# PREPARATION AND CHARACTERIZATION OF POTASSIUM BASED CLAY CATALYST FOR BIODIESEL PRODUCTION

by

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14768

Dissertation submitted in partial fulfillment of

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Universiti Teknologi PETRONAS

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# CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Chemical Engineering Programme
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Approved by,

______________________
(Dr Muhammad Ayoub)

UNIVERSITI TEKNOLOGI PETRONAS
BANDAR SERI ISKANDAR, PERAK
January 2015

# 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.

________________________________

AHMAD HANIF BIN DRAMAN

# ABSTRACT

Biodiesel is an alternative fuel for diesel engines consisting of the mono alkyl ester of fatty acids that is produced from the vegetable oils or animal fats. Most of the biodiesel is made from the reaction of methanol, solid catalyst and palm oil, under trans-esterification process. The usage of heterogeneous catalyst is very important to increase the yield of biodiesel in this process, plus make it more environmental friendly and economically viable. In fact, there are many researchers still focusing on the use of heterogeneous catalysts for biodiesel production, especially solid base catalyst. From the previous research, this type of catalyst is more effective compare to solid acid catalyst. However, there are still some gap exist in the preparation of solid base catalyst, that can lead to a higher conversion of biodiesel in the trans-esterification process. Thus, a potential application of Potassium based MK-10 clay as a most effective catalyst for biodiesel production had been studied. KOH and $K_2CO_3$ have been prepared by wet impregnation method with the MK-10 clay catalyst. The ratio between different types of Potassium with MK-10 clay catalyst is 1:10. The characterization of both Potassium based MK-10 clays has been conducted by X-Ray Diffraction (XRD), Thermal Gravimetric Analysis (TGA) and Brunauer-Emmett-Teller (BET). The effects of the catalyst on the yield of biodiesel were investigated. The highest yield of biodiesel recorded was 72% with KOH/MK-10 catalyst. It was obtained at reaction time 4 hour, 2% wt catalyst, methanol to oil ratio of 10, and the reaction temperature at 60°C. Further studied on yield of biodiesel was done using KOH/MK-10 with different reaction temperature. The optimum temperature recorded for highest yield of biodiesel was at 60°C for 10 hour.

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In addition, special thanks to Muhammad Ariff Firdaus and Tan Wei Heng, which are my partner under Dr Muhammad Ayoub for always helping me during the course of this final year project. Starting from searching the information and discussing about our project together so that we can understand, until doing experiments, writing reports, and meeting with supervisor, they were always there so that we can complete this project together. Besides that, not to forget, my special thanks goes to my parents and family, who had always given me a lot of support and advice in completing my project. Without them I doubt that I will have the strength to complete this project in time.

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# CHAPTER 1
# INTRODUCTION

## 1.1 Background of Study

In the industry nowadays, catalysts are the most important substance that had been used to produce lots of things surrounds us. As stated by the Louise Lerner, almost everything that have in our daily life are depends on the catalyst. For example, cars, laundry detergent, cheddar cheese and so on. He also said that, catalyst is the one that can break down paper pulp to produce the smooth paper in the magazine. On top of that, he also adds that catalyst can clean the contact lenses and turn the milk into yogurt as well as turn the petroleum to the plastic bags and others. Therefore, it can say that, the usage of catalyst are very wide in the chemical industry process to produce a lot of things that can benefits and help us in our daily life.

Basically, the definition of catalyst is a substance that speeds up the chemical reaction, but it is not consumed by the reaction. On the other hand, from the definition of Louise Lerner in his article, he stated that catalyst speed up a chemical reaction by lowering the amount of energy so that the process can be faster to obtain the product. The way it works is by providing an alternative reaction pathway to produce the product. This alternative route will cause the activation energy of the reaction become lower, hence will increase the rate of the reaction.

There are many reasons why a catalyst is widely used in the industry. Firstly, the use of catalyst in the reaction is very environmental friendly. This is because, when the presence of catalyst is exist, most of the reactants are converted to the products, thus, the amount of waste generated is reduced. Besides that, the use of catalyst also causes the cost for the reaction and the process is very low. This is because most of the processes need the supply of energy so that it can reach until the activation energy of the reaction. However, the use of catalyst reduce the activation energy of the reaction, so the energy that need to supply is reduced, thus, cost for the usage of the energy also reduced. In addition, the use of catalyst will reduce the time consuming to get the product. This is due to the alternative path made by the catalyst that is shorter from the actual reaction.

On the other hand, biodiesel is a liquid fuel which is similar with the petroleum diesel, in terms of combustion properties, but, it is free from sulphur and makes it as a cleaner burning fuel compare to petroleum diesel (Chopade et al. 2011). Biodiesel can be a viable alternative to the current petroleum-derived diesel because it is a clean burning and biodegradable fuel, which it is produced from the non-food plant or algal oils or animal fats (Knothe). The biodiesel is a mono alkyl ester of fatty acids that is produced from vegetables oil or animals fats, which needs undergo some modification and process because of it contains saturated and unsaturated fatty acid (Talebian-Kiakalaieh et al., 2013). There are many methods for modification of vegetable oils which are the dilution, thermal cracking (pyrolysis), trans-esterification and micro emulsification (Talebian-Kiakalaieh et al., 2013). However, majority of the scientist agreed that the best method for biodiesel production is trans-esterification (Kulkarni et al. 2006).

## 1.2 Problem Statement

In the trans-esterification process, the catalyst that normally used is heterogeneous solid catalyst, and it can be divided into two, which are base catalyst or acid catalyst. From the commercial point of view, solid base catalyst is more effective compare to solid acid catalyst and enzymes (Chopade et al. 2011). However, according to Chopade et al, the solid base catalyst need to undergo more details research to prove that it is more effective compare to solid acid catalyst. Thus, the presence of the gap still exists for the preparation of the catalyst in the purpose of biodiesel production. In other words, the researchers and scientist are still looking to find and produce the best solid base catalyst to lead a higher conversion of biodiesel in this trans-esterification process.

## 1.3 Objectives

The objectives of this research are:

- To prepare solid base catalyst by using different types of Potassium with MK-10 clay.
- To study the characteristics of all prepared Potassium base catalyst for biodiesel production.
- To determine the best effective catalyst that produce high yield of biodiesel production.

## 1.4 Scope of Study

Basically, the study for this project can be focused on three parts which are preparation of catalyst, characterize the catalyst and biodiesel production. For the first part, in preparing the catalyst, the author will use an experimental approach. The different type of Potassium (KOH and $K_2CO_3$) and Montmorillonite K-10 clay catalyst will be prepared by using wet impregnation method and will be used in this project.

Next, characterization of the catalyst will use an analytical approach to study the characteristics of the catalyst. The analytical equipments that will be used are X-Ray Diffraction, Thermal Gravimetric Analysis, and Brunauer-Emmett-Teller.

Lastly, all catalyst will be tested in biodiesel production experiment to determine the most effective catalyst that will give higher yield of biodiesel with constant parameters – reaction time, reaction temperature, methanol to oil ratio and weight of catalyst. Then, further analysis and studies of the most effective catalyst with different reaction temperature will be carried out to determine the yield of biodiesel.

# CHAPTER 2

# LITERATURE REVIEW

Catalyst can be divided into two main types which are heterogeneous catalyst and homogenous catalyst. Heterogeneous catalyst is the catalyst that form different physical phase with the reactants in the reaction. Typical heterogeneous catalyst inorganic solids such as metals, metals salt, oxides and sulfide. However, they may also be organic materials such as organic hydroperoxides, enzymes and ion exchangers. Basically, the suitable practical, which give high impact and consumption, of heterogeneous catalyst is in the form of solid, meanwhile the suitable practical of reactants is in the form of liquid or gas (Rothernberg, 2008). The example of application of heterogeneous catalyst is the hydrogenation of fatty acid which is normally used for the production of margarine. In addition, homogeneous catalyst is a catalyst that forms in the same phase with the reactants in the reaction. One of the examples of the application of homogeneous catalyst is the destruction of atmospheric ozone. In this case, catalyst and reactant are in the form of gas. Thus, in other words the difference between the homogenous catalyst and heterogeneous catalyst are the forms of the catalyst with the reactants, which same phase and different phase, respectively.

However, in the biodiesel production, the scientist and researchers are often use heterogeneous solid catalyst, rather than homogenous catalyst. This is because, heterogeneous solid catalyst are easily separated from the products, while, water washing process and neutralization process can be avoided (Feng Guo and Zhen Fang, 2011). The thermal stability of the heterogeneous solid catalyst is very good and it is very stable. Plus, the selectivity of the catalyst towards the reaction can be either good or poor, depending on the multiple active site that have on the catalyst (Farnetti, et al). However, homogeneous catalyst is hard and difficult to separate it from the product mixture because of the similar phase with the product. According to the (Farnetti, et al), a major drawback of the homogenous catalyst is the difficulty of their recovery from the reaction medium. Meanwhile, the thermal stability of homogeneous catalyst is very poor, but, the selectivity of the catalyst is very good and excellent, because of single active site (Farnetti, et al). Thus, in the biodiesel production, the suitable catalyst that can be used to make sure the production are environmental-friendly and economically viable is heterogeneous catalyst. The comparison of homogeneous and heterogeneous can be seen in the Table 1 below:

Table 1 Comparison of homogeneous and heterogeneous catalysis (Helwani et al, 2009)

| **Factors** | **Homogeneously Catalysis** | **Heterogeneously Catalysis** |
|---|---|---|
| **Reaction rate** | Fast and high conversion | Moderate conversion |
| **After treatment** | Catalyst cannot be recovered | Can be recovered |
| **Processing methodology** | Limited used of continuous methodology | Continuous fix bed operation possible |
| **Presence of water/FFA** | Sensitive | Not sensitive |
| **Catalyst reuse** | Not possible | Possible |
| **Cost** | Comparatively costly | Potentially cheaper |

In heterogeneous catalysis, there are some of operating parameters that are very important and need to be considered in biodiesel production such as, temperature, extent of catalyst loading, mode of mixing, alcohol/oil molar ratio, presence/absence of impurities in the feedstock and the time of reaction (Chopade et al, 2011 & Helwani et al, 2009). Feng Guo and Zhen Fang have mentioned that heterogenous process can be run in a continuous mode with a packed bed continuous flow reactor and the catalyst can be recycle and reused for certain number of times. On top of that, heterogeneous solid catalyst can be divided into two types which are acid catalyst or base catalyst.

