Biodiesel Production from Palm Oil over Potassium Based Montmorillonite-K10 (MK10) Clay Catalyst

by

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Dissertation submitted in partial fulfilment of the requirements for the
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CERTIFICATION OF APPROVAL

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(CHEMICAL ENGINEERING)

Approved by,

____

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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.

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MUHAMMAD ARIFF FIRDAUS BIN OTHMAN

ABSTRACT

The heterogeneous catalyst Montmorillonite MK10 clay (MK10) and potassium modified MK10 were prepared for biodiesel production through transesterification process. The catalyst MK10 was modified with different salt of potassium such as Potassium Hydroxide (KOH), Potassium Nitrate (KNO_3), and Potassium Carbonate (K_2CO_3). These prepared catalyst then tested for activity of biodiesel production through transesterification reaction. The process variable used is the same for each catalyst as to check which gives higher yield at the same operating condition. Operating parameters used for this experiment are: catalyst 2wt%., Temperature at 60℃ , methanol to oil molar ratio 10:1, and reaction time of 2 hours using the same alcohol and feed stock which are methanol and palm oil. The optimum yield of fatty acid methyl ester were found to be potassium hydroxide (KOH). Based on the results obtained, the catalyst potassium hydroxide based Montmorillonite K10 clay catalyst (KOH/MK10) will be producing higher yield compare to potassium carbonate (KCO_3/MK10), and potassium nitrate (KNO_3/MK10) catalyst with at temperature of 60℃, 10:1 of methanol to oil ratio, 2 hours reaction time and 2 weight % of catalyst used. In addition, 5.0% of KOH metal loading on the MK-10 clay gives better performance while the temperature tested on catalyst, 60℃ is the best operating temperature giving out better performance for modified KOH/MK10 catalyst compare to other temperature which is 30℃, 50℃ and 70℃ tested. In term of stability of the catalyst, modified KOH/MK10 clay catalyst can only be used a few times and replaced with new catalyst as the performance of the catalyst dropped with respect of the cycles.

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CHAPTER 1
INTRODUCTION

1.1 Background Study

Biodiesel is one of the alternative renewable sources that can replace the commercial fossil fuel diesel that will be depleted in the near future. The need to seek renewable sources of energy has grown rapidly in this age, as population growth required more energy in demand. Biodiesel is safe and easy to process as the method can be done locally even at home as the raw feed can be found abundantly whether it is edible or non-edible. Basically, it is known as fatty acid methyl ester (FAME) and produced together with glycerol from the reaction between alcohol and free fatty acid. Only fatty acid methyl ester will be taken to be used for fuel while the by product, glycerol can be used for other purpose. The reaction take place is reversible, therefore, any possible parameter that can be used to push forward the system to produce more fatty acid methyl ester and reducing the production of glycerol and the reactant.

Biodiesel are clean, biodegradable, as less sulphur and toxic gases were released, reducing common gas emission such as carbon dioxide released to atmosphere compare to fossil fuel diesel which contain high content of sulphur that can pollute the air if not treated well. In fact, biodiesel give many advantages to the industry by reducing the dependence to the crude oil, reducing the emission of greenhouse gases because of closed carbon dioxide cycle, lower combustion emission profile especially SOx and NOx, providing good potential improvement to the rural area economic, no need for engine modifications and can be blended with current petroleum-based diesel with any ratio [2]. Currently, research had been done to seek the most optimum method to maximize the production of biodiesel to the highest content for future benefit.

Currently, about 95% of world biodiesel consumption are from edible oil which is available everywhere in large scale from agricultural industry [1]. Despite of that, the demand of edible oil is quite high, therefore, the competition between biodiesel production and consumer demand for food purpose give the alternative to seek for non-edible oil. There are various sources of non-edible oil that can be used to produce biodiesel such as mustard oil, sesame oil, waste cooking oil, coconut oil, castor oil, linseed oil etc. [1].

In this research, biodiesel will be produced via the reaction of palm oil with methanol in the presence of potassium based clay catalyst to yield for fatty acid methyl esters and glycerol. In term of alcohol used, methanol is used compared to other alcohol with higher carbon number such as ethanol, isopropanol and butanol because it is the simplest and cheapest alcohol available on the market. There are many different processes that can be used to produce biodiesel which is: acid-catalyzed transesterification, base-catalyzed transesterification, enzyme-catalyzed transesterification and other method [2]. However, in this paper, will be focusing on producing biodiesel using base-catalyzed method as the palm oil used have Free Fatty Acid (FFA) which fall in base condition. Thus, by using this method, base catalyst will be used with certain required condition to meet high purity and yield of Fatty Acid Methyl Ester such as catalyst percentage used in weight percent, methanol to oil ratio, reaction temperature, and reaction time .

1.2 Problem Statement

Biodiesel is currently a phenomenon around all countries including Malaysia as to reduce the dependence on fossil fuel diesel locally or foreign oil. Currently, biodiesel is in high cost of production due to less commercialization compare to local diesel which is far cheaper. The problem is the need to find suitable catalyst to maximize the yield is still in progress as not many catalyst used give more than 90% yield. As stated above in the topic, this research is to seek the yield and purity of fatty acid methyl ester based on the potassium which will be varies impregnated into the clay. Palm oil quality for free fatty acid (FFA) content, is suitable for base reaction transesterification process as it have low value of FFA. Palm oil is vegetable oil which is suitable for production of biodiesel as it is abundant and have low demand from the user for edible oil. There are various catalyst being used and clay is one of the heterogeneous catalyst. In this research, Montmorillonite K10 (MK10) clay will be used together with lithium base compound as the catalyst for biodiesel production.

