EFFECT OF ALKALINE-CATALYZED IN HOMOGENEOUS REACTION OF BIODIESEL PRODUCTION FROM WASTE COOKING OILS USING ULTRASONIC BATH-CLEANER

MOHD SYAFIQ BIN SALIM

UNIVERSITI MALAYSIA PAHANG

"I/We* hereby declare that I/We* have read this thesis and in my/our* opinion this thesis is sufficient in terms of scope and quality for the award of the Degree/Master/Doctor of Philosophy of

....Chemical Engineering....".

| Signature | : |
|--------------------|---|
| Name of Supervisor | : Miss. Shalyda Binti Md. Shaarani@Md. Nawi |
| Date | : 14 May 2008 |

* Delete as necessary

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MOHD SYAFIQ BIN SALIM

A report submitted in partial fulfillment of the requirement for the award of the Degree of Bachelor in Chemical Engineering

Faculty of Chemical and Natural Resources Engineering Universiti Malaysia Pahang

MAY 2008

I declare that this thesis entitled "Effect of Alkaline-Catalyzed in Homogeneous Reaction of Biodiesel Production from Waste Cooking Oils Using Ultrasonic-Bath Cleaner" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any degree.

| Signature | : | |
|-------------------|---|-----------------------|
| Name of Candidate | : | Mohd Syafiq Bin Salim |
| Date | : | 14 May 2008 |

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ABSTRACT

Many years of research have been done in order to find a new alternative renewable fuel such as biodiesel to replace the diesel fuel. Biodiesel was used instead of conventional diesel fuel because there is a highly concern and awareness for environmental protection and due to increase of the petroleum price. Hence the aimed of this research is to investigate the feasibility of waste cooking oils (WCOs) used as feedstock to produce biodiesel by alkaline-catalyzed process. The performance of alkaline-catalyzed such as sodium methoxide (NaOCH3) was investigated towards biodiesel yield and selectivity (methyl ester conversion) of product by using ultrasonic bath-cleaner. This transesterification process was conducted with a molar ratio of methanol-oils used fixed to (6:1). In order to obtain the optimum condition for biodiesel production, three stages of experiment with different parameter setting such as catalyst concentration (0.5 to 2.5 wt %), temperature (40 to 80°C) and reaction time (20 to 60 min) were performed through this transesterification process. The results indicated that, catalyst concentration was the major effects affecting biodiesel yield and methyl ester conversion. However, temperature and reaction time were related together in which the time required for reaction completion varied significantly with reaction temperature. The results showed that the optimum condition for biodiesel production can be achieved at catalyst concentration of 1.0 wt %. The temperature and reaction time was conducted at 60°C and 40 minutes which indicated the most product yield as well as methyl ester conversion can be reached within the values range from (70 to 75 %) and (88 to 90 %) respectively.

ABSTRAK

Dalam tempoh tahun yang lama, pelbagai penyelidikan telah dijalankan untuk mencari sumber alternatif bahan api yang boleh diperbaharui seperti biodisel bagi menggantikan sumber yang sedia ada seperti minyak disel. Penggunaan biodisel bagi menggantikan minyak disel adalah penting kerana mendapat perhatian dan kesedaran yang tinggi mengenai alam sekitar serta berlaku kenaikan harga pasaran petroleum dunia. Oleh yang demikian, tujuan utama penyelidikan ini adalah untuk mengkaji keupayaan sisa minyak masak dalam penghasilan biodisel dari proses tindakbalas pemangkin alkali. Prestasi pemangkin alkali seperti sodium metoksida telah dikaji terhadap hasil biodisel dan juga pertukaran kepada metil ester dengan menggunakan medium ultrasonik reaktor. Proses transesterifikasi ini telah dijalankan dengan nisbah tetap metanol kepada sisa minyak masak iaitu (6:1). Oleh kerana untuk mendapatkan keadaan yang optima bagi penghasilan biodisel, tiga peringkat eksperimen dengan parameter yang berlainan seperti kepekatan mangkin (0.5 ke 2.5 %), suhu tindakbalas (40 ke 80°C) dan juga masa tindakbalas dari 20 ke 60 minit telah dijalankan dalam proses transesterifikasi. Keputusan daripada proses tranesterifikasi telah menunjukkan bahawa kepekatan katalis merupakan faktor utama yang memberi kesan terhadap hasil biodisel dan juga pertukaran metil ester. Walaupun begitu, suhu dan juga masa tindakbalas adalah bergantung di antara satu dengan yang lain dimana masa yang diperlukan untuk melengkapkan proses tindakbalas berbeza terhadap suhu tindakbalas. Keputusan akhir menunjukkan bahawa, keadaan yang optima bagi penghasilan biodiesel boleh dicapai pada kepekatan katalis (1.0 %), manakala suhu juga masa tindakbalas dijalankan pada 60°C dan 40 minit dimana hasil masing-masing bagi produk akhir (biodisel) berserta metil ester boleh dicapai dalam lingkungan antara 70 ke 75 % dan 88 ke 90 %.