## 2.1 Heterogeneous Solid Acid Catalyst

Basically, the usage of liquid acid in the process will produce some problems which are corrosion and environmental hazard. But, solid acid catalyst has high potential to replace liquid acid because it can eliminate those problems (Chopade et al, 2011 & Helwani et al, 2009). Heterogeneous acid catalyst can catalyze simultaneously both esterification and transesterification that showing higher value of FFAs and water, compare to basic homogenous catalyst. Even though this acid catalyst are performed less active during the process, but they are much favorable for low-qualified oil feed stocks that has high FFAs (Feng Guo and Zhen Fang, 2011).

## 2.2 Heterogeneous Solid Base Catalyst

This solid base catalyst that use in the transesterification for biodiesel production had been studied intensively over the last decade. According to Feng Guo and Zhen Fang, they stated that solid bases is referring mainly to the Brønsted basic and Lewis basic activity centers that can supply electrons (or accept protons) for (or from) reactants. In biodiesel production, the oil that is used as a reactant must be a low-qualified oil or fat with low Free Fatty Acid (FFA) and water. This is because if the FFA value in the oil is higher, when react with the solid base catalyst, the transesterification process will be disturb because of the formation of soap or saponification process occur between the reaction of base catalyst and FFA. The oil that used should not contain more than 1% of FFA for alkaline-catalyzed transesterification reaction, but, if the level is exceeds this number, the formation of soap will inhibit the separation of the ester from the glycerin and also reduce the ester conversion rate (Canakci and Van Gerpen, 2001). However, the catalytic efficiency of conventional heterogeneous base catalyst is relatively low and needs to be improved (Feng Guo and Zhen Fang, 2011). The advantages and disadvantages of base catalyzed transesterification reaction can be seen in the Table 2 below:

Table 2 Advantages and disadvantages of base catalyzed trans-esterification (Helwani et al, 2009)

| Advantages | Disadvantages |
|---|---|
| Approximately 4000 times faster than acid catalyzed transesterification | Glycerides and alcohol must be substantially anhydrous, otherwise it will leads to saponification, which reduces the catalytic efficiency, forms gel and causes difficulty in separation of glycerol. |
| The FFA content of the oil should be as low as possible | |
| Methoxides are more effective than | The molar ratio of methanol to oil has |

| | |
|---|---|
| hydroxides | to be 6:1 or higher instead of stoichiometric 3:1 ratio |

There are many solid base catalysts that were used in the biodiesel production, such as zeolites, γ-Alumina, clays and many more. For this research, the catalyst that is use is Montmorillonite clay.

## 2.3 Montmorillonite clay catalyst

From the last decade until now, chemist had struggle and attempted to minimize the waste by designing the new and more environmentally friendly methods for synthesizing useful organic compounds. This movement, so called "Green Chemistry" has produced an array for improved methodologies, including the use of clays as chemical catalyst (Navjeet Kaur et al, 2012). Montmorillonite clays have been used as catalyst in many organic reaction and it is also have several advantages over classical acids, such as strong acidity, non-corrosive properties, cheapness, mild reaction conditions, high yields and selectivity, and the ease of setting and working-up (Habibi and Marvi, 2006). Because of its structure, montmorillonite tends to adsorb organic compounds and this contributes to its ability to catalyze a variety of organic reactions. In addition, montmorillonite clay is easily recovered and can be reused in the reaction (Li et al, 1966). In montmorillonite clay, both Bronsted and Lewis acidic catalytic sites are available, thus its natural occurrence as well as ion exchange properties allow it to function efficiently as a catalyst (Navjeet Kaur et al, 2012).

According to the Nagendrappar, montmorillonite lattice is composed of a sheet of octahedrally coordinated gibbsite $[Al_2(OH)_6]$ sandwiched between two sheets of tetrahedrally coordinated silicate $[SiO_4]^{4-}$ sheets. Then the three-sheet layers are repeating continuously, while the interlayer space will hold the key to the chemical and also the physical properties of the clay (Nagendrappar, 2002).

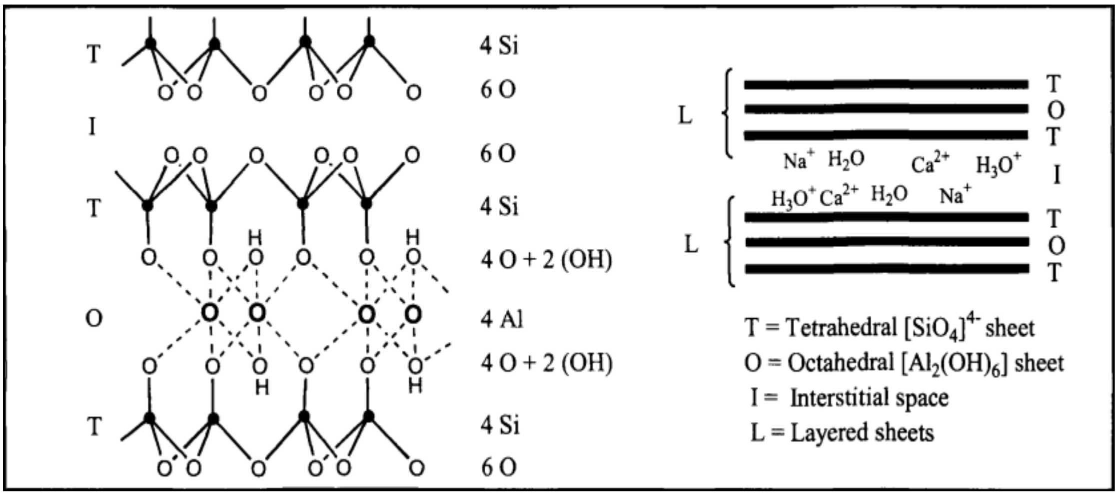


Figure 1 The structure of montmorillonite (Nagendrappar, 2002)

On top of that, according to Navjeet Kaur et al, the advantage of the usage of clay in organic synthesis can be seen as follows:

- Safe to handle, reusable, inexpensive and can prevent waste.
- It may lower the activation energy by stabilizing the transition state.
- It also may act as a general acid or base
- Environmentally benign
- The reaction that use clay are extremely easy to “work-up”, since it is not dissolve in the solvent.

Figure 2 Montmorillonite clay

In preparing the catalyst, there are many methods that are commonly used by the scientist or researchers in their project. Since, catalyst plays a key role in the industry, thus, the preparation of the catalyst plays a dominant role in catalysis research in the past years. Plus, the activity of the catalyst in an organic reaction is influenced by the way of how it is prepared and its pretreatment conditions. So, there are several methods that are found by these researchers to make sure the catalyst produced can perform it task perfectly in the process. The common used methods are impregnation, precipitation, ion exchange and many more. However, the most preferred method is impregnation method.

In the traditional procedures used in preparing the catalyst, there are two types of preparation routes, which are precipitation and impregnation. In the precipitation route, a new solid phase is obtained by the concept of “blending” of proper reagents, which is precipitating agents, from a liquid medium. The resulting precipitate is transformed in subsequent preparation stages into the active catalyst. Meanwhile the impregnation route is explained briefly in the next section below.

## 2.4 Impregnation Method

In the impregnation method, according to Schwarz et al (1994), a solid phase is used as a support to the catalytically active materials, which mounted and stabilized on it. In other words, a certain volume of the active element in the catalyst is doped with the solid support. As a result, the mechanical properties of the catalyst are controlled by the pre-existing support. However, the technique can be referred as incipient wetness impregnation if the volume of the solution is either equal or less than the pore volume of the support (Schwarz et al 1994). This technique is used and followed by drying, when the interaction strength of the active substances in solution with the support is weak. This is to make the loadings of the active substance onto the support is high. In addition, the common technique used in preparing the catalyst is wet impregnation method.

### 2.4.1 Wet Impregnation Method

This technique is also known by soaking or dipping. As stated by Schwarz et al (1994), in this technique, an excess solution is used with the solid catalyst. After certain period of time, the solid is separated from the solution and the excess solvent is removed by drying. However, the amount of the active substance mounted onto the porous solid support, its concentration profile within the carrier grains, and its chemical environment on the support surface depends significantly on the conditions during the early steps in catalyst preparations (Schwarz et al 1994).