1.3 Objective of Project

The main objective of this final year project is:

- To study the activity of each catalyst on converting palm oil into fatty acid methyl ester (biodiesel) produced
- To find the maximum yield of biodiesel using different type of catalyst
- To compare and select the most suitable catalyst for biodiesel production based on the results obtained from transesterification process
- To find the effect of catalyst on biodiesel at high temperature

1.4 Scope of Research Work

The scopes of this research work is to study the effect of potassium based catalyst on the production of fatty acid methyl ester at the constant operating condition which is reaction time, catalyst concentration, oil-to-fuel ratio and temperature at to the palm oil used to produce biodiesel. Once the product had been formed after reaction completed, the biodiesel will be analysed to study the yield, density, composition, viscosity, fatty acid methyl ester content, pour point, flash point, total glycerol and cetane index.

CHAPTER 2
LITERATURE REVIEW

2.1 Introduction

Biodiesel is non-petroleum based diesel fuel which can be derived from animal-fat based or vegetable oil that consists of mono alkyl esters of long chain of fatty acid. Technically, it is a reaction between animal fat or vegetable oil with alcohol with the presence of catalyst to produce fatty acid methyl esters as main product and glycerol as by-product. Biodiesel can be blended with petroleum fuel as its chemical and physical properties are nearly the same with commercial diesel oil which can be used on normal diesel engine without any modification required. In this section will discuss in details about biodiesel production and parameters required according to the ASTM D 6751standard [3].

2.2 Biodiesel Production

In production of biodiesel is to synthesize it from triglyceride plant or animal oil with a simple alcohol chain such as methanol or ethanol for a process known as transesterification. Currently, commercial diesel price will rise due to depleting storage of crude oil, therefore, biodiesel is the best alternative to replace diesel in term of renewable sources. Besides that, due to environmental issue from the burning of fossil fuel emitted by the vehicles it is a very applicable to replace it with biodiesel which emit environmental friendly gases.

Diesel was once founded by Rudolph Diesel, a German engineer introduce the engine diesel and using vegetable oils for his source of fuel to test his engine performance [4]. Researchers had found that vegetable oils can be the source of renewable energy for alternative of diesel, however, by using raw vegetable oils can cause many problems to the engine such as deposits on the engine internal surfaces, piston ring sticking and injector coking due to its increased viscosity and low volatility properties [5]. Although, there were problem associated with vegetable oils, the problem can be solved by using other method by converting raw vegetable oils into alkyl ester by transesterification process [5][6].

Recently, vegetable oils are becoming hot topics among researchers especially for palm oil as it had been mass produced with cheaper production cost while having green environmental effects and benefits to current situation. With the increase of petroleum fuel price and crude oil, give the driving force to seek interest in vegetable oils while maintaining the current storage of fossil fuel. There are many types of vegetable oils that can be used other than palm oil such as peanut oil, sesame oil, soybean oil, cottonseed oil, sunflower oil and others as potential biodiesel fuel alternative [7].

Table 2.1: Physical and Chemical Properties of Biodiesel (American Standard Test Material, 2001)

Vegetable oil methyl ester	Kinematic viscosity (mm^2/s)	Cetane number	Lower heating value (MJ/l)	Cloud point (°C)	Flash point (°C)	Density (g/l)	Sulfur (wt %)
Peanut[a]	4.9 (37.8°C)	54.00	33.60	5.00	176.00	0.88	-
Soybean[a]	4.5 (37.8°C)	45.00	33.50	1.00	178.00	0.89	-
Soybean[b]	4.0 (40°C)	45.7-56	32.70	-	-	0.880 (15°C)	-
Babassu[a]	3.6 (37.8°C)	63.00	31.80	4.00	127.00	0.88	-
Palm[a]	5.7 (37.8°C)	62.00	33.50	13.00	164.00	0.88	-
Palm[b]	4.3-4.5 (40°C)	64.3-70	32.40	-	-	0.872-0.877 (15°C)	-
Sunflower[a]	4.6 (37.8°C)	49.00	33.50	1.00	183.00	0.86	-
Tallow[a]	-	-	-	12.00	96.00	-	-
Rapeseed[b]	4.2 (40°C)	51-59.7	32.80	-	-	0.882 (15°C)	-
Used rapeseed[c]	9.48 (30°C)	53.00	36.70	-	192.00	0.90	0.00
Used corn oil[c]	6.23 (30°C)	63.90	42.30	-	166.00	0.88	0.00
Diesel fuel[b]	12-3.5 (40°C)	51.00	35.50	-	-	0.830-0.840 (15°C)	-
JIS-2D[c] **(Gas oil)**	2.8 (30°C)	58.00	42.70	-	59.00	0.83	0.05

2.3 Methods of Producing Biodiesel

The quality that need to be focused on is the Free Fatty Acid (FFA) content inside of the oil used will determine to use which process route and suitable catalyst. Every vegetable oils that being prepared as the feed of biodiesel production will be tested and analysed for the density, kinematics viscosity, free-fatty acid content, moisture content and fatty acid composition as being stated by Intarapong, P et al. [9]. There are various method that can be used such as pyrolysis, micro-emulsification and transesterification.

Pyrolysis is a process of heating an organic material such as biomass without the presence of oxygen that will decompose into combustible gas and charcoal. The product of pyrolysis can separated into three which are as pyrolysis oil (bio-oil), bio-char (solid form) and syngas. However, pyrolysis process need a very high temperature about 500 ℃ which will yield about 60-70 wt% of bio-oil which is not feasible as it need equipment that can withstand high heat [10]. Besides that, micro-emulsification is a method to reduce the viscosity of the vegetable oil. Low viscosity of the fuel will improve the efficiency of the diesel engine, but still other problems occur due to the properties of the vegetable oil itself that are not very suitable to the normal engine with no modification. Emulsion can be define as dispersion of oil in water or water in oil which is known as macro-emulsion. In addition, micro – emulsion is a stable dispersion of oil in water and water in oil which use surfactant for both emulsion to enable oil and water to mix. Transesterification is the other method that is called alcoholysis which is a chemical reaction between vegetable oil or animal fat with alcohol to produce glycerol and esters in with the presence of catalyst. This research will focused on the production of biodiesel using transesterification processes as palm oil is suitable for this method as being done by other researchers which will be discussed in further details in the next section.