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CHAPTER 1

INTRODUCTION

1.1 Overview of Research

Since there is highly concern and awareness for environmental protection against the pollutions coming from the vehicles gases and due to high price of conventional fossil diessel fuel, many years of research have been done in order to find a new alternative renewable fuel and sustainable energy sources such as biodiesel to replace the petrol-diesel fuel. Furthemore, biodiesel can be used in most modern engine without or little modifications. There are a lot of advantages by using biodiesel instead of conventional diesel fuel which are environmental benefits, less toxicity for humans because the raw materials used to produce it are natural and renewable making it biodegradable and non-toxic. The biodiesel combustion produced lower carbon monoxide (CO) gases and almost zeros sulfur emmisions.

Biodiesel is derived from a feedstock of vegetable oils or animal fats by direct tranesterification process of triglycerides with a short chain alcohol/ monoalcohol (methanol or ethanol) in the present of acidic or basic catalysts to produce esters of fatty acids (methyl ester or ethyl ester) and glycerol (glycerine). In transesterification process, the main ingredient is oil itself which related to the relative high price of the oils used. Therefore a lot of possible feedstocks were carried out such as waste cooking oils (WCO) or waste vegetable oils (WVO), soapstocks and also acid oils to substitute the refine oils. The common problem related to these crude oils or low-grade oils is the

present of high free fatty acids (FFAs) and water which contributed to the sites reaction such soaps formation when react with homogeneous basic catalyst either sodium hydroxide (NaOH) or potassium hydroxide (KOH). Higher production cost required due to difficult of the downstream separation and purification of biodiesel.

Both homogeneous and heterogeneous catalysts can be carried out in the tranesterification reaction, but mostly in the commercial biodiesel production from transesterification process was proceed by using homogeneous basic (NaOH or KOH) catalyzed which conducted much faster reaction rates with minimal side reactions in order to obtain higher conversions of biodiesel (Lopez *et al*, 2005; Dossin *et al*, 2006).

Recently, the new research has been reported that, heterogeneous solid catalysts such as alkaline earth metal oxides and alkoxides, alkaline metal supported on alumina, zeolite and anion exchange resin can be used to transesterifying the triglycerides into (monoalkyl esters) biodiesel (Xuejun Liu *et al*, 2007). The advantages of using the heterogeneous catalysts are, they not corrosive which contributed to the environmental friendly, present fewer disposal problems and easier to separate from liquid product which gave to the lower production costs and the catalysts also can be recycled and reused in order to reduce cost of regenerated catalysts (Gryglewicz, 1999; Tanabe *et al*, 1999; Corma *et al*, 2005). However, the succesful of heterogeneous catalyst in achieving high conversion of methyl ester is still under research.

