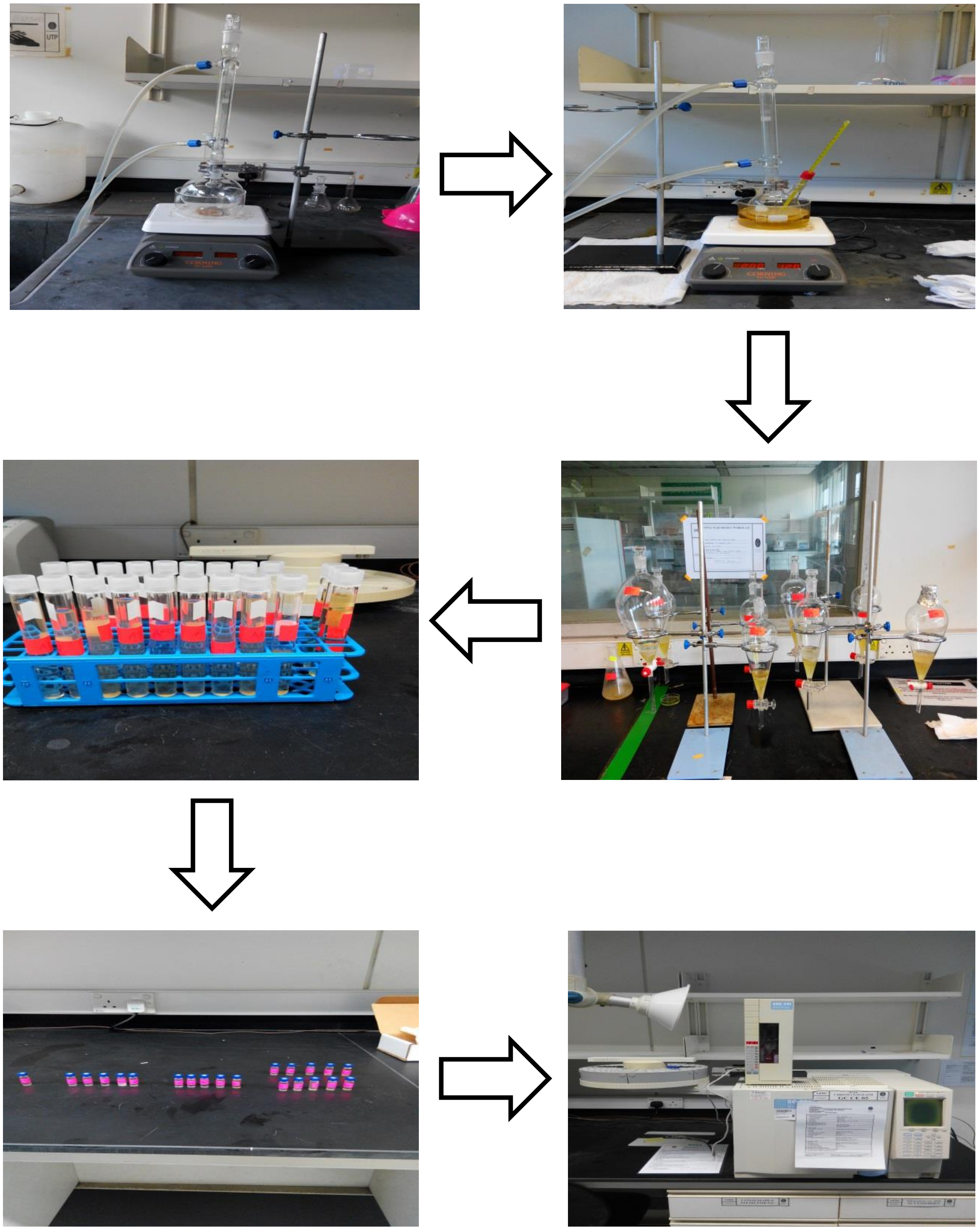
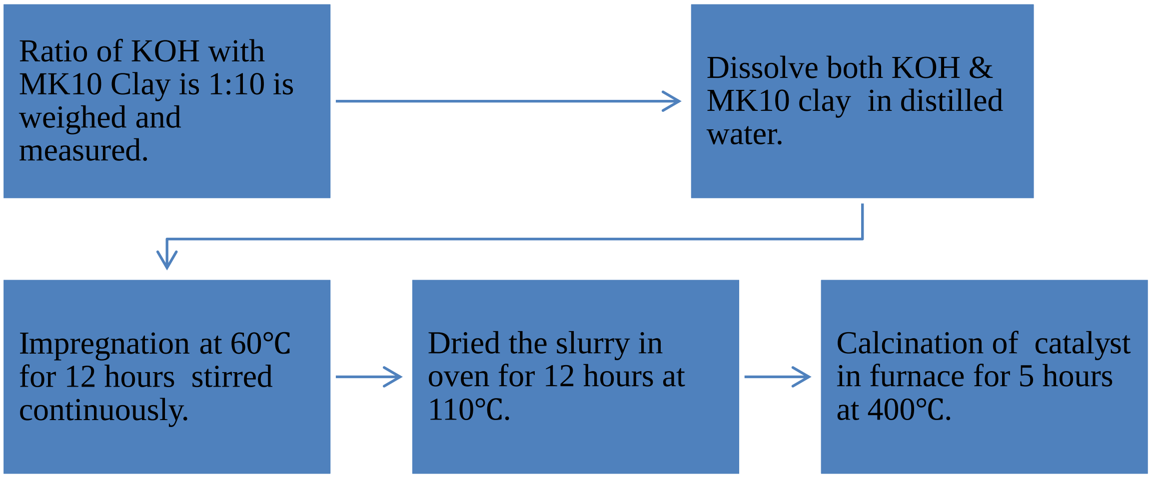