2.4 Transesterification Process of Biodiesel

Transesterification is a reaction between triglyceride lipid molecule with alcohol to produce alkyl ester and glycerol. During the early days, researchers were using raw vegetable oil to be used as burning fuel inside the diesel engine. However, problems rise due to the properties of vegetable oil that was not up to the petroleum diesel standard that can damage the diesel engine. Thus, by using transesterification method, it can be seen that vegetable oil can be refine to a better fuel that is comparable with fossil fuel diesel in term of the quality of the alkyl ester produced. For biodiesel production in this research, palm oil will be the triglyceride that will be reacted with methanol in the presence of potassium based clay catalyst to produce methyl ester and by-product of glycerol. One mole of triglyceride react with three mol of alcohol to produce the product mixture.

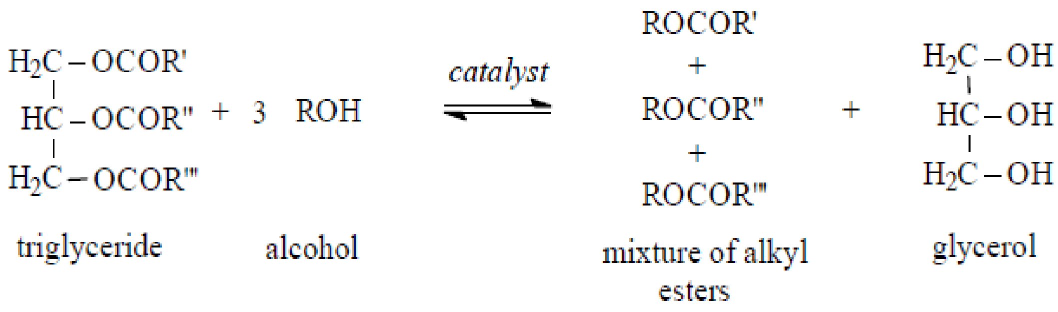

Figure 2.1: Transesterification of vegetable oils [11]

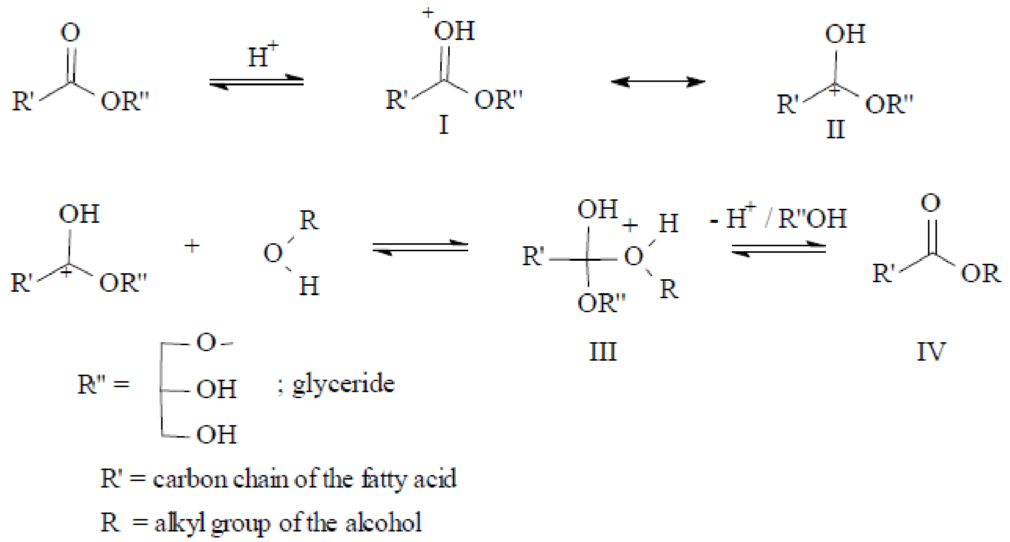

Figure 2.2: Mechanism Acid-catalyzed transesterification of vegetable oils [11]

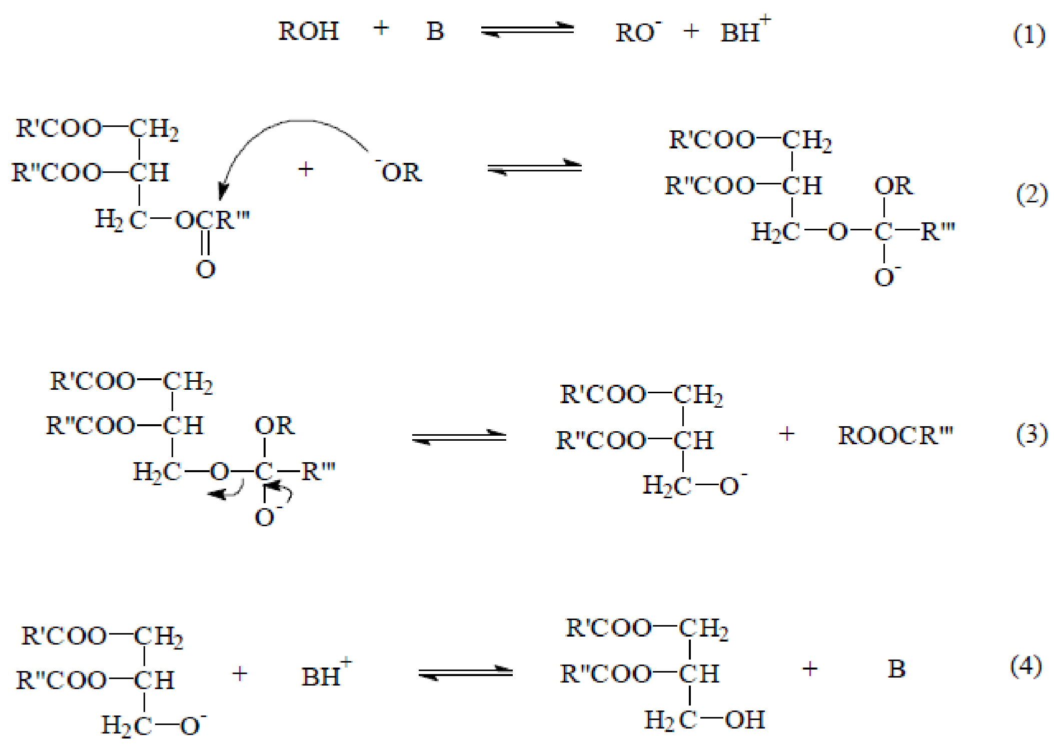

Figure 2.3: Mechanism of base-catalyzed transesterification of vegetable oil [11]