## 2.5 Biodiesel Production

In biodiesel production, the main raw materials that involve in the trans-esterification process are alcohol, vegetables oil or animal fats and catalyst. All of these raw materials have their own condition that will affect the yield of biodiesel whether high or low. The suitable catalyst that can be used in this process can be identified as per discussed in the previous section. The correct factors in selecting the suitable catalyst can improve the reaction rate as well as final yield. Meanwhile, the vegetable oil or animal fats must consist of either saturated or unsaturated fatty acids (Talebian-Kiakalaieh et al., 2013). The determination of percentage of free fatty acid or FFA is very important to make sure the yield of biodiesel is higher as well as the formation of soap can be avoided, depends on the catalyst used (Canakci and Van Gerpen, 2001). On top of that, as stated by Talebian-Kiakalaieh et al. (2013), there are many different types of alcohol that can be used in this process, however, many of the research favor the used of methanol is because of it is more feasible due to the low cost and can save the money, as well as it have physical and chemical advantages (i.e shortest chain alcohol and being polar), that is suitable for this trans-esterification reaction (Talebian-Kiakalaieh et al. 2013, and Ma & Hanna, 1999).

In addition, the yield of biodiesel can be calculated using the following equation (F. E. Soetaredjo et al. 2011):

$$yield(\%) = \frac{weight\ of\ biodiesel \times total\ weight\ \%\ of\ FAME\ in\ sample}{weight\ of\ palm\ oil} \times 100\ (1)$$

### 2.5.1 Effect of Loading Ratio of Catalyst in Biodiesel conversion

According to the research made by F. E. Soetaredjo et al. (2011), the loading ratio of KOH in bentonite clay can affect the yield of biodiesel. Increasing amount of KOH will provide more active site on the catalyst to react with palm oil to produce biodiesel. The optimum loading ratio of KOH over bentonite, which gives best performance, is 1:4 (F. E. Soetaredjo et al., 2011). However, the further increase of KOH amount will reduce the performance of biodiesel production. This is due to the high formation of Al-O-K compound that have lower catalytic activity (F. E. Soetaredjo et al., 2011).

### 2.5.2 Effect of methanol to oil molar ratio

The effect of methanol to oil ratio is also affect the yield of biodiesel. This can be explained by the concept of Le'Chatelier. The trans-esterification process is reversible. The higher amount of alcohol to oil ratio will shift the equilibrium to the product side and make the conversion higher. From the research made by Talebian-Kiakalaieh et al. (2013), the methanol to oil molar ratio that gives higher yield of biodiesel is 70:1, and the conversion does not give any effect beyond that.

### 2.5.3 Effect of Catalyst

The reaction conversion of biodiesel is increase with the amount of catalyst used is increase from 5% to 10% wt. This is due to the high surface area of reaction, as well as higher amount of active site on the catalyst that increases the speed of reaction and increase the conversion. However, the amount of catalyst beyond 10 %wt will cause the conversion unchanged but increase the production cost (Talebian-Kiakalaieh et al. 2013).

### 2.5.4 Effect of Temperature

According to the research made by Talebian-Kiakalaieh et al. (2013), the effect of higher temperature which is exceed 65°C, it cause the conversion of biodiesel decreased. This is because, during the heating process, there are three types of chemical reaction occur when the temperature is keep getting higher which are oxidative, hydrolytic and themolytic, which from these reaction, it forms some undesirable components which have a negative effect to the conversion of biodiesel.

Thus, based on the previous research regarding biodiesel production, the catalyst that is very effective for the reaction is solid basic catalyst. The base catalyst is chosen because of lots of advantages that it have compare to the acid catalyst. In addition, since biodiesel is in the liquid phase, it is highly encourage using solid catalyst for the reaction to make sure the separation process of the product with the catalyst is easier and less cost will be use. In fact, there are many types of solid base catalyst, but from the research, there are lots of advantages if using clay as a catalyst for the trans-esterification process. This is due to the advantages that clay catalyst have, which is suitable for this project. Plus, the common preferred method in preparing the catalyst is the wet impregnation method.

Other than that, the conversion of biodiesel is mainly affected with several parameters, which are methanol to oil ration, reaction temperature, weight of catalyst and reaction time. With the perfect condition for each parameter, the yield of biodiesel produce is in the maximum level.

# CHAPTER 3

# METHODOLOGY

This chapter explains in detail all the related procedures during conducting the experiment. Overall process flow diagram of the research methodology to study about preparation and characterization of catalyst and biodiesel production in current research is presented in research methodology section. Next, these projects are divided into three parts: first, the preparation of the catalyst by using experimental approach, second, characterization of the catalyst and lastly, biodiesel production.

## 3.1 Research Methodology

The methodology used in conducting this research project is based on the discovery and experiment. First, all the important information regarding based catalyst and biodiesel are gathered together from the previous journal and paper work, and compiled it in the literature review. Then, the research continues with conducting the experiment to produce the potassium based clay catalyst sample to undergo the next steps which are characterizing them. After that, the effectiveness of all prepared catalyst in producing high yield of biodiesel is tested and the result is obtained. Lastly, all results are analyzed and reported.

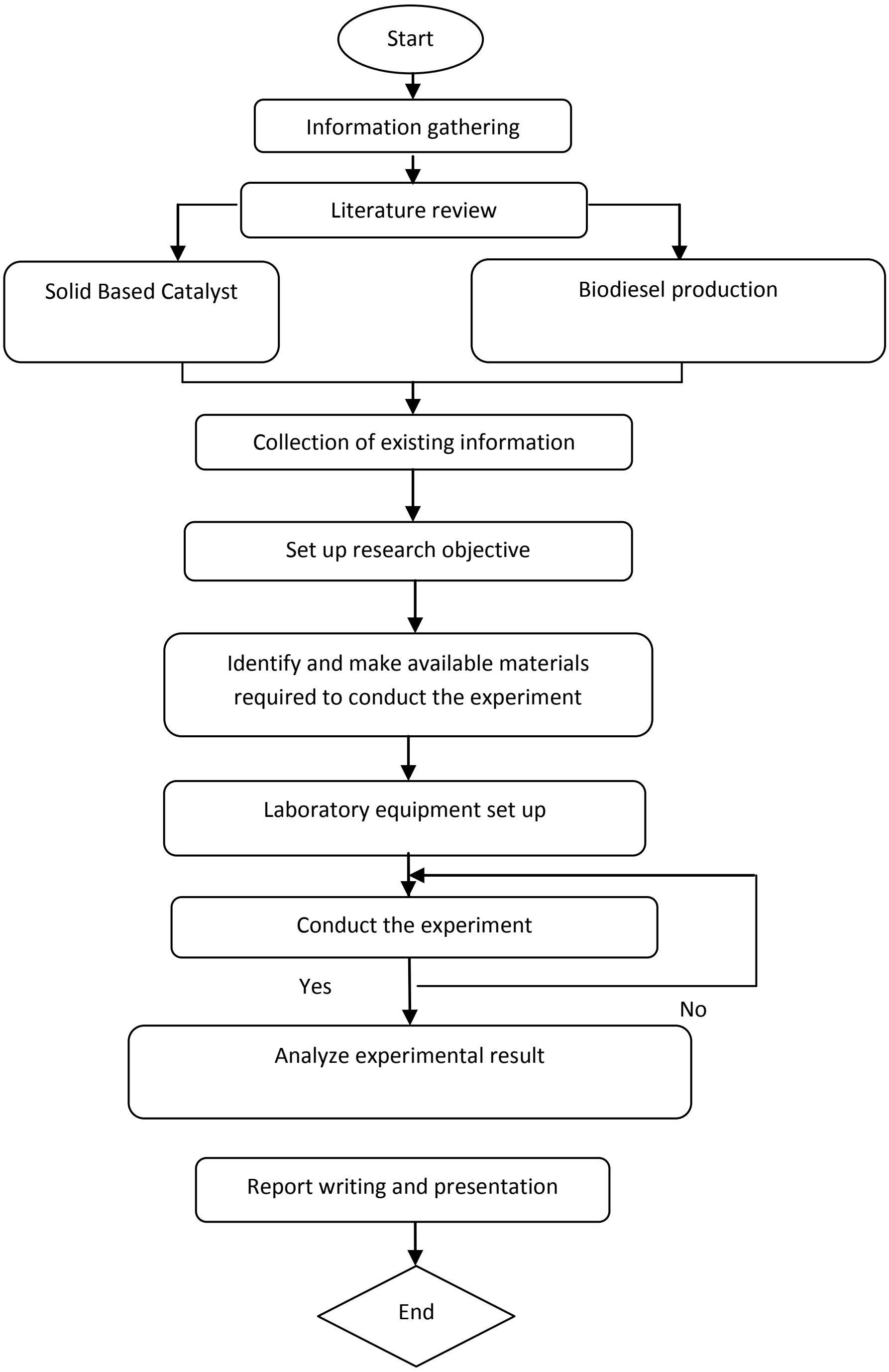


Figure 3 Flowchart of the Potassium Based Clay Catalyst Project

## 3.2 Preparation of the Catalyst

For this research, two catalysts will be prepared by using different type of potassium as an active site, which are Potassium Carbonate, and Potassium Hydroxide. Meanwhile, the catalyst that will be used as based is Montmorillonite K10 clay. These substances will undergo Wet Impregnation method that will conducted in the laboratory. The ratio between Potassium substances and MK-10 clay is 1:10. The apparatus and procedure for the preparation of the catalyst can be seen as follow:

### 3.2.1 Apparatus

The beaker is used to dissolve both Potassium substances and MK-10 clay with distilled water. Plus, the Potassium solution will pour into the burette and retort stand will be used to hold the burette containing Potassium solution. Then, the electric heater is used to heat the mixture till 60°C and magnetic stirrer to stir the mixture continuously. The temperature of the mixture is measure by using thermometer. In addition, weighing machine is used to weight the amount of MK-10 clay and Potassium substances. Then filter paper and petri dish are used to dry the slurry in the oven.