Figure 3: Reaction Procedure of Transesterification Process

3.2 CATALYST PREPARATION

Montmorillonite K-10 clay catalyst is prepared by calcination of MK-10 clay in the furnace for 5 hours at 400°C.

KOH/MK-10 clay catalyst is prepared using wet impregnation method. Below is the procedure in block diagram of preparing KOH/MK-10 clay catalyst.



Ratio of KOH with MK10 Clay is 1:10 is weighed and measured.

Dissolve both KOH & MK10 clay in distilled water.

Impregnation at 60°C for 12 hours stirred continuously.

Dried the slurry in oven for 12 hours at 110°C.

Calcination of catalyst in furnace for 5 hours at 400°C.

3.3 GC-FID ANALYSIS

Reference materials and samples were analyzed by a gas chromatograph (Perkin Elmer Autosystem XL, USA), equipped with a silica capillary column (Nukol^{TM} fused with the dimension of 0.53 mm i.d. x 15 m length x 0.50 µm film thickness (Supelco, USA) and a flame ionization detector (FID). Helium was used as the carrier gas. The injector temperature was set at 220^{o}C and the detector temperature maintained at 250^{o}C. Meanwhile, the column temperature was kept constant at 110 C. The analysis of FAME for each sample was carried out by dissolving 100 microliters of diluted sample (FAME sample and n-hexane) into 100 microliters of internal standard solution (concentration = 1 g/l). 1µl of this mixture was then injected into the GC.

Total weight of methyl esters in the sample is the sum of all types of FAME in the sample. For palm oil sample, there are five types of FAME, methyl myristate, methyl palmitate, methyl stearate, methyl oleate and methyl linoleate. Weight of each ester in the sample is calculated based on the peak area of the FAME.

$$Weight\ (g) = \frac{R_{SD} \times [ME\ pure]_{SD} \times D_f}{R_{SP}}$$

Where:

R_{SD} = Ratio of peak area of ester to peak area of internal standard in the standard references.

R_{SP} = Ratio of peak area of ester to peak area of internal standard in the sample

$[ME\ pure]_{SD}$ = Concentration of the ester in the standard reference

D_f = Dilution factor of the sample

$$R_{SD} = \frac{\text{Peak area of ME in the standard reference}}{\text{Peak area of internal standard (IS) in the standard reference}}$$

$$R_{SP} = \frac{\text{Peak area of ME in the sample}}{\text{Peak area of internal standard (IS) in the sample}}$$