2.5 Transesterification Catalyst

Based on the journal and research paper, it can be seen that quite numerous method that can be used to produce methyl ester using suitable catalyst, which also depend on the vegetable oil used according to Free Fatty Acid (FFA) content. Among the process that are commonly used for transesterification are acid-catalyzed process, base-catalyzed process, lipase catalyzed process and non-ionic base catalyzed processes [11]. Catalyst also can be categorized as homogeneous and heterogeneous. Homogeneous catalyst usually will have a separation problem once reaction completed as the catalyst is in the same phase with the product liquid. However, different case for heterogeneous catalyst which is in solid form and easily can be separated with the product at the end transesterification process. This research will be using potassium base impregnated into Montmorillonite 10 (MK10) clay as the catalyst which will be prepared earlier for the production of biodiesel purpose.

Commonly it is either base-catalyzed process or acid-catalyzed will be chosen as the process path. However, it is favourable to choose base-catalyzed process because transesterification of vegetable oils is faster and give higher yield compare to acid-catalyzed process [11]. This is because alkaline catalyst are less corrosive than acid compound such as hydroxides and metal alkoxides. Other requirement that need to be fulfilled is the complete absence of water, as presence of water will cause hydrolysis and cause soap formation which will reduce yield of methyl ester. Saponification which is undesirable reduce the formation of fatty acid methyl ester and cause the separation between glycerol become difficult due to formation of emulsions [12].

2.6 Comparison between Biodiesel and Diesel Fuel

Biodiesel and diesel have same common usage which are the burning fuel for the engine. Both of these fuel can be compared into certain categories to see which is the best, whether the alternative or the current existing. In this research paper stated the comparison between pure biodiesel and the petroleum diesel in terms of performance and exhaust emissions. Discuss in this paper are performance comparative analysis which stated that biodiesel have lower vapour pressure compare to petroleum diesel which results in less cavitation [13]. Besides that, biodiesel have greater lubricant properties compared to petroleum diesel due to the lower sulphur content inside [14]. Supported by other research paper from [15], reported that biodiesel excel in lubricity due to the presence of oxygen molecules as the polarity was introduced.

Besides that, in term of emission of both diesel product, depend on raw materials used and production processes. From a paper, it is reported that diesel engines best fuel should be biodiesel and its blends as they combustion product release the lowest greenhouse gases on life cycle basis [16]. Moreover, carbon monoxide and particulate emission were reduced when using biodiesel fuel which give it the best fuel that is environmental friendly and clean [16].

It can be concluded that, biodiesel fuel give many advantages to the environment, energy and economic impacts. Biodiesel give huge impact if it is implemented worldwide as it will reduce greenhouse gases emission, while reducing air pollution used by vehicles, easily degradable without any special treatment, carbon neutral and higher combustion efficiency. Besides that, in term of economic impacts to the citizen around the area and nation, this will provide job opportunity in the rural area, while increasing farmer's income and the sustainability. Therefore, more effort will be put to enhance the technology in this field. In addition, in term of energy, fossil fuel consumption will be reduced and altogether reduce the dependency to petroleum products. Biodiesel is also one of the renewable energy and can be domestically distributed as the process can be done locally and give the reliability as the supply of clean energy [17].

CHAPTER 3

METHODOLOGY

3.1 Introduction

There are many method that can be used to produce biodiesel according to the free-fatty acid content and feed used. In this case, refined palm oil is used as the raw feed and by following the method of base catalyzed process as the Free Fatty Acid (FFA) for palm oil is less than 3 w.t% of FFA which fall in the base-catalyzed transesterification region.

3.2 Project Flow Chart

Preliminary Studies

Literature Review on existing studies from journals, books and other reliable resources

Understanding biodiesel production process

Understanding transesterification process

Understanding type of catalyst used and the process involved

↓

Experimental Tests

Identifying the suitable experimental procedures for producing

Conduct test on the free-fatty acid content on the palm oil

Conduct experiment by varying the catalyst used to calculate yield of the product

↓

Data Collection

Tabulation of data

Analyse and compare between the methyl ester produce with standards and previous experimentation using different catalyst

↓

Conclusion

Conclusion of the outcome and findings

Project report preparation

3.3 Materials and Equipment for Biodiesel Production

These are the materials and equipment that will be used in the biodiesel production:

Table 3.1: List of materials and apparatus used in biodiesel production

Materials	**Apparatus**
Palm oil	Three-necked flask
MK10 clay Potassium Hydroxide (KOH) Potassium Nitrate (KNO_3) Potassium Carbonate (KCO_3)	Oil Bath
Methanol	Magnetic Stirrer
	PID Controller
	Heater Plate
Water	Retort Stand and Clamp
	Sample bottle
	Thermometer

Usually, the common used alcohol for biodiesel production is methanol due to low cost and simple hydrocarbon structure. Other alcohol can also be used such as ethanol, butyl, isopropanol and others. Basically, the parameter controlled with respect to alcohol is the water content, as water will interferes with the transesterification process and giving poor yield and high percentage of soap formation, triglycerides and free fatty acid which make separation between product, by-product and unreacted reactant difficult.