### 3.2.2 Preparing KOH/MK-10

Potassium Hydroxide and MK-10 clay are weighted, and then put in the beaker. Both substances had been dissolved with distilled water. The Potassium Hydroxide solution had been poured into the burette and placed on top of the beaker containing clay solution. Then, the beaker is put on the electric heater, and the magnetic stirrer is put inside the beaker. The mix of Potassium Hydroxide solution with MK-10 clay solution had been set at 60°C and under continuous stir for 12 hour, based on the Figure 4.

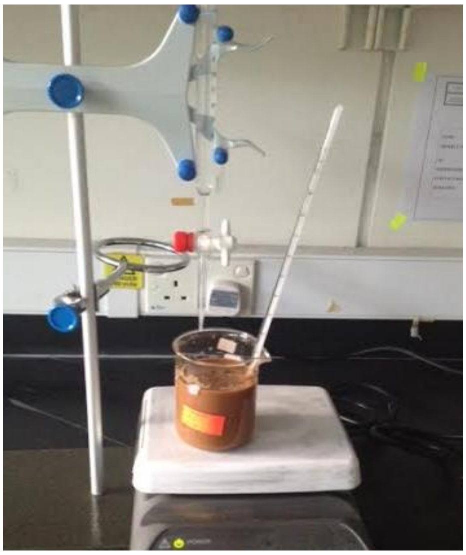


Figure 4 Apparatus Setup for Mixing KOH with MK-10 at 60°C for 12 hour

The slurry had been collected after completing the impregnation process and dried in the oven for 12 hour at 110°C, based on Figure 5. Then, the catalyst had been calcined for 5 hour at 400°C in the furnace. After that, the KOH/MK-10 catalyst had been prepared.

Figure 5 The Catalyst is dried in the oven for 110°C for 12 hour

### 3.2.3 Preparing $K_2CO_3$/MK-10

Potassium Carbonate and MK-10 clay are weighted, and then put in the beaker. Both substances had been dissolved with distilled water. The Potassium Carbonate solution had been poured into the burette and placed on top of the beaker containing clay solution. Then, the beaker is put on the electric heater, and the magnetic stirrer is put inside the beaker. The mix of Potassium Carbonate solution with MK-10 clay solution had been set at 60°C and under continuous stir for 12 hour. The slurry had been collected after completing the impregnation process and dried in the oven for 12 hour at 110°C. Then, the catalyst had been calcined for 5 hour at 400°C in the furnace. After that, the $K_2CO_3$/MK-10 catalyst had been prepared.

## 3.3 Characterization of the Catalyst

In this part, the analytical equipments that are use in the characterization process can be seen as follow:

### 3.3.1 X-Ray Diffraction

Powder X-ray Diffraction pattern of MK-10 with the KOH/MK-10 and $K_2CO_3$/MK-10 can be recorded on a Bruker D8 Advance XRD at 40 kV and 30 mA using Cu Kα radiation over the 2θ range of 5 - 90°. The process is started by switch on the machine. Then, the set the kV by adjusting the kV dial until the value is reached 40 kV. After that, the value of mA is set by adjust the mA dial to the desired value of mA which is 30 mA. Then, the sample is inserted into the machine. Next, the diffraction experiment of the sample is been done by the computer to analyze and obtained the graph. The equipment can be seen in the Figure 6.

Figure 6 Bruker D8 Advance XRD equipment

### 3.3.2 Thermal Gravimetric Analysis

The maximum temperature of the MK-10 and Potassium/MK-10 catalyst that can sustain in the trans-esterification process can be determined by using Perkin Elmer Pyris 1 TGA Analyzer, with the range temperature range 30°C - 800°C at a heating rate 10°C/min. The equipment is switch on and the sample is put on the sample pan. Then, push the button of raising the furnace in the software. Next, stabilize the weight of the sample by pressing the zero weight buttons to zero the balance of the sample. Then, enter the starting temperature and wait for the temperature to stabilize and press the start button. After complete the analysis, the sample had been removed from the equipment and close the software and switch off the equipment. The equipment can be seen in the Figure 7.

Figure 7 Perkin Elmer Pyris 1 TGA equipment

### 3.3.3 Brunauer-Emmett-Teller

The BET analysis is done by using Micromeritics ASAP 2020 equipment. The surface area is calculated using adsorption data at relative pressure ranging from 0 to 1.0. The analysis is started by put the sample in the equipment and verifies the parameters inside the software. Then, click start to begin the experiment. Next, the result of adsorption isotherm graph is obtained.

## 3.4 Biodiesel Production

After preparing all of the catalyst and characterize them, the catalyst need to undergo the next experiment to determine the most effective catalyst between MK-10, KOH/MK-10 and $K_2CO_3$/MK-10 that can lead to a higher yield of biodiesel in trans-esterification process. In this process, the methanol is used and palm oil is selected to produce Fatty Acid Methyl Ester or biodiesel. There are four parameters that need to be considered to make sure the production is favored and effective, which are reaction time, reaction temperature, methanol to oil ratio and weight of catalyst. In determining the most effective catalyst, all these parameters are keep in constant as follows:

| | |
|---|---|
| ❖ Reaction Time | : 4 hour |
| ❖ Reaction Temperature | : 60°C |
| ❖ Methanol to Oil Ratio | : 10:1 |
| ❖ Weight of Catalyst | : 2% wt |

The apparatus and the procedure of the experiment are explained in the next section below.

### 3.4.1 Apparatus

The reaction of the palm oil, methanol and catalyst will be in the 3-neck bottle flask that equipped with thermometer, to measure the temperature of the reaction. Then, reflux condenser is put on top of the flask to condense the vapor inside the flask. Moreover, oil bath is used to maintain the temperature of the reaction to 60°C by submerged the flask in it. Plus, electric heater and magnetic stirrer are used to heat the reaction and stir continuously the mixture. The methanol, palm oil and catalyst had been weighted by using weighing machine. Separating funnel is used to separate the palm oil with glycerin.

### 3.4.2 Procedure for Biodiesel Production (Different Catalyst)

The apparatus is set up based on the Figure 8. Oil bath is prepared and put on the electric heater. Then, the palm oil had been weighed and poured into the 3 neck bottle flask and submerged it into the oil bath and equipped with the reflux condenser. Next, the palm oil is heated to 60°C and the temperature was kept constant. After that, the methanol and MK-10 catalyst had been weighed and put into the flask to mix with palm oil by using magnetic stirrer. Then, the experiment is run for 4 hour with constant temperature of 60°C.

Figure 8 Apparatus setup for biodiesel production

After 4 hour, the transesterified oil is allowed to settle overnight in separating funnel based in the Figure 9. Two layers will be produced and the biodiesel is collected and analyzed. Then, the procedure is repeated by using different catalysts which are KOH/MK-10 and $K_2CO_3$/MK-10.

Figure 9 The transesterified oil is settled for overnight

### 3.4.3 Procedure for Biodiesel Production (Different Reaction Temperature)

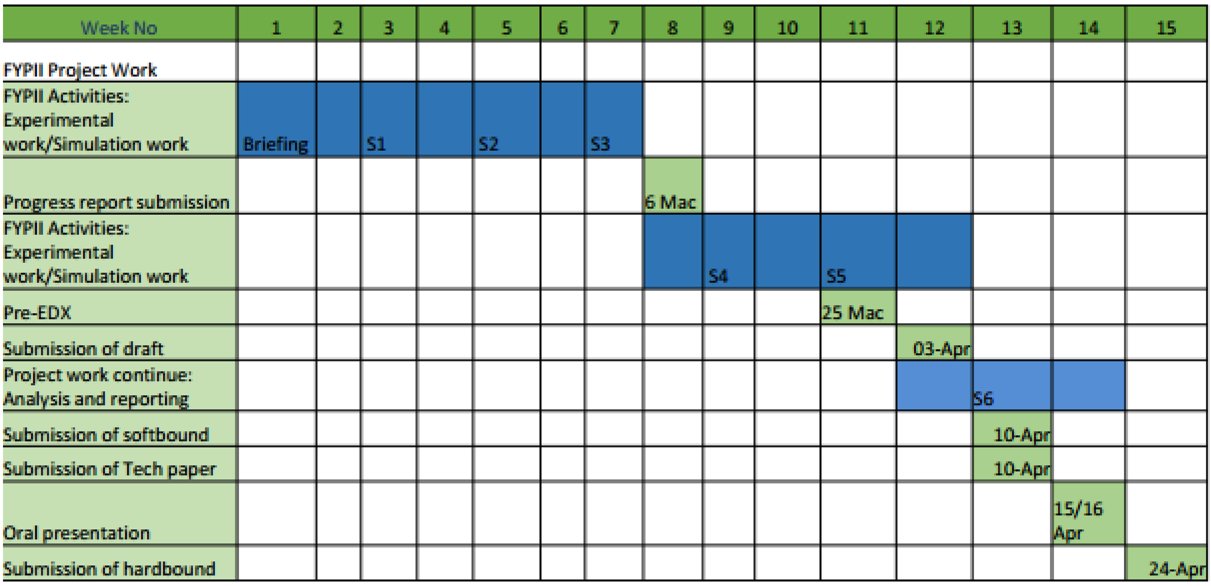
The apparatus is set up based on the Figure 8. Oil bath is prepared and put on the electric heater. Then, the palm oil had been weighed and poured into the 3 neck bottle flask and submerged it into the oil bath and equipped with the reflux condenser. Next, the palm oil is heated to 50°C and the temperature was kept constant. After that, the methanol and KOH/MK-10 catalyst had been weighed and put into the flask to mix with palm oil by using magnetic stirrer. Then, the experiment is run for 2 hour with constant temperature of 50°C. After 2 hour, the transesterified oil is allowed to settle overnight in separating funnel based in the Figure 9. Two layers will be produced and the biodiesel is collected and analyzed. Then, the procedure is repeated by varying the temperature at 50°C, 60°C, 70°C and 80°C for every 4 h, 6 h, 8 h and 10 h

The results obtained for the characterization of all prepared catalyst as well as the results for biodiesel will be discussed in the next chapter.