1.2 Problem Statement

In biodiesel production, many researchers and engineers do a lot of efforts in order to improve the quality of biodiesel. Since there was highly concern on environmental awareness against pollutions coming from vehicles the problematic here is to replace the conventional diesel fuel by biodiesel as fuel which gives more beneficial on economy and ecological. In addition, the raw materials use in synthesizing biodiesel is renewable and cheaper than conventional diesel fuel. However, the raw materials coming from vegetable oils or highly grade oils contributed to the high cost production, so other feedstocks were considered such as waste cooking oils or waste vegetable oils to replace this high price of oils in order to reduce the production cost (Marchetti *et al*, 2007)

Although feedstocks used coming from waste cooking oils is considered to be reduced in biodiesel production cost, there was a major problem occured which indicates that highly free fatty acids (FFAs) presence in this raw materials but consequently they need a high quality feedstock such as virgin or refined oils (Lopez *et al*, 2005). The effect of free fatty acids present in this raw material will contribute to the water and soap formations when homogeneous base catalyst such NaOH reacted with FFAs. Initially, high amount of FFAs must be treated before any further reaction take place.

Since, conventional homogeneous catalyst reaction gives a lot of advantages towards faster reaction rate and high conversion yield, there have some weaknesses with this catalyst because it cannot be recovered and must be neutralized after the reaction and also their sensitivity to the presence of water and FFAs.

1.3 Objective of Study

The objective of this research is to obtain the optimum yield and selectivity towards biodiesel production from waste cooking oils in homogeneous basic-catalyzed reaction by using ultrasonic cleaner.

1.4 Scope of Study

The scopes of this research are:

- To examine the effect of catalyst concentration, temperature and reaction time towards the optimum yield and selectivity of biodiesel.
- To analysis the sample product on their biodiesel yield, moisture content and conversion of methyl ester in order to obtain the optimum condition for biodiesel production.

In this research, the catalyst concentration range within 0.5 to 2.5 wt%. The temperature condition will be in the range of 40° C to 80° C in order to investigate the performance of catalyst at low temperature. The reaction time will be conducted from 20 to 60 min.

CHAPTER 2

LITERATURE REVIEW

2.1 Historical Background on Biodiesel Production

Biodiesel is a liquid fuel source largely compatible petroleum based on diesel fuel and was introduced in year 1900 at World's Fair when Otto Company was invented the diesel engine by using bio-chemical base compound generally known as vegetable oils which converted into diesel fuel for combustion in diesel engine. A famous German inventor who responsibles to the invention of diesel engine is Rudolf Christian Karl Diesel was born in 1858 in Paris. In 1893, he published a paper describing an engine with combustion within a cylinder, the internal combustion engine.



Figure 2.1 Rudolf Christian Karl Diesel

In 1894, he filed for a patent for his new invention, dubbed the diesel engine. Rudolf Diesel was almost killed by his engine when it exploded. However, his engine was the first that proved that fuel could be ignited without a spark. He operated his first successful engine in 1897 (Steiger Verlag, 1984). In year 1912, Rudolph Diesel was certainly aware of the possibility on his experimented of using the vegetable oils as a fuel to his engine. During presentation of the British Institute of Mechanical Engineers, Rudolph Diesel presented a lot of efforts in this area and remarked that "Fat oils from vegetable sources can be used may seem insignificant today, but such oils may perhaps become in course of time of the same importance as some natural mineral oils and the tar products are now." (Knothe *et al*, 2001).

Nowadays, since many researchers and enthusiasts engineer thought about awareness of environmental protection against pollutants such as corbon monoxide (CO), carbon dioxides (CO₂) and sulphur content coming from fuel combustion of vehicle will effect to the global warming and also due to high price of conventional diesel fuel, a lot of efforts have been done in order to find an alternative renewable source such as biodiesel to replace the petroleum based fuel.