Table 3.2: Ranges of operating conditions for transesterification reaction [20]

SELECTION PARAMETERS	RANGES		
	Low	Middle	High
Catalyst concentration (% w/w)	0.2% - 1%	>1% - 3%	>3% - 15%
Molar ratio alcohol/oil	3:1 - 6:1	>6:1 - 12:1	>12:1 - 80:1
Temperature (°C)	50 - 60	>60 - 100	>100 – 200
Yield (%)	20 – 70	>70 - 90	> 90 – 100
Reaction time (hours)	0.16 – 1	>1 - 2	> 2 – 40

3.4 Experimental Work

Catalyst Preparation

There are various method that can be done to produce biodiesel via experiment provided that all materials and equipment are sufficient. The method will depend on the free fatty acid (FFA) and followed by the catalyst used as the higher the basicity of vegetable oil, the better the yield of methyl ester. The catalyst will be prepared first before being used to test and producing the FAME. Firstly, take the KOH and MK10 clay in a ratio of 1:10 weighed and measured. Then, dissolve both of KOH and MK10 clay in distilled water to mix both evenly. The process of impregnation occur at 60℃ for 12 hours and stirred continuously using magnetic stirrer. Once impregnation were finished, proceed to the next step which is to dry the slurry in oven for 12 hours at temperature of 110℃. After 12 hours, the catalyst will undergoes calcination in furnace at temperature of 400℃ for 5 hours. Thus, after calcination finished, the catalyst can be used in biodiesel production using palm oil and methanol as reactant.

Transesterification Process

Transesterification process of palm oil method can be done with the following steps below for base-transesterification biodiesel production. A sample of palm oil were taken, weighed and placed in a 250-ml three-necked flask, which is equipped with magnetic stirrer (300 rpm) and a reflux condenser. Reflux condenser is used to improve the purity of the fatty acid methyl ester formed. The palm oil is then heated to a temperature about 60℃ and stirred to ensure the heat is fully dispersed to the palm oil. Temperature of 60℃ is taken due to methanol boiling point which is about 64.7℃ means if the reaction were taking place at higher than this temperature, in example, 70℃, it will reduce the amount of FAME produced as methanol had converted into gaseous form. Next, take methanol with measured quantities of modified catalyst (potassium based clay catalyst) dissolved in it by vigorously stirring, then methanol were added to the three-necked flask for transesterification process to be carried out.

The reaction was carried out for the desired reaction time in this case is 2 hours of reaction time until the reaction complete with constant temperature of 60℃. Once the time had reached the desired limit, the transesterifed oil then cooled and allowed to settle overnight in a separating funnel. Next, the transesterification process results can be seen in two liquid phases which are methyl ester and crude glycerine inside the separating funnel. Crude glycerine which is the heavier part is separated after complete settling in separating funnel can be removed as only methyl ester will be used for analysing purposes. The remaining ester will be washed with water several times until ester layer becomes clear. This is done to remove any water-soluble substances as the system had reached equilibrium once the transesterification process complete. The biodiesel now can be collected and stored for further analysis with Gas Chromatography (GC) to check the parameters and compare with the standards.

Gas Chromatography Test

The samples were analysed using 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). The carrier gas used were Helium gas.The operating condition for testing is the injector temperature was set at 220 ^{o}C and the detector temperature maintained at 250 ^{o}C. Besides that, the column temperature need to be kept constant at 110 ^{o}C. Then, analysis of FAME for each sample was carried out by dissolving 100 microlitres 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.

3.5 Analysis of the Product

Once the biodiesel had been completely separated from glycerol and washed, it will be taken for further analysis. These are the parameters that will be checked to be compared with the ASTM D6751 standard which are Ester content, kinematic viscosity, density, flash point, cloud point, pour point, acid value, yield and water content also the purity of the biodiesel produced. Yield of methyl ester can be calculated using the following formula:

$$YIELD = \frac{W\ (BIODIESEL)}{W\ (OIL)}$$

3.6 Design of Experiment

As shown below is the apparatus setup for batch reactor process of transesterification process of biodiesel using palm oil as feed and lithium based clay as catalyst. Type of catalyst used will be Potassium Hydroxide (KOH), Potassium Nitrate (KNO_3), Potassium Carbonate (KCO_3) impregnated into Montmorillonite K10 clay, Montmorillonite K10 clay, potassium hydroxide (KOH), and sodium hydroxide (NaOH) to compare the yield between the catalysts used.

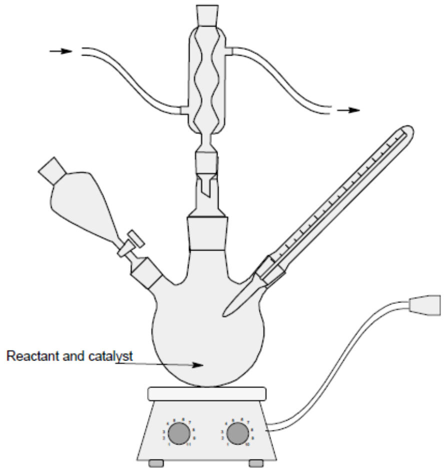

Figure 3.1: Transesterification process apparatus setup [18]

Figure 3.2: Experimental Setup inside the laboratory

Gantt chart and project timeline

No.	Detail/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Selection of Project Topic														
2	Preliminary Research work of Biodiesel Production from palm oil over potassium based clay catalyst														
3	Submission of extended proposal						●								
4	Proposal defence														
5	Project work continue														
6	Submission of interim draft report													●	
7	Submission of interim report														●

Project Milestone ●

No.	Detail/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Project Work Continues														
2	Submission of Progress Report							●							
3	Project Work Continues														
4	Pre-SEDEX										●				
5	Submission of Draft Final Report											●			
6	Submission of Dissertation												●		
7	Submission of Technical Paper												●		
8	Viva													●	
9	Submission of Project Dissertation														●

Project Milestone ●

CHAPTER 4

RESULT AND DISCUSSION

4.1 Data Gathering and Analysis

From the experiment conducted, it can be expected that the results are as follows. Based on the results obtained, it will be compared with the ASTM standards as to check whether the yield fatty acid methyl ester (FAME) produced using different type of catalyst MK10 based is within the acceptable range or not.