Chemicals	Purity	Supplier	Purpose of use
Methanol	100%	J.T.Baker	Solvent
n-hexane	99.99%	Merck	Solvent
Palmitic acid methyl ester	99.00%	Nu-chek prep Inc	Standard of methyl ester
Myristic acid methyl ester	99.00%	Nu-chek prep Inc	Standard of methyl ester
Stearic acid methyl ester	99.00%	Nu-chek prep Inc	Standard of methyl ester
Oleic acid methyl ester	99.00%	Nu-chek prep Inc	Standard of methyl ester
Linoleic acid methyl ester	99.00%	Nu-chek prep Inc	Standard of methyl ester
Heptadecanoic acid methyl ester	99.50%	Sigma-Aldrich	Internal standard of methyl ester
Refined cooking palm oil	FFA (0.3) Moisture content (0.75)	Local distribution	Source of triglyceride

Table 1: List of chemicals and materials used in transesterification process and FAME analysis

3.4 KEY PROJECT MILESTONE

Week	**Task**	**Status**
1-12	Experimental lab work	Completed
8	Progress report submission	Completed
11	Pre-SEDEX presentation	Completed
12	Submission of draft	Completed
12-14	Analysis and reporting of experiment result	Completed
13	Submission of softbound dissertation	Completed
13	Submission of technical paper	Completed
14	Oral presentation	Completed
15	Submission of hardbound dissertation	Completed

3.5 GANTT CHART

No	Activities	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	Experimental lab work.	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	
2	Meeting with supervisor for the lab work discussion.	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	
3	Progress report submission								🟦							
4	Pre-SEDEX presentation											🟦				
5	Submission of draft												🟦			
6	Analysis and reporting of experiment result												🟦	🟦	🟦	
7	Submission of softbound dissertation													🟦		
8	Submission of technical paper													🟦		
9	Oral presentation														🟦	
10	Submission of hardbound dissertation															🟦

CHAPTER 4

RESULT AND DISCUSSION

4.1 RESULTS

4.1.1 Effect of methanol/oil molar ratio on conversion

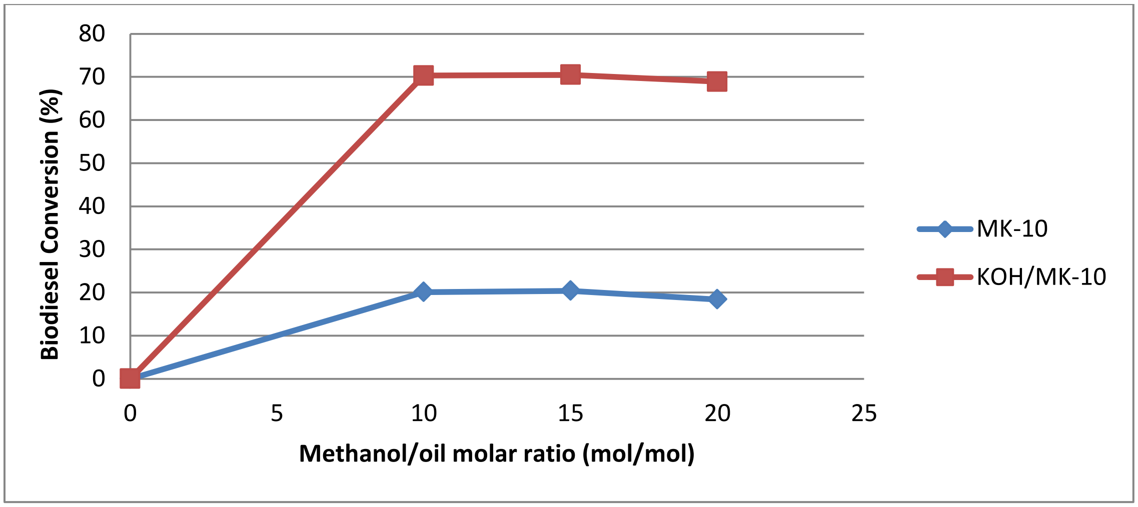


Figure 4: Graph of Methanol/Oil Molar Ratio vs. Biodiesel Conversion

The reaction conditions are 2wt%, reaction time of 2 hours, and reaction temperature of 60^{o}C. The methanol/oil molar ratios used are 10:1, 15:1, and 20:1. The highest conversion achieved are 70.5% for KOH/MK-10 clay catalyst while 20.4% for MK-10 clay catalyst when the methanol/oil ratio is 15:1.