2.2 Raw Materials

Generally, the renewable feedstocks of vegetable oils (polyunsaturated fats) or animal fats (polysaturated fats) used in biodiesel production. Polyunsaturated fats are in liquid form while polysaturated fats in solid form at room temperature. However, the vegetable oils extracted from plant that are composed of triglycerides (triacylgycerides) was used because it contains similar fuel properties to diesel fuel except the higher viscosity and low oxidative stability that must be encountered before being converted into biodiesel. So, the vegetable oils that mostly used in transesterification reaction includes pure plant oils (PPOs) or straight vegetable oils (SVOs) and waste vegetable oils (WVOs) or usually known as waste cooking oils (WCOs) (Knothe *et al*, 2001).

Triglycerides or triacetin is the simplest and flexible component of lipid which this amphiphilic molecule contains a polar glycerol backbone and 3 non-polar methyl groups (Lopez *et al*, 2005).



Figure 2.2 General structure of trigleceride

The chemical formula is CH₂COOR-CHCOOR'-CH₂-COOR", where R, R', and R" are long alkyl chains. The three fatty acids RCOOH, R'COOH and R"COOH can be all different, all the same, or only two the same.

The three non-polar of methyl groups formed a hydrophobic layer while the tail or backbone which contains long alkyl chains acted as hydrophilic layer. In spite of that, the triglycerides can be served as substituent in transesterification reaction of alcoholysis in the present of catalyst.

2.2.1 Pure Plant Oil (PPO)/ Straight Vegetable Oil (SVO)

Pure plant oils (PPO) or commonly known as straight vegetable oils is not a byproduct of other industries either coming from domestic usage or restaurant. Actually, the straight vegetable oils is a highly grade of oil extracted primarily from plant, usually seeds of oilseed plants. In addition, straight vegetable oils contain very low levels of free fatty acids (FFAs) thus increases the conversion yield and also further separation and purification process can be easier.

2.2.2 Waste Vegetable Oil (WVO)/ Waste Cooking Oil (WCO)

The feedstock coming from waste vegetable oils or commonly known as waste cooking oils is one of the alternative sources among other higher grade or refine oils. Since, biodiesel have advantages itself there also has one disadvantage in biodiesel production which is related to the relative high price of the oils used. Waste cooking oil is easy to collect from other industries such as domestic usage and restaurant and also cheaper than other oils (refine oils), hence by using the waste cooking oils as the raw material will reduce the cost in biodiesel production (Canakci and Van Gerpen, 2001).

Furthermore, when we deal with waste cooking oils actually we are facing the problem with significants amount of free fatty acids (FFAs) content. Canakci and Van Gerpen (2001) found that, if the free fatty acids (FFAs) level is less than 15% it is called *yellow grease* while the amount of FFAs in animal fats may exceed to 30% and some other very low quality feedstocks such as trap greases may approached to 100% of FFAs amount. Typically, by using waste cooking oils usually contained 2-7% of FFAs.

The higher amounts of free fatty acids (FFAs) presented will effected the biodiesel production by soap formation thus give difficulty to the downstream separation and purification process.





2.3 Solvent

In transesterification reaction the conventional alcohol such a short chain alcohol (monoalcohol) was used as the solvents to convert the triglycerides into fatty acid alkyl esters (biodiesel). Short chain alcohol was used instead of long chain alcohol because they can be served as strong nucleophilic attack when reacted with catalyst especially basic-catalyst (Hanna *et al*, 1999).

Mostly, methanol (CH₃OH) and ethanol (C₂H₅OH) were utilized in biodiesel production (Marchetti *et al*, 2007). Marchetti recommended that ethanol as a solvent in the transesterification due to its less toxicity for humans because ethanol can be obtain from natural source hence produced 100% of renewable fuel. On the other hand, methanol also provided faster reaction rate which affected the biodiesel yield. However, some authors proposed that different short-chain alcohol varying from methanol, ethanol, 1-propanol and 1-butanol showed the same promising resulted towards conversion yield but with difference of reaction time to reach the final equilibrium process (Kusdiana *et al*, 2001; Warabi *et al*, 2004).

2.4 Catalyst

Oyama and Somorjai (1986) reported over 2000 years ago that catalysts have been done especially in food industries such as making of wine, cheese and bread. Generally, catalyst is a substance that affects the rate of reaction by promoting a different molecular path (mechanism) for the reaction. It provided a lower energy barrier thus affected both the yield and selectivity. Catalysts can either accelerate or slow the rate of reaction but it does not affect the equilibrium.