Table 4.1: ASTM D 6751 -02 Standard [19]

ASTM D 6751–02 Requirements

S/No	Property	Method	Limits	Units
1.	Flash point, closed cup	ASTM D 93	130 min	°C
2.	Water and sediment	D 2709	0.050 max	% volume
3.	Kinematic viscosity, 40°C	D 445	1.9–6.0	mm2/s
4.	Sulphated ash	D 874	0.020 max	wt. %
5.	Total Sulphur	D 5453	0.05 max	wt. %
6.	Copper strip corrosion	D 130	No. 3 max	
7.	Cetane number	D 613	47 min	
8.	Cloud point	D 2500		°C
9.	Carbon residue	D 4530	0.050 max	wt. %
10.	Acid number	D 664	0.80 max	mg KOH/g
11.	Free glycerol	D 6584	0.020	wt. %
12.	Total glycerol	D 6584	0.240	wt. %

Table 4.2: Operating Parameters of each catalyst

Operating Parameter	Potassium Hydroxide /MK10	Potassium Carbonate/MK10	Potassium Nitrate/MK10	MK10 Clay
Catalyst wt.%	2%	2%	2%	2%
Reaction Temperature, ℃	60	60	60	60
Reaction Time, Hours	2	2	2	2
Oil-to-methanol ratio	1:10	1:10	1:10	1:10

Based on the table above, the operating parameters are set to be the same for all catalyst including raw MK10 clay as to observe and analysed the activity of the catalyst affecting the performance of biodiesel production. From the result obtained, it can be deduced that catalyst with highest amount of fatty acid methyl ester (FAME) produced is the best catalyst to be used at these conditions which is 2% catalyst weight, 60℃ reaction temperature, 2 hours reaction time and 1:10 oil-to-methanol ratio.

4.2 Results and Discussion

The results for each product based on different catalyst used which are Potassium based chemical impregnated on MK-10 clay catalyst and MK-10 clay. According to the standard, the content of total glycerol in biodiesel allowed is only 0.24%, which means need to control the conversion of biodiesel up to certain level.

Three solid catalysts (KNO_3/MK10, KOH/MK10, and K_2CO_3/MK10) had been tested for transesterification of palm oil to evaluate the catalytic activity of each catalyst. Basically, the parameter that will be kept constant is temperature at 60℃, catalyst used at 2 wt. %, reaction time of 3 hours and methanol to oil ratio 10:1. In this experiment, the yield and the content of FAME using different catalyst will be analysed and compared with the standards as stated in Table 4. The highest yield of FAME will determine which catalyst is the best to be used in industry for mass production purpose. The result is yet to be tested by Gas chromatography to identify the component inside the biodiesel from palm oil produced whether it is within the standard specified.

Table 4.3: Yield of FAME by transesterification experiment

Catalyst	**Expected Yield (FAME),%**	**Type of catalyst**
MK10 Clay	10.5	Heterogeneous
Potassium Hydroxide / MK10	71	Heterogeneous
Potassium Nitrate / MK10	63	Heterogeneous
Potassium Carbonate / MK10	45	Heterogeneous

Based on the literature review, it can be seen that the results expected can be analysed using Gas Chromatography to determine the amount of FAME. By using KNO_3/ZrO_2 and KNO_3/KL Zeolite catalyst compared to other base catalyst used on the transesterification of palm oil kernel. According to the literature review with operating condition of methanol to oil ratio 6:1, 3wt% of catalyst,(based on vegetable oil) with pressure of 50 bar and temperature of 200℃ and 350 rpm stirrer[21], here is the result obtained:

Table 4.4: Crude palm oil transesterification by solid catalysts [21]

No.	Catalyst	M.E. Content (wt. %)	M.E. Yield (wt. %)
1	-	32.3	30.4
2	ZrO_2	69.0	64.5
3	ZnO	98.9	86.1
4	SO_4^{2-}/SnO_2	95.4	90.3
5	SO_4^{2-}/ZrO_2	95.8	90.3
6	KNO_3/KL.zeolite	77.8	71.4
7	KNO_3/ZrO_2	78.3	74.4

Besides that, by using Potassium Carbonate loaded on silica (K_2CO_3/SiO_2) of palm oil transesterification to produce Fatty Acid Methyl Ester (FAME), the results obtained from the literature was yielding about 98.10% with reaction time of 3h, temperature of 60℃, methanol to oil molar ratio of 20:1, with catalyst amount of 4wt%. Fatty Acid Methyl Ester (FAME) produced are quantified using Gas chromatography to analyse the peak formed. [22]

The expected results of Fatty Acid Methyl Ester (FAME) using Potassium Hydroxide (KOH) loaded on ZrO_2 can also be referred to the literature by giving yield of 99.69% using the operating condition of temperature 65℃, 2 hours reaction time, 20wt% catalyst loading, methanol to oil ratio 15:1, 5wt% catalyst and stirrer speed of 300 rpm.[23] The experiment results with transesterification of palm oil using heterogeneous catalyst (KNO_3/MK10, KOH/MK10, and K_2CO_3/MK10) will be compared to the present work of other literatures and diesel standard ASTM D6751.