Oil to Methanol Ratio	Mass of Palm Oil Used (g)		Mass of Biodiesel Produced (g)		Total wt% of FAME in Sample		Biodiesel Yield (%)	
	KOH/MK-10 Clay	MK-10 Clay	KOH/MK-10 Clay	MK-10 Clay	KOH/MK-10 Clay	MK-10 Clay	KOH/MK-10 Clay	MK-10 Clay
1:10	50	50	41.19	26.73	85.33	37.6	70.3	20.1
1:15	50	50	39.46	25.89	89.34	39.4	70.5	20.4
1:20	50	50	40.90	22.49	84.24	35.3	68.9	18.4

Table 2: Biodiesel yield with different oil to methanol ratio

4.1.2 Effect of catalyst amount on conversion

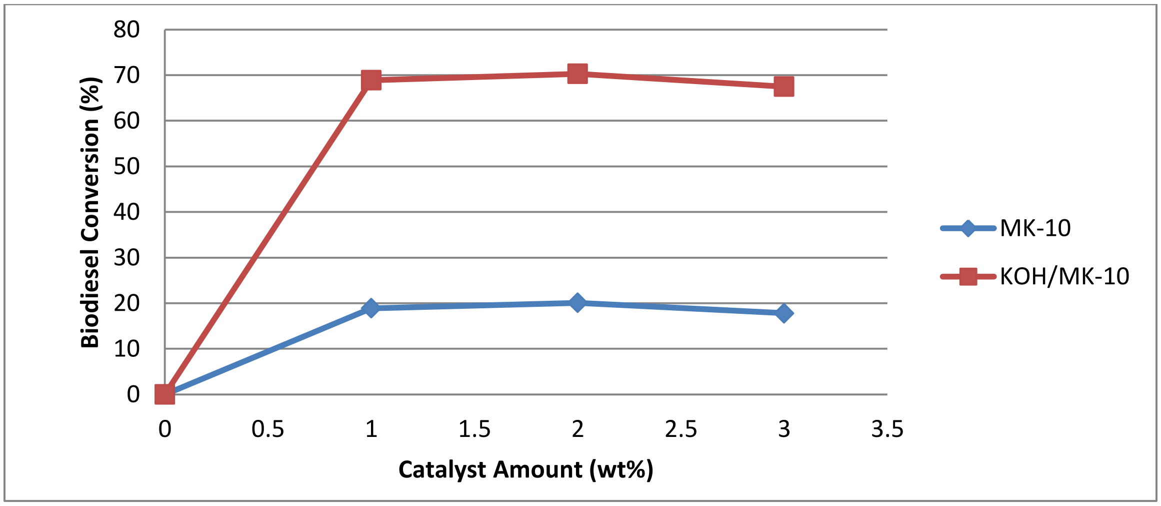


Figure 5: Graph of Catalyst Amount vs. Biodiesel Conversion

The reaction conditions are methanol/oil ratio of 15:1, reaction time of 2 hours, and reaction temperature of 60^{o}C. The amounts of catalyst used are 1wt%, 2wt%, 3wt%. The highest conversion achieved is 70.3% for KOH/MK-10 clay catalyst while 20.1% for MK-10 clay catalyst when the amount of catalyst used is 2wt%.

Catalyst Amount (wt%)	Mass of Palm Oil Used (g)		Mass of Biodiesel Produced (g)		Total wt% of FAME in Sample		Biodiesel Yield (%)	
	KOH/MK-10 Clay	MK-10 Clay	KOH/MK-10 Clay	MK-10 Clay	KOH/MK-10 Clay	MK-10 Clay	KOH/MK-10 Clay	MK-10 Clay
1.0	50	50	41.26	26.54	83.50	35.6	68.9	18.9
2.0	50	50	41.19	26.73	85.33	37.6	70.3	20.1
3.0	50	50	41.33	26.02	81.66	34.2	67.5	17.8