Since in the biodiesel production, there were different types of catalyst used which a conventional way of homogeneous catalytic and the new way of heterogeneous catalytic and also the enzymatic catalyst process.

Homogeneous catalytic process involved one phase only in which a catalyst is soluble in solution with at least one of the reactants. Such in synthesizing of biodiesel, liquid basic (NaOH or KOH) and acidic (H₂SO₄ or HCl) catalysts are used as homogeneous catalyzed reaction (Lopez *et al*, 2005; Dossin *et al*, 2006). The liquid-liquid phase reaction provides almost all homogeneous catalysts dissolved in the solvents thus gives faster reaction rate towards conversion yield.

However, there was a way to improve the quality and the value of biodiesel production by using the heterogeneous catalytic process (Bournay *et al*, 2005). Heterogeneous catalytic process involves more than oen phase reaction, usually the catalyst is a solid and the reactants and products are in liquid or gaseous form. Eventhough heterogeneous catalyst showed an economically attractive and their reusibility compared to homogeneous catalyst, it should be noticed that the active site on the surface of this catalyst was sensitively to the presence of moisture and carbonyl group. Both moisture and carbonyl group presence in the surrouding atmosphere will be attracted to the surface active-site thus interupted the reaction process. So that, care

must be taken during preparation and the storage of this heterogenous catalyst in order to avoid any particles attached to the active-site.

There also have a different way of synthesizing biodiesel by using bio-catalyst such as lipase enzyme instead of chemically catalyst. Bio-catalyst such an enzyme is a high molecular weight protein or protein-like substance that acts on substrate (reactant molecule) to transform it chemically at a greatly accelerate rate than the uncatalyzed rate (Shuler and Kargi, 2002). The authors founded that the enzymatic reaction also the same as the chemical catalyzed which provide an alternate pathway for the reaction by lowering the activation energies (Shuler and Kargi, 2002). The enzymes affected the reaction rate towards chemical equilibrium but they are not consumed during the reaction take place.

Shuler and Kargi (2002) claimed that the enzymatic reaction apart from other catalyzed reactions is the formation of an enzyme-substrate complex (E.S). In the case of biodiesel, the substrate (triglycerides) binds with a specific active site of the lipase-enzyme to form this complex (E.TGs). This is an important property of enzymes that they are specific which one enzyme can usually catalyze only one type of reaction.

The mechanism of enzymatic reaction provides two models for substrateenzyme interactions which are the *lock* and *key model* and the *induced fit model* (Levine and LaCourse, 1967). The lock and key model was preffered because of the stereospecific effects of one enzyme acting on one substrate. However, the induced fit model is the most useful model because both the enzyme molecule and the substrate molecules are distorted. Distortions of the enzyme-substrate occured by stressing and weakening the bond to make the molecule more susceptible to rearrangement or attachment.

2.5 Biodiesel Production Process

The precaution must be taken to monitor the amount of water and free fatty acids in the incoming oil or fat. If the free fatty acid level or water level is too high it may cause problems with soap formation and the separation of the glycerin by-product downstream. Hence, if the waste vegetable oils or waste cooking oils used in transesterification reaction it must be purified first in order to remove dirt and other non-oil materials found.

Initially, the catalyst-mixing process included typically of either alkali (NaOH or KOH) or acid (H₂SO₄ or HCl) catalyzed which added directly and dissolved with alcohol (methanol, ethanol) in the reactor at time and temperature condition.

The alcohol/catalyst mix then is charged with oils feedstock (vegetable oils, waste vegetable oils, animal fats) thus proceed further reaction via tranesterification process. The transesterification reaction was kept in closed-vessel system to prevent the loss of alcohol. Neutralization process needed if the feedstocks used contained high level of FFAs. The free fatty acids (FFAs) were neutralized by titration of standard solution of base in order to determine the concentration of FFAs present in feedstocks.