4.2.1 Different Potassium Component Effect vs. Yield

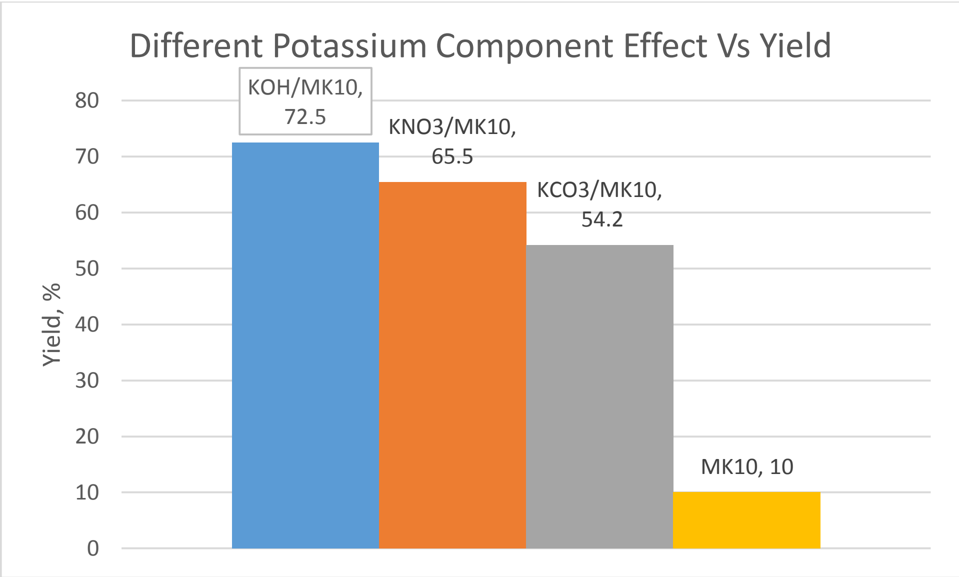

Figure 4.1: Bar chart of Different Potassium component effect on the yield of FAME

Based from the chart in figure 6, it can be see that modified KOH/MK10 give the highest yield compare with other catalyst used which is about 72.5 % yield, while modified KNO3/MK10 give about 65.5%, modified KCO3/MK10 give only 54.2% while MK10 clay only give about 10% yield of Fatty Acid Methyl Ester (FAME). This concluded that modified KOH/MK10 is the better catalyst in heterogeneous form of catalyst as KOH in homogeneous give very high conversion of Fatty Acid Methyl Ester (FAME) which is about 95.5%. However, the problem lies in separating the homogeneous catalyst with the Fatty Acid Methyl Ester (FAME) produced as both in liquid form and miscible with each other compared by using heterogeneous which is easy to separated. Therefore, modified KOH/MK10 are chosen compared to other catalyst tested due to its higher yield conversion, easy to separate because of the heterogeneous properties and it is economical as the MK10 clay is abundant and inexpensive to be found in the market.

4.2.2 Metal Loading Effect of KOH/MK10 vs Yield

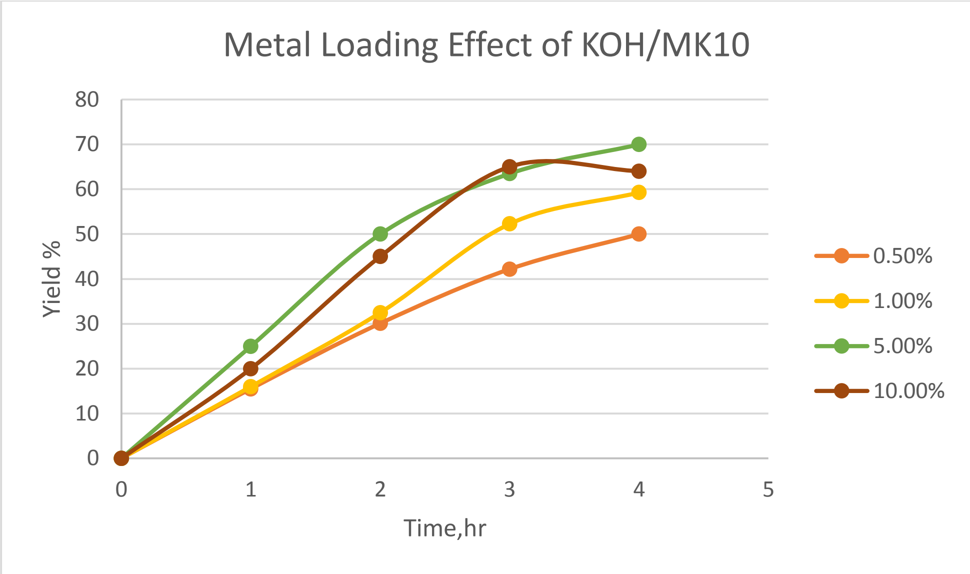

Figure 4.2: Graph on metal loading effect of KOH/MK10

As in Figure 6, modified KOH/MK10 catalyst was chosen to be tested further for the properties the catalyst have. The first one is to test the metal loading effect of the modified catalyst KOH/MK10 as shown in figure 6 above. This metal loading effect test is to check the suitability of the potassium used based on the loading percent on the MK-10 clay by using 0.5% 1.0%, 5.0% and 10% of metal loading. Thus, based from the results obtained in the line graph tabulated for each of metal loading, it can be interpreted that 5.0% metal loading is the optimum for KOH as it gives better result compared with other loading such that 0.5% which is lowest and 1.0% as the second lowest in performance. We can see some irregularities in 10% loading as it rise up to about 65% then decrease in performance. This is due to the structure of the catalyst itself if the is too much KOH impregnated into MK-10 clay, it will hinder the active sites for conversion of palm oil used as raw feed to be converted into biodiesel (FAME). Thus, it can be concluded that 5.0% of KOH loading on the MK-10 clay gives better performance compare to other loading percentage.