Table 3: Biodiesel yield with different catalyst amount

4.1.3 Effect of reaction time on conversion

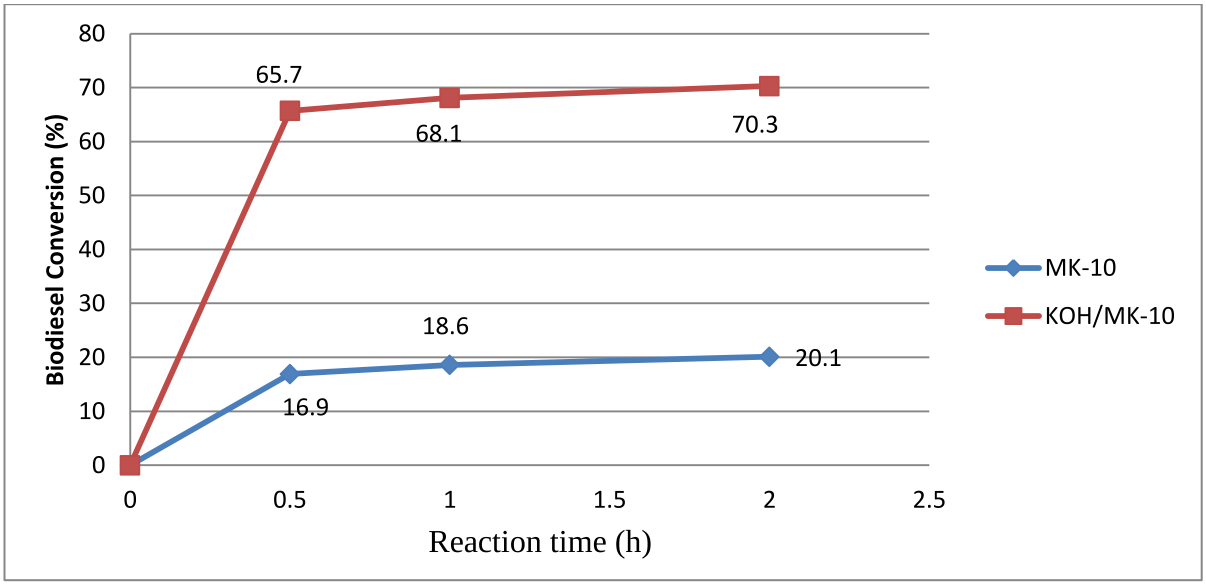


Figure 6: Graph of Reaction Time vs. Biodiesel Conversion

The reaction conditions are methanol/oil ratio of 15:1, catalyst amount of 2wt%, and reaction temperature of 60°C. The reaction times are 0.5 hour, 1 hour, and 2 hours. The highest conversion achieved is 70.3% for KOH/MK-10 clay catalyst while 20.1% for MK-10 clay catalyst when the reaction time is 2 hours.

Reaction Time (hrs)	Mass of Palm Oil Used (g)		Mass of Biodiesel Produced (g)		Total wt% of FAME in Sample		Biodiesel Yield (%)	
	KOH/MK-10 Clay	MK-10 Clay	KOH/MK-10 Clay	MK-10 Clay	KOH/MK-10 Clay	MK-10 Clay	KOH/MK-10 Clay	MK-10 Clay
0.5	50	50	41.99	28.34	78.23	29.82	65.7	16.9
1	50	50	41.93	27.42	81.21	33.91	68.1	18.6
2	50	50	41.19	26.73	85.33	37.6	70.3	20.1