In separation phase two major products exist which are glycerin and biodiesel. Each has a substantial amount of the excess methanol that was used in the reaction. The reacted mixture is sometimes neutralized at this step if needed. The glycerin phase is more denses than biodiesel phase and the two can be gravity separated with glycerin simply drawn off the bottom of the settling vessel. In some cases, a centrifuge is used to separate the two materials faster (Bournay *et al*, 2005). Once the glycerin and biodiesel phases have been separated, the excess alcohol in each phase is removed with a flash evaporation process or by distillation. In others systems, the alcohol is removed and the mixture neutralized before the glycerin and esters have been separated.

In either case, the alcohol is recovered using distillation equipment and is reused. Care must be taken to ensure no water accumulates in the recovered alcohol stream. The glycerin by-product contains unused catalyst and soaps that are neutralized and sent to storage as crude glycerin. In most cases the salt is left in the glycerin. Water and alcohol are removed to produce 80-88% pure glycerin that is ready to be sold as crude glycerin.

Once separated from the glycerin, the biodiesel is sometimes purified by washing gently with warm water to remove residual catalyst or soaps, dried, and sent to storage. In some processes this step is unnecessary. This is normally the end of the production process resulting in a clear amber-yellow liquid with a viscosity similar to petrodiesel. In some systems the biodiesel is distilled in an additional step to remove small amounts of color bodies to produce a colorless biodiesel. The summary on biodiesel production routes is depited as showned in figure 2.4.



Generally, the biodiesel production occurred by using the following steps:

Figure 2.4 General biodiesel production routes

2.6 Process of Synthesizing Biodiesel

Many researchers and engineers proposed that there are different processes which can be applied to synthesize biodiesel which are direct use and blending, microemulsion process, thermal cracking and the most conventional way is transesterification process. However, there are a lot of methods can be done through transesterification process such as based-catalyzed transesterification (Dorado *et al*, 2002; Lotero *et al*, 2005), acid-catalyzed esterification (Mittelbach *et al*, 1996; Lopez *et al*, 2005), integrated acid-catalyzed pre-esterification of FFAs and based-catalyzed transesterification (Canakci *et al*, 2001; Ramadhas *et al*, 2005), enzyme-catalyzed (biocatalyst) transesterification (Wei and Du, 2004), hydrolysis and supercritical alcohol transesterification (Saka *et al*, 2001).

2.6.1 Direct Use and Blending

The direct use of vegetable oils in diesel engines is not favorable and problematic because it has many inherent failings. Eventhough the vegetable oils have familiar properties as biodiesel fuel it required some chemical modification before can be used into the engine. It has only been researched extensively for the past couple of decades, but has been experimented with for almost a hundred years. Although some diesel engines can run pure vegetable oils engines, turbocharged direct injection engines such as trucks are prone to many problems. Energy consumption, with the use of pure vegetable oils, was found to be similar to that of diesel fuel. For short term use ratios of 1:10 to 2:10 oil to diesel have been found to be successful (Ma, 1999).

2.6.2 Thermal Cracking (Pyrolysis)

Pyrolysis is the conversion of one substance into another by means of applying heat i.e. heating in the absence of air or oxygen with temperatures ranging from 450° C– 850° C. In some situations this is with the aid of a catalyst leading to the cleavage of chemical bonds to yield smaller molecules. Unlike direct blending, fats can be pyrolyised successfully to produce many smaller chain compounds. The pyrolysis of fats has been investigated for over a hundred years, especially in countries where there is a shortage of petroleum deposits. Typical catalysts that can be employed in pyrolysis are SiO₂ and Al₂O₃. The ratios of light to heavy compounds are temperature and time dependent.

The equipment for pyrolysis or thermal cracking is expensive for modest throughputs. Although, the products are chemically similar to pyrochemically based diesel, oxygen removal from the process decreases the products benefits of being an oxygenated fuel. This decreases its environmental benefits and generally produces more fuel similar in properties of gasoline than diesel, with the addition of some low value materials.