## 3.5 Key Milestones

The key milestones for the second half of this project which is, Final Year Project II can be seen as follows:

Table 3 The Key Milestone for this project in FYP II



| Week No | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| FYPII Project Work | | | | | | | | | | | | | | | |
| FYPII Activities: Experimental work/Simulation work | Briefing | 🟦 | S1 | 🟦 | S2 | 🟦 | S3 | | | | | | | | |
| Progress report submission | | | | | | | | 6 Mac | | | | | | | |
| FYPII Activities: Experimental work/Simulation work | | | | | | | | 🟦 | S4 | 🟦 | S5 | 🟦 | | | |
| Pre-EDX | | | | | | | | | | | 25 Mac | | | | |
| Submission of draft | | | | | | | | | | | | 03-Apr | | | |
| Project work continue: Analysis and reporting | | | | | | | | | | | | 🟦 | S6 | 🟦 | |
| Submission of softbound | | | | | | | | | | | | | 10-Apr | | |
| Submission of Tech paper | | | | | | | | | | | | | 10-Apr | | |
| Oral presentation | | | | | | | | | | | | | | 15/16 Apr | |
| Submission of hardbound | | | | | | | | | | | | | | | 24-Apr |

### 3.6 Gantt Chart

The Gantt chart for this project can be referred as in the table below:

Table 4 Gantt Chart for this project

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Shipping of Chemicals | ■ | ■ | ■ | ■ | ■ | ■ | | | | | | | | |
| Meeting with Supervisor | Based on the schedule had been arranged with the SV | | | | | | | | | | | | | |
| Start Preparing Catalyst | | | | | | | ■ | ■ | | | | | | |
| Make Progress Report | | | | | | | | ■ | | | | | | |
| Characterize Catalyst | | | | | | | | | ■ | ■ | | | | |
| Pre-SEDEX | | | | | | | | | | | ■ | | | |
| Biodiesel Production | | | | | | | | | | | ■ | | | |
| Draft Submission Report | | | | | | | | | | | | ■ | | |
| Submission of Softbound & Tech Paper | | | | | | | | | | | | | ■ | |
| Oral Presentation | | | | | | | | | | | | | | ■ |
| Hardbound Submission | | | | | | | | | | | | | | ■ |

# CHAPTER 4

# RESULTS AND DISCUSSION

This chapter discusses on the results obtained from the experiments conducted previously. After undergone the procedure in preparing the catalyst and analyze them with the analytical equipment, the results obtained for studying the characteristics of the MK-10 clay, KOH/MK-10 and $K_2CO_3$/MK-10, will be discussed in the next section.

## 4.1 XRD Pattern

The XRD analysis is basically to check the presence of the active material, which is Potassium on the MK-10 clay. In addition, this analysis also provide with other important information that can help the researchers to clearly understand the characteristics of the sample prepared. The information are:

- Lattice parameters
- Phase identity
- Phase purity
- Crystallinity
- Crystal structure
- Percent phase composition

However, the XRD analysis cannot provide certain information about the sample such as the exact amount of the element in that sample, the details element that has in the sample and others. All of this information can be obtained in a graph, when the Potassium based clay catalyst and parent Montmorillonite K-10 clay catalyst are run in the XRD equipment.

The XRD pattern of the parent MK-10 clay, KOH/MK-10 and $K_2CO_3$/MK-10, which is prepared with the ratio of 1:10, is given in the Figure 10. The element that present in the sample can be determined through the reflections of the peak and also with the detail information that stated in that graph. The reflections of the peak that give the information about the planes, which are (001), (003) and (130 – 200) proves that the presence of Montmorillonite in the parent MK-10 clay, as well as in the KOH/MK-10 and $K_2CO_3$/MK-10. Since the loading ratio of KOH and $K_2CO_3$ is 1:10, thus the XRD pattern of both catalysts is quite similar with the parent MK-10. This pattern proves there are still presences of the MK-10 structure inside the Potassium based clay catalyst, and the structures are not collapsed. However, there are still difference between 2 prepared catalyst and parent MK-10 graph in the terms of peak reflection, to describe the existence of the active components which is KOH and $K_2CO_3$ in the MK-10 clay. This is confirms that the preparations of the catalyst is quite perfect, which the both Potassium components are well dope into the pore area in the parent clay structure.

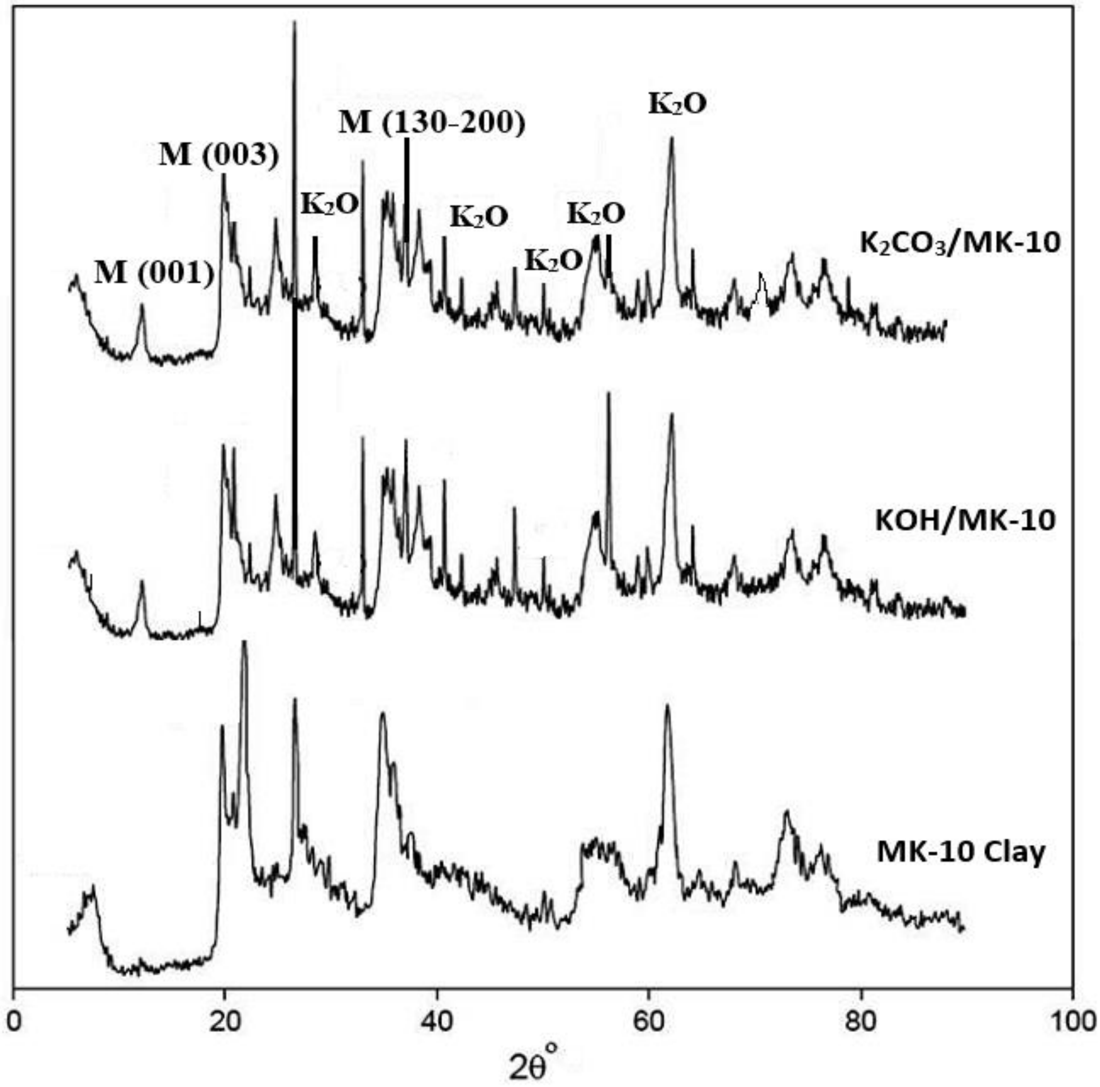


Figure 10 The XRD patterns of MK-10 clay, KOH/MK-10 and $K_2CO_3$/MK-10

However, the diffraction peak of the prepared Potassium catalyst that had been observed, which have different peak with the parent clay can be assigned to KOH or $K_2CO_3$, or $K_2O$. If the active components use in the preparation of catalyst is come from Potassium group (KOH and $K_2CO_3$), the chance to appear the new phase in the XRD pattern which is known as $K_2O$ is possible. This is because there is a possibility for the KOH or $K_2CO_3$ is not well dispersed on the parent MK-10 clay surface or structure during the preparation. Then during the calcinations at temperature of 400°C, the potassium hydroxide and the potassium carbonate are converted into the $K_2O$ (Noiroj et al, 2009 and Gálvez et al). In addition, the diffraction peak of the $K_2O$ for both KOH/MK-10 and $K_2CO_3$/MK-10 is observed around at $2\theta = 30°$, 43°, 50°, 55° and 63°.

## 4.2 Thermal Stability of Catalyst

The study of thermal stability of the catalyst by using Thermal Gravimetric Analysis equipment is to determine the maximum temperature that can catalyst sustain in the process before breaking down. Basically, thermal stability is the ability of a substance to maintain its properties as nearly unchanged as possible on heat. This information regarding thermal stability is important for engineers so that they can know the temperature ranges of which substances can be used.