Table 4: Biodiesel yield with different reaction time

4.1.4 Effect of reaction temperature on conversion

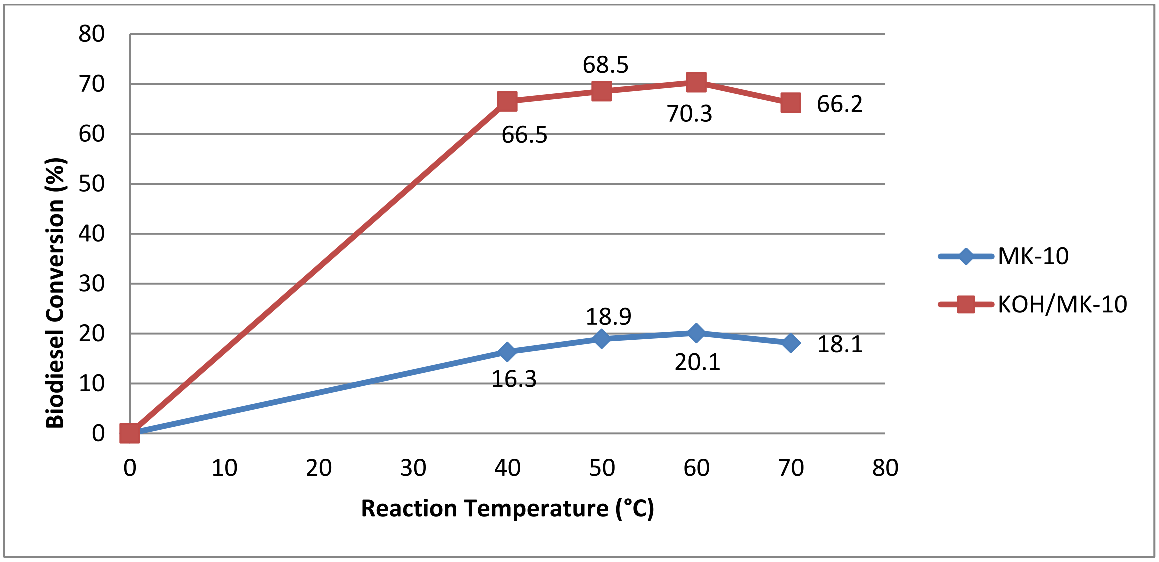


Figure 7: Graph of Reaction Time vs. Biodiesel Conversion

The reaction conditions are methanol/oil ratio of 15:1, catalyst amount of 2wt%, and reaction time of 2 hours. The reaction temperatures are 40^{o}C, 50^{o}C, 60^{o}C, and 70^{o}C. The highest conversion achieved is 70.3% for KOH/MK-10 clay catalyst while 20.1% for MK-10 clay catalyst when the reaction temperature is 60^{o}C.

Reaction Temperature (°C)	Mass of Palm Oil Used (g)		Mass of Biodiesel Produced (g)		Total wt% of FAME in Sample		Biodiesel Yield (%)	
	KOH/MK-10 Clay	MK-10 Clay	KOH/MK-10 Clay	MK-10 Clay	KOH/MK-10 Clay	MK-10 Clay	KOH/MK-10 Clay	MK-10 Clay
40	50	50	41.45	27.02	80.22	30.16	66.5	16.3
50	50	50	40.35	25.68	84.89	36.8	68.5	18.9
60	50	50	41.19	26.73	85.33	37.6	70.3	20.1
70	50	50	39.82	25.93	83.12	34.9	66.2	18.1

Table 5: Biodiesel yield with different reaction temperature

Catalyst	**Maximum Biodiesel Yield (%)**	**Optimized Parameters**			
		Palm Oil/Methanol Molar Ratio (mol/mol)	Reaction Time (hr)	Reaction Temperature (°C)	Catalyst Amount (wt%)
KOH/MK-10	70.5	1:15	2	60	2
MK-10	20.4	1:15	2	60	2

Table 6: Optimized parameters for maximum biodiesel yield

4.2 DISCUSSION

4.2.1 Effect of methanol/oil molar ratio

Transesterification required 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. As represented by the graph of conversion % versus methanol/oil molar ratio above, we can see that when methanol/oil molar ratio increased, the conversion was increased considerably from 70.3% to 70.5% for KOH/MK-10 clay catalyst while 20.1% to 20.4% for MK-10 clay catalyst when the methanol/oil ratio increased from 10:1 to 15:1 and the conversion decreased when the ratio is 20:1 for both catalyst. The conversion reached the maximum which is 70.5% for KOH/MK-10 clay catalyst while 20.4% for MK-10 clay when methanol/oil molar ratio reached 15:1. Thus, an excess methanol feed is only effective to certain extent only.

4.2.2 Effect of catalyst amount

The conversion of biodiesel increased with the increased of catalyst amount from 1 wt% to 3 wt% as shown in the graph of conversion % versus catalyst amount above. The biodiesel conversion increased gradually when amount of catalyst is increased from 1wt% to 2wt%. The highest conversion is 70.3% for KOH/MK-10 clay catalyst while 20.1% for MK-10 clay catalyst when catalyst amount added is 2wt%. However, the biodiesel conversion decreased with further increase of catalyst amount. This is most probably due to slurry (mixture of catalyst and reactants) became too slurry. It gives rise to mixing problem and higher power consumption demand for adequate stirring.

4.2.3 Effect of reaction time

From the graph of conversion % versus reaction time above, the biodiesel conversion reached the peak when the reaction time is 2 hours. When the reaction time increased from 0.5 hour to 1 hour, the biodiesel conversion is increasing and reached the peak at 2 hours. The highest conversion is 70.3% for KOH/MK-10 clay catalyst and 20.1% for MK-10 clay catalyst when the reaction time is 2 hours. The biodiesel conversion can be considered as almost constant after 2 hours because the equilibrium conversion had been reached.