4.2.3 Temperature vs Efficiency of KOH/MK10

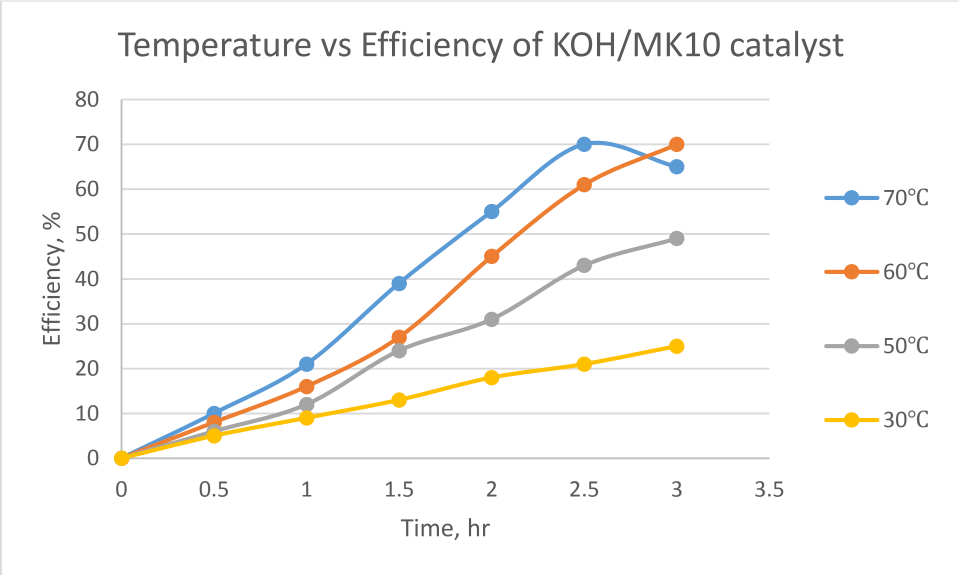

Figure 4.3: Graph of Temperature vs Efficiency of KOH/MK10 catalyst

Besides that, further test was conducted on modified KOH/MK10 catalyst for its efficiency on different temperature range which is 30℃, 50℃, 60℃, and 70℃ of operating temperature. As shown in figure 8 above, it can be seen that the efficiency is very low in activity at relatively 30℃, while it slightly increase when testing the catalyst in experiment on 50℃ which is nearly around 50% efficiency. As the temperature were increased to 60℃, it can be seen that the catalyst performance rise up until 70% and maintained while if the temperature were increased to 70℃, it can be seen it reached up to 70%, however decreased after that. This shows that the efficiency decreased at high temperature as boiling point of methanol as about 60℃, means after 60℃, it will start to change phase from liquid into gas phase which makes the conversion of palm oil into biodiesel decreased compared at temperature of around 60℃, as stated in the literature review. Thus, from the results above, it can be concluded that 60℃ is the best operating temperature for modified KOH/MK10 catalyst.

4.2.4 Stability Effect of KOH/MK10 vs Efficiency

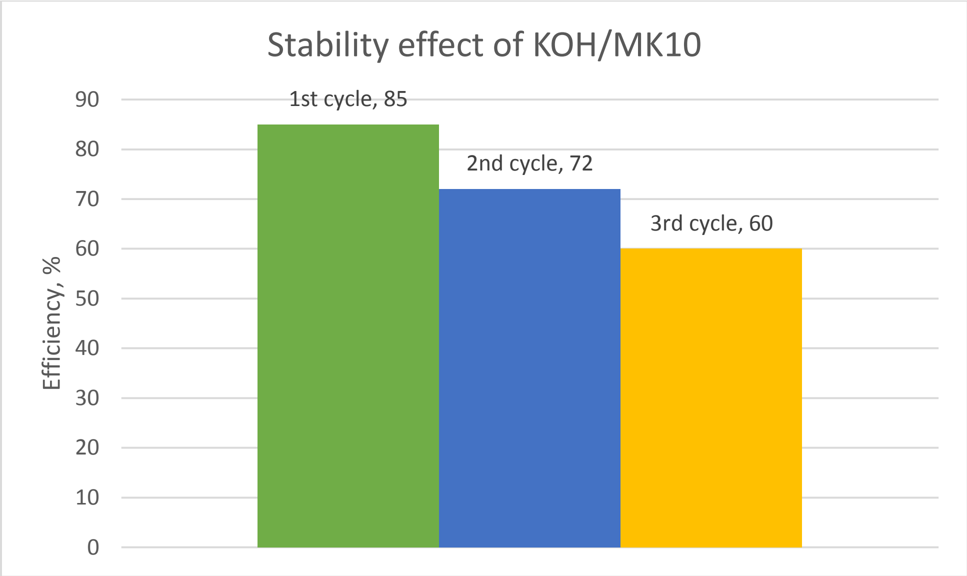

Figure 4.4: Bar chart of stability effect of KOH/MK10

Stability effect refers to the reusability of the catalyst after first time used. The purpose of stability test is to check the catalyst efficiency on the conversion of biodiesel in a few cycle. Based on figure 9, it can be seen that in first cycle or first use of the KOH/MK10 catalyst, the efficiency is about 85%. As the next experiment conducted using the same catalyst, in second cycle, it can be seen that the efficiency dropped to 72% and further tested in third cycle, the efficiency dropped gradually in the next cycle expectedly. Therefore, it can be concluded that the catalyst KOH/MK10 can only be used a few times and need to be replaced with new catalyst as the performance of the catalyst dropped with respect of the cycles.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

It can be concluded that potassium hydroxide based Montmorillonite K10 clay catalyst (KOH/MK10) produce higher yield compare to potassium carbonate (KCO_3/MK10), and potassium nitrate (KNO_3/MK10) catalyst with temperature of 60℃, 10:1 of methanol to oil ratio, 2 hours reaction time and 2 weight % of catalyst used. In addition, 5.0% of KOH metal loading on the MK-10 clay gives better performance compare to other loading tested. In term of temperature tested on catalyst, it can be concluded that 60℃ is the best operating temperature giving out better performance for modified KOH/MK10 catalyst compare to other temperature which is 30℃, 50℃ and 70℃ tested. Besides that, in term of stability of the catalyst, modified KOH/MK10 clay catalyst can only be used a few times and need to be replaced with new catalyst as the performance of the catalyst dropped with respect of the cycles. Methanol should be in excess as to move the reaction forward because transesterification process is a reversible process which means when reaction taking place, there is possibility of product will revert back to reactant which will reduce the yield.

As for recommendation, it is highly recommended to reproduce the experiments using different type of catalyst and operating parameters such as high and low temperature, different stirring speed in RPM, oil-to-alcohol ratio and catalyst wt.%. Besides that, it would be highly suggested to further check the content of biodiesel produced to see the type of component presents as final product. Besides that, it is better to check the fatty acid methyl ester yield using different type of oil which is inedible and abundant with economical price.

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APPENDICES

Separation of Biodiesel and Glycerine in Separating Funnel

Series of samples undergo separation in separating funnels