To determine the thermal stability of the prepared sample, the sample is tested with temperature heat range from 30°C to 800°C. Then, the result of the sample, MK-10, KOH/MK-10 and $K_2CO_3$/MK-10 can be characterized based on the graph in Figure 11, Figure 12 and Figure 13. From the graph in Figure 11, the moisture content of parent MK-10 clay is 9.035%. This is shows that, the water content in the parent MK-10 is high if it is compared with the prepared KOH and $K_2CO_3$. This is due to the parent clay does not undergoes the calcinations process in the procedure, so the water content in the parent clay is high. Plus, the free spaces in the pore volume also provide the water to fill in the space on the structure of MK-10 clay, hence increase the moisture content of the parent clay.

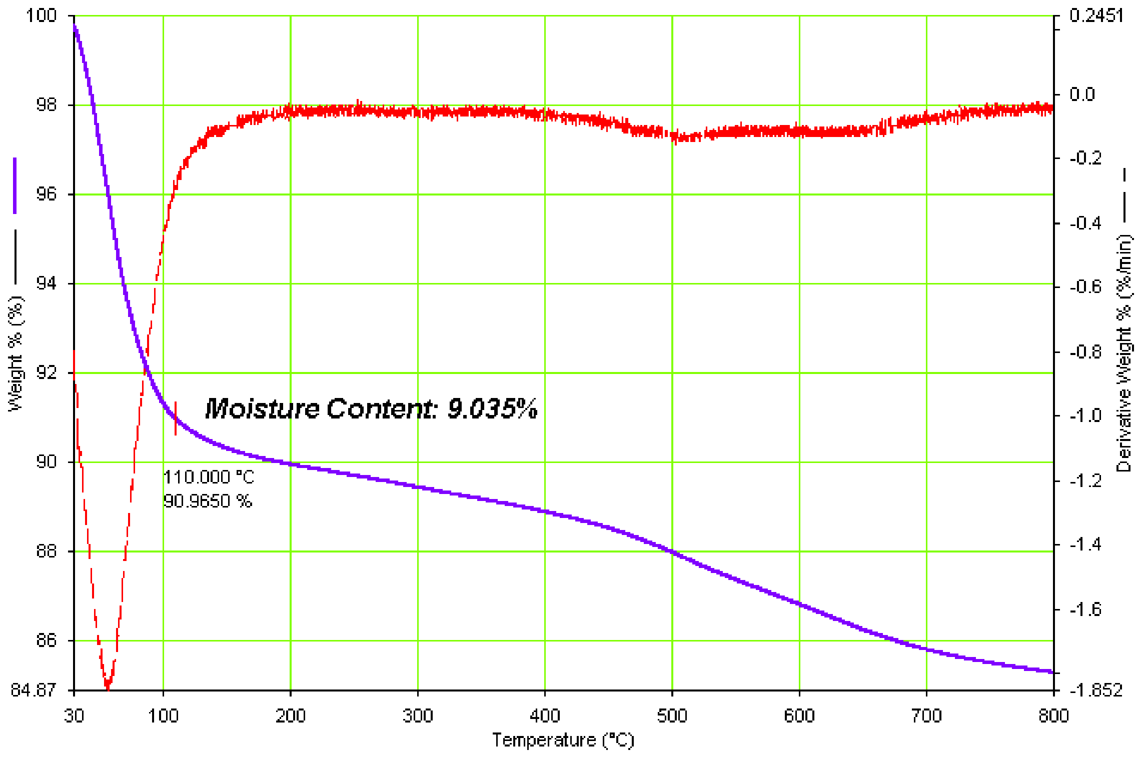


Figure 11 The TGA curve for parent MK-10 clay

However, when the MK-10 clay sample is tested in the TGA equipment, the weight loss of the sample is dropped drastically at temperature range from 30°C - 100°C. This is due to the dehydration of the water content on the parent clay surface that causes the weight of the sample decrease. Then, the line is continuously decreased until the final weight of the parent clay is 85% at temperature 800°C.

Meanwhile, the TGA curve for KOH/MK-10 can be seen in the Figure 12. The graph shows that the moisture content of the sample is 2.9035%. This is confirm that the water content inside the surface of the structure is less, due to the less space of the pore volume on the parent clay that had been filled by the KOH. In addition, the results from calcinations process at 400°C during the preparation method also caused some of the water content vaporize and reduce the moisture content in the sample. Moreover, the weight loss of the sample is decrease gradually from 30°C - 500°C, and slightly dropped drastically at temperature range from 500°C - 630°C. This trend of the line proves the evaporation of the impurities inside the sample that reduce the weight of the sample. In fact, the red line indicates the derivative weight on the sample shows that there is slightly decrease with the weight at temperature of

600°C. This condition can confirmed that the sample is start to decompose and breaking down.

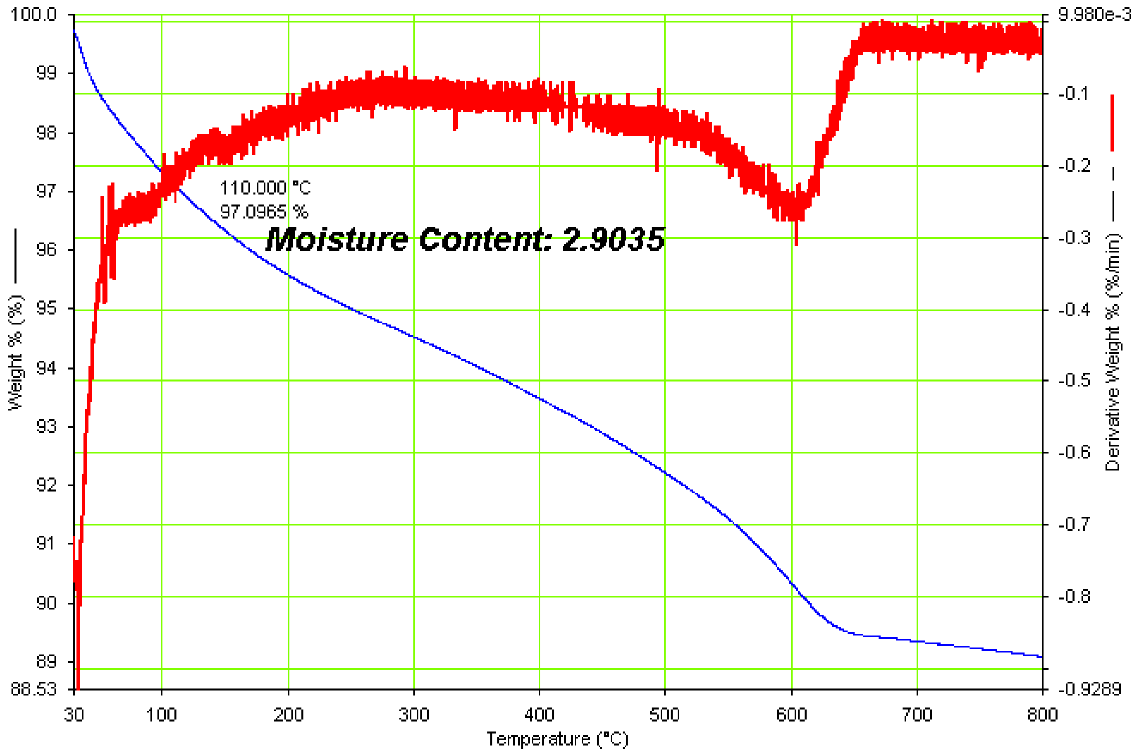


Figure 12 The TGA curve for KOH/MK-10

On the other hand, the graph of TGA for $K_2CO_3$/MK-10 sample can be seen in the Figure 13. For this sample, the moisture content is 4.2884%, which is quite higher compare to KOH/MK-10 sample. This is due to the pore volume of the sample is higher compare to the KOH/MK-10, which provide some space for water to fill in that space. That is the reason why the moisture content is slightly higher compare to KOH/MK-10. However, it is still lower than the moisture content of the parent MK-10 clay, due to the calcinations process in the preparing method that cause the water content to dehydrate from the surface of the sample.

Besides that, the blue line that referring to the weight loss is decreased gradually start from the temperature of 30°C - 680°C, significant to the dehydration of Carbon Dioxide content inside the sample. However, for the derivative weight line, the line is slightly decreased of the derivative weight at temperature of 680°C, as well as the weight loss. This is confirms that the sample is start to breakdown and decompose at temperature of 680°C.