4.2.4 Effect of reaction temperature

From the graph of conversion % versus reaction temperature above, it is shown that biodiesel conversion increased from 40°C to 60°C and decreased after 60°C. The highest conversion is 70.3% for KOH/MK-10 clay catalyst while 20.1% for MK-10 clay catalyst when the reaction temperature is 60°C. The elevation of temperature of reaction will increase the rate of reaction of transesterification and hence increase the yield of biodiesel but only up to certain extent. The conversion % decreased after the temperature is elevated to more than 60°C. This is because when the temperature reached the boiling point of methanol which is 64.7°C, methanol's bubbles will form and hence prevent the mass transfer on the phase interface and decreased the conversion% of biodiesel. Besides that, it is also due to the reaction is more favorable to saponification rather than transesterification when the reaction temperature is elevated more than 60°C.

4.2.5 Effect of type of catalyst

There are two types of catalyst using in the transesterification included KOH/MK-10 clay catalyst and MK-10 clay catalyst. This is the first time for the use of MK-10 clay catalyst in the transesterification process of palm oil into biodiesel. It is proven that KOH/MK-10 clay catalyst is a very efficient catalyst in the transesterification process. KOH is the active site while MK-10 clay provides support and bigger surface area for the transesterification process to occur. The highest biodiesel yield is 70.5% using KOH-MK-10 clay when the operating conditions are 60°C reaction temperature, 2 hours reaction time, 2wt% catalyst, and oil/methanol ratio of 1:15. However, MK-10 clay itself is a poor catalyst in the transesterification process. The highest biodiesel yield achieved is only 20.4% clay when the operating conditions are 60°C reaction temperature, 2 hours reaction time, 2wt% catalyst, and oil/methanol ratio of 1:15. Thus, it is proven that KOH/MK-10 clay catalyst is a much better catalyst than MK-10 clay itself in the transesterification process since MK-10 clay is more suitable to become supporting agent in transesterification process.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

The use of KOH/MK-10 clay and MK-10 clay as catalyst in the biodiesel production using palm oil is very rare. However the use of KOH/MK-10 clay and MK-10 clay catalyst to produce biodiesel is feasible because it is an environmental friendly heterogeneous solid base catalyst compared to homogeneous catalyst and methanol is a low cost alcohol which fulfills the objective of the project which is to have an economic and environmental friendly reaction.

Besides that, the use of KOH/MK-10 clay and MK-10 clay catalyst for transesterification reaction is a very interesting area to study about because the researches on this are very rare. Palm oil is used as the raw material because palm oil is one of the major productions in Malaysia and it very easy to get palm oil anywhere.

The biodiesel yield is dependence on the reaction parameters such as molar ratio of palm oil to methanol, catalyst amount, reaction time, and reaction temperature. The highest biodiesel achieved using modified KOH/MK-10 clay is 70.5% while 20.4% using MK-10 clay under the same optimum reaction parameters of palm oil/methanol molar ratio of 1:15, 2 hours reaction time, 60°C reaction temperature, and 2wt% catalyst. Through the experimental works, it is also proven that KOH/MK-10 catalyst is a much better catalyst compare to MK-10 clay catalyst in the transesterification process of palm oil to biodiesel.

For future recommendation, we can increase the parameters for the transesterification process such as different wt% loading of KOH/MK-10 clay catalyst, stirring speed and etc. Besides that, we can also increase the range parameters such as reaction time, we can conduct the transesterification process using 1 hour, 3 hour, and so on. It is also applicable to other parameters such as catalyst amount, reaction temperature, and oil/methanol molar ratio. Furthermore, we can also characterize the biodiesel for its flash point, pour point, boiling point, density, specific gravity, viscosity and etc. Finally, we can also test the biodiesel produced on vehicles which is using diesel engine in order to test whether the biodiesel produced is working or not.

In conclusion, biodiesel still cannot replace fossil fuel completely because of expensive production cost and low efficiency of biodiesel compared to fossil fuel petroleum. However, the world now is getting more and more polluted due to emission of carbon dioxide and other toxic gases from the combustion of fossil fuel petroleum. Thus, biodiesel which is an environmental friendly biofuel will replace fossil fuel in the future through the optimization of biodiesel production using effective catalyst and suitable operating conditions in order to lower the production cost and increase the efficiency of biodiesel.

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APPENDICES

Appendix 1: Two Neck Bottle Flask