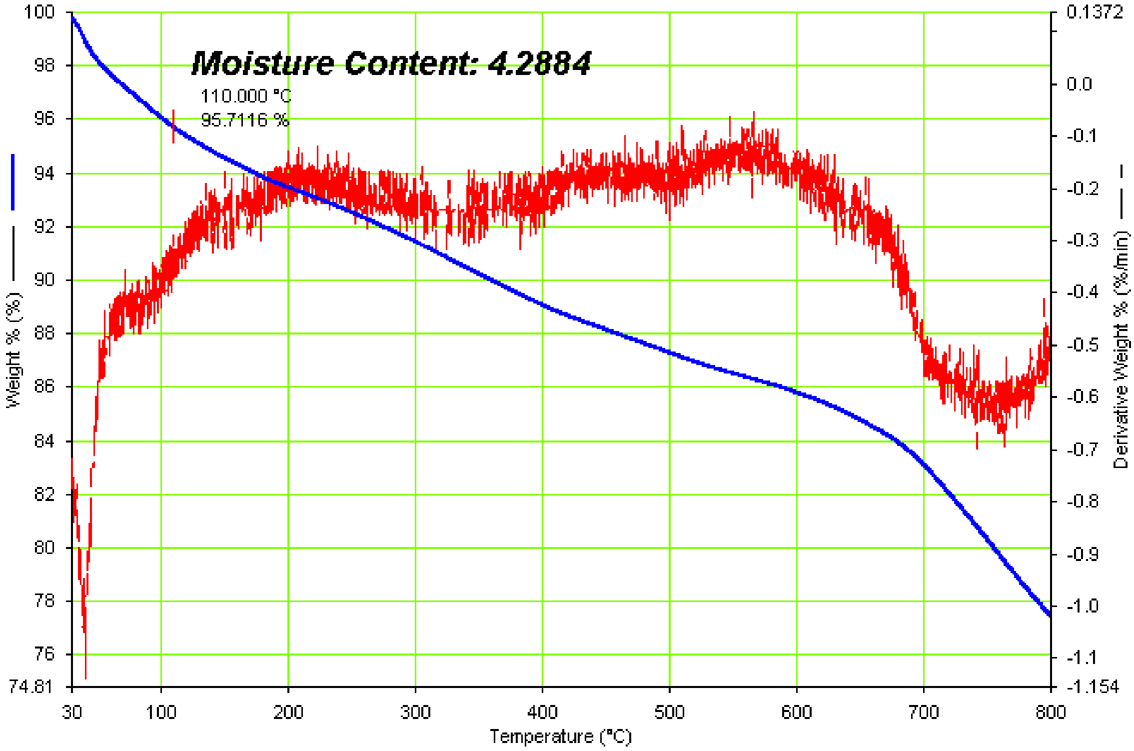


Figure 13 The TGA curve for $K_2CO_3$/MK-10

### 4.3 BET Surface Area and Pore Volumes of Catalyst

The results of all three samples that obtained after had being tested in the BET equipment, are summarized in the Table 5. For parent MK-10 clay, the BET surface area is 194 $m^2/g$ and the pore volumes is 0.37 $cm^3/g$. Generally, the surface area and pore volumes of the catalyst will be decreased when the catalyst is loading with active substance. This is because of, during impregnation, the molecule of active substance will filled the available pores in the catalyst, which will lead to a decrease of the surface area of catalyst. This indicated that the presence of the molecule of active substances on the surface of the catalyst, and also on the surface of the pores within the catalyst particles (F. E. Soetaredjo et al., 2011).

Table 5 The surface area, pore volume and pore size for MK-10 clay, KOH/MK-10 and $K_2CO_3$/MK-10

| Catalyst | Surface Area ($m^2$/g) | Pore Volume ($cm^3$/g) | Pore Size (A) |
|---|---|---|---|
| **Clay MK-10** | 194 | 0.37 | 54 |
| **KOH/MK-10** | 174 | 0.32 | 47 |
| **$K_2CO_3$/MK-10** | 167 | 0.33 | 42 |

The surface area for both KOH/MK-10 and $K_2CO_3$/MK-10 are 174 $m^2$/g and 167 $m^2$/g, respectively. From the result obtained, it is clearly shows that the surface areas for both samples were decreased as compared to the parent MK-10 clay. This is because, during the impregnation process, the KOH and $K_2CO_3$ molecules are filled the available pores on the parent MK-10 surface, which is lead the decreasing of the surface area of the catalyst. Thus, this is support that the fact of the successful intercalation process between KOH and $K_2CO_3$ with the parent MK-10 clay. However, the surface area of $K_2CO_3$/MK-10 sample was lower than the KOH/MK-10 sample. This is might be due to the structural geometry and the size of the $K_2CO_3$ molecule is bigger compare to KOH molecule. Even though the ratio is same for both molecule, but with different size and geometry cause the different value in the surface area.

Besides that, the pore volumes for KOH/MK-10 sample is 0.32 $cm^3$/g, meanwhile, pore volumes for $K_2CO_3$/MK-10 sample is 0.33 $cm^3$/g. Both of them have lower pore volumes compare to the parent MK-10 clay. This is also due to the both potassium molecules were filled in the pores on the parent clay, which cause the volumes to be decreased.

In addition, the textural characterization of all these samples was study by using adsorption isotherm at a temperature lower than or nearly equal to critical temperature. Plus, the reaction between the adsorbent and adsorbate to produce the adsorption process is control by using pressure, based on Le-Chatelier’s principle. Normally, $N_2$ gas is used as adsorbate. The Figure 14 shows the $N_2$ adsorption and desorption isotherm graph of the parent MK-10 clay, KOH/MK-10 and $K_2CO_3$/MK-10. When the gas pressure is increase, the adsorption process is favored, so the gas is started to fill in the pores on the adsorbent (the catalyst samples). The amount of volume of gas adsorbed is depending on the limited number of vacancies on the surface of the adsorbent, even the pressure is keep increase. It means that if all of the pore sites are fully occupied with the gas and further increasing of the pressure will give no difference in the adsorption process. Basically, the volume of the gas adsorbed that can obtained from the graph will shows the surface area and pore volumes of the 3 samples, through applying the BET equations.

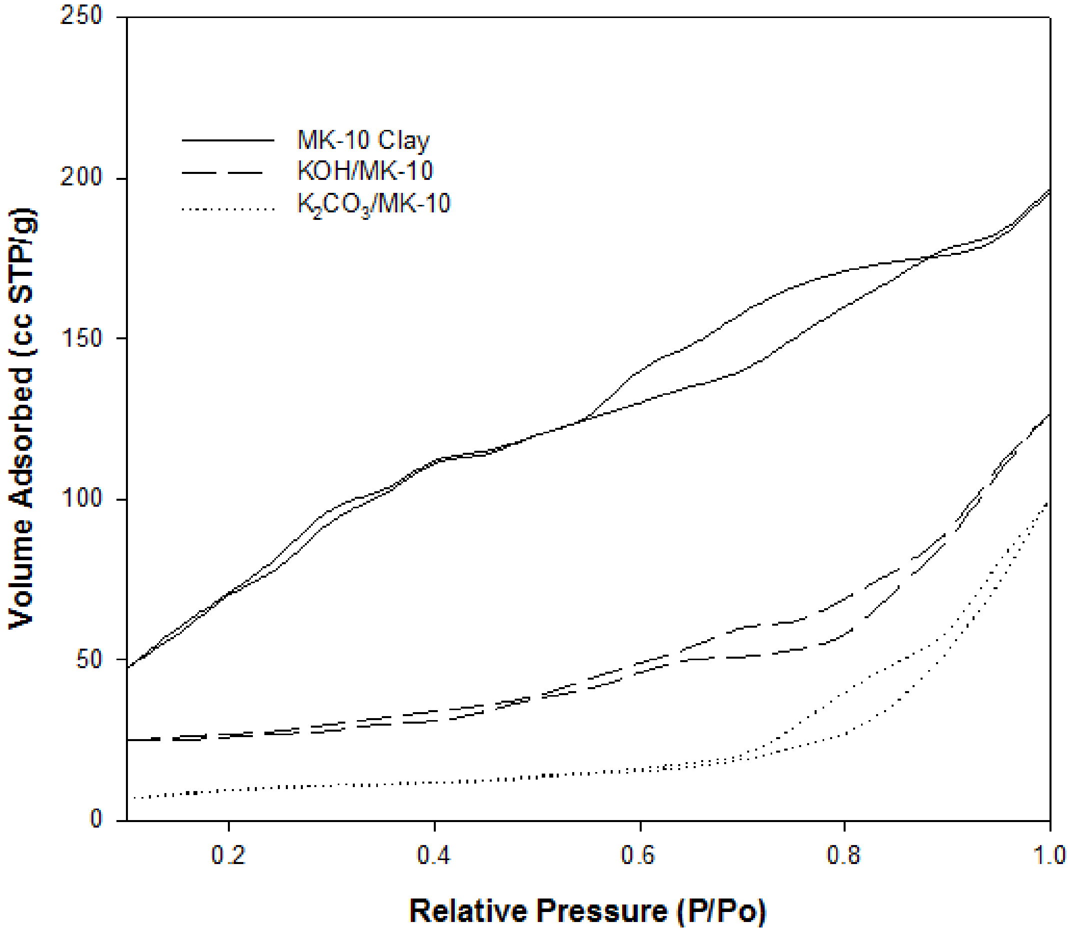


Figure 14 $N_2$ adsorption isotherm graph of MK-10 clay, KOH/MK-10 and $K_2CO_3$/MK-10

From Figure 14, the hysteresis loop for parent MK-10 clay shows the Type I isotherm, meanwhile, the hysteresis loop for KOH/MK-10 and $K_2CO_3$/MK-10 are agreed to Type III isotherm, according to the IUPAC nomenclature. The parent MK-10 clay hysteresis loop shows the ability of the sample to absorb the gas in the large amount when the pressure is increase, corresponding to the large amount of available pores and pore volumes on the sample. However, since the parent clay is loading with two Potassium molecule in the pores, the pore volumes of the sample tested are decrease, and hence it is shows the ability of the sample to adsorbing the gas also decrease, as been proven in the Figure 14.

## 4.4 Biodiesel Production

The catalytic activity of the 3 samples of the catalyst in trans-esterification of palm oil had been done in order to investigate the effectiveness of the catalyst to produce biodiesel. It has been measured from the percentage yield of fatty acid methyl ester (FAME) produce from the reaction. In order to determine the percentage yield, the important parameters had needed to be constant and the 3 different catalysts (MK-10 clay, KOH/MK-10 and $K_2CO_3$/MK-10) are the variables. The constant parameters that need to be considered are methanol to oil ratio, reaction time, weight percent of the catalyst, and the reaction temperature. Each of the parameters has their optimum condition that can give higher yield of FAME. However, to determine this optimum condition for each parameter, more detail experiment and research need to be carried out. For the first experiment to check the percentage yield of the FAME, the operating condition of the parameters can be seen as follow:

- Methanol to oil ratio : 10:1
- Reaction time : 4 hour
- Weight percent of the catalyst : 2% wt
- The reaction temperature : 60°C

The percentage yield of biodiesel production by using MK-10 clay, KOH/MK-10 and $K_2CO_3$/MK-10 catalysts can be seen in the Figure 15.

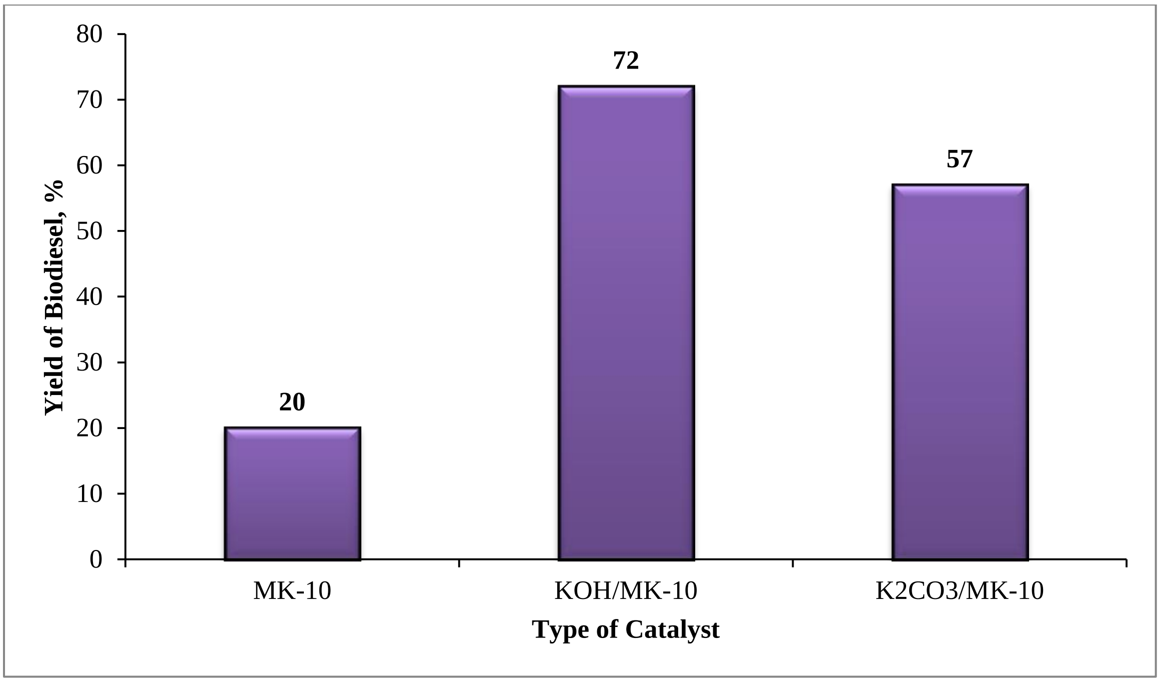


Figure 15 The percentage yield of biodiesel

From the graph above, it is clearly shows that the production of biodiesel with the usage of KOH/MK-10 catalyst produces the highest yield, which is 72%. Meanwhile, the use of $K_2CO_3$/MK-10 catalyst leads to a 57% of biodiesel production. Therefore, further detailed experiment has been carried out with the KOH/MK-10 use as catalyst to study the yield of biodiesel with constant condition of weight percent of catalyst and the methanol to oil ratio. The variable parameter that needs to be studied is temperature which is start from 50°C – 80°C. The graph of this experiment can be seen in the Figure 16. From the graph obtained, it is show that the percentage yield of biodiesel at temperature of 60°C has the highest yield compare to other temperature. The yield is increase continuously start from 38% at time = 2 hour, until 82% at time = 10 hour. Meanwhile, at reaction temperature of 50°C, the yield is continuously increased higher than reaction temperature of 60°C (from 2 hour to 6 hour). However, at time start from 6 hour to 10 hour, the yield of biodiesel at 50°C is decreased lower than temperature of 60°C.

On the other hand, the temperature of 70°C and 80°C have lower percentage yield of biodiesel than at temperature of 60°C. It is recorded that the lowest yield of biodiesel is at temperature of 80°C. This is because, at this temperature, the catalytic activity of the catalyst with the palm oil and methanol is not at optimum condition, hence, produce lower yield of biodiesel. Therefore, it can be say that, the optimum temperature that lead to higher yield of biodiesel is at 60°C.

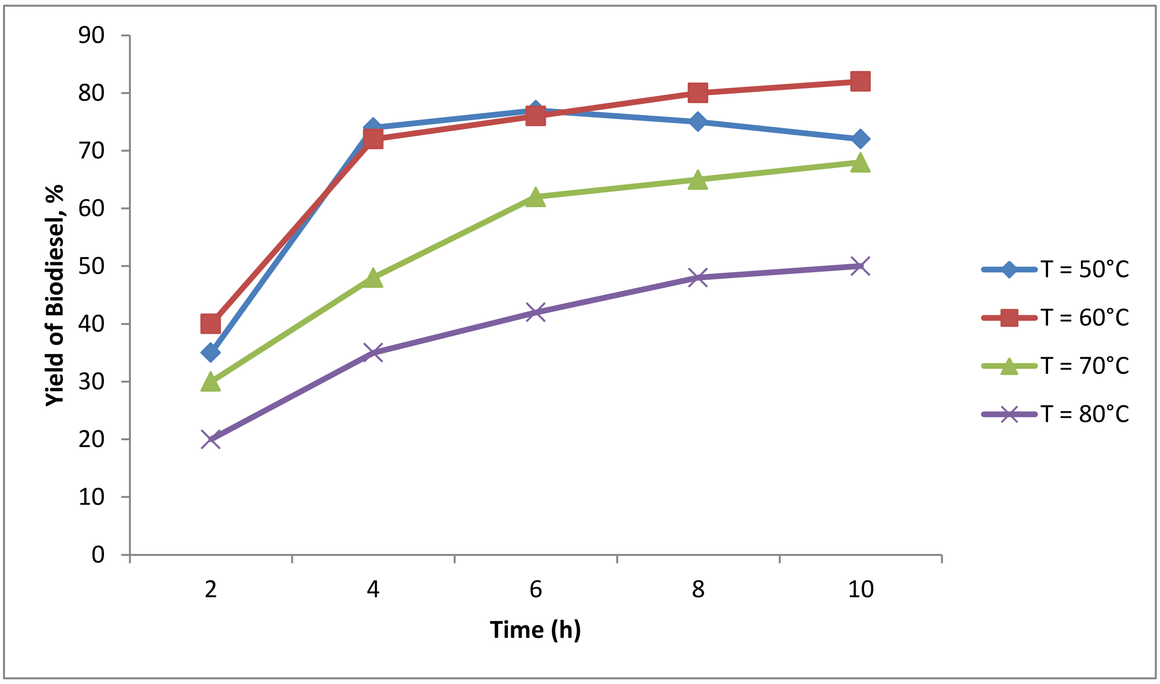


Figure 16 The percentage yield of biodiesel with different reaction temperature

# CHAPTER 5

# CONCLUSION AND RECOMMENDATION

## 5.1 Conclusion

As a conclusion, the objectives of this project were achieved successfully. The preparation of KOH and $K_2CO_3$ over MK-10 was done by wet impregnation method. The characteristics of the catalyst were studied.

The additional peaks on the XRD pattern of KOH/MK-10 and $K_2CO_3$/MK-10 proves the existence of KOH and $K_2CO_3$ substances, respectively, and the impregnation of both substances on the MK-10 were succeed.

On top of that, in the terms of thermal stability of the catalyst, it is show that the maximum temperature for the catalyst can sustain before breakdown and decompose is around 600°C for KOH/MK-10 and 680°C for $K_2CO_3$/MK-10.

Besides that, the surface area of MK-10 clay recorded is 194 $m^2/g$ and its pore volume is 0.37 $cm^3/g$. From the results obtained, the surface area and pore volumes for both KOH/MK-10 and $K_2CO_3$/MK-10 were decreased compare to parent clay. This is confirmed the presence of the Potassium substances on the surface of the MK-10. This is due to Potassium substances filled the available pores on the parent MK-10 during the impregnation process.

In trans-esterification of palm oil by using MK-10 clay and 2 Potassium based clay catalysts, the highest yield of biodiesel produce is 72% with KOH/MK-10 catalyst, followed by 57% with $K_2CO_3$/MK-10. This had been carried out at operating parameters of reaction time 4 hour, 2% wt catalyst, methanol to oil ratio of 10, and the reaction temperature at 60°C. Then, further experiments had been done by using KOH/MK-10 to study the effect of temperature on the yield of biodiesel. The results obtained shows that the optimum temperature that can produce higher yield of biodiesel is at 60°C with 81% of biodiesel. The reaction temperature of 70°C and 80°C lead to a lower yield of biodiesel due to the catalytic activity is not at the optimum condition.

## 5.2 Recommendation

In general, there are many previous research prove that base catalyst are more effective than acid catalyst. Thus, there is more research need to be done in studying the basic catalyst. In addition, the study of the different ratio of the Potassium substances on the MK-10 clay need to be done to determine the perfect ratio of Potassium with clay, that can produce higher yield of biodiesel in the trans-esterification process.

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