2.6.3 Transesterification Process

Transesterification process involved reaction between triglyceride (triacylglyceride) and alcohol usually short chain alcohol such as methanol or ethanol in the present of catalyst. Generally, there are two types of catalyst used in the transesterification either basic or acidic catalyst.

Actually, overall process in the transesterification of triglycerides (TGs) with alcohols proceeds via three reversible reactions route. The stoichiometry of alcohol to oil molar ratio is (3:1). However, an excess alcohol required to improve the reaction towards the desired products. The alcohol-oil molar ratio that should be used varies from (N= 1:1, 6:1) and actually, (6:1) alcohol-oil molar ratio mostly used giving an excellent conversion without using great amount of alcohol. (Lopez *et al*, 2005) proposed that the first transesterification reaction took placed where a molecule of triglyceride is converted into diglyceride intermediate and produced a molecule of fatty acid alkyl ester (FAME). Thereafter, diglyceride is converted into monoglyceride intermediate by transesterification process and produced a molecule of fatty acid alkyl ester. Finally, the last monoglyceride intermediate was converted into alkyl ester and produced co-product of glycerol (glycerine).

The detailed information about transesterification conversion of triglyceride into diglyceride, monoglyceride, alkyl ester and glycerol has been discussed in based-catalyzed mechanism later.

Hence, the transesterification process involved three reaction routes with three intermediates which produced three molecules of fatty acid alkyl ester (FAME) and a molecule of glycerol (glycerine).



2.6.3.1 Based-Catalyzed Transesterification

Mostly, the commercial biodiesel is currently produced from transesterification of soybean oil (straight vegetable oil) by using the homogeneous strong base (NaOH or KOH) catalyzed process. Some authors recommended the amount of catalyst that should be added varies from 0.5% to 1% w/w (Barnwall *et al*, 2005; Srivastava *et al*, 2000) but Hanna (1999) claimed that valued of catalyst should be used between 0.005% and 0.35% w/w. These economical strong base-catalyzed is less corrosive than homogeneous acid catalyst such as sulphuric acid (H₂SO₄) and proceeds at much higher rate which yields about 98% conversion. In addition, the process conditions required low temperature usually take place is 60°C but depends on the type of catalyst, different temperature gives different degrees of conversion and low pressure which gives the reaction faster with minimal side effect.

Some researcher found that, temperature range varies between 25°C to 120°C. Using of acidic catalyst, provided a slow reaction and unfavorable because the price of these catalyst is an expensive. Unfortunately, this based-catalyzed mechanism required feedstocks containing low levels of free faty acids (FFAs) and no water present such higher grades oil to ensure that direct conversion occurred with no intermediate compounds such soap formation and glycerines. In addition, since the strong alkaline was used as the catalyst, there still have weaknesses in catalyst recovery and must be neutrallized at the end of reaction.

Detailed explanation of mechanism on transesterification of homogeneous based-catalyzed process which occurred by chemical reacting of trigyceride or triacylglyceride (substance of animal fats or vegetable oils) with short chain alcohol (methanol or ethanol) in the present of catalyst (NaOH or KOH) to produce the esters of fatty acids (alkyl ester) which known as biodiesel and high value co-product of glycerol.

The triglyceride which made of three molecules of fatty acids and a molecule of glycerol (trihydric alcohol) was transesterified by alcohol-catalyst mixture. Commonly, the strong base (NaOH/ KOH) is dissolved with alcohol before adding to the triglyceride. The alcohol will be deprotonate with a base to serve it as the strong nucleophile.

Once the alcohol mixture is made, it is addad to the triglyceride. The reaction follows the replacement of alkyl group on the triglyceride in series of reactions.



At the double bond between carbon and oxigen (C=O), slightly positive charge located at carbon atom while negatively charge located at oxigen atom. This charge will attract the RO⁻ to reaction site. This yields a transition state that has a pair of electrons from the C=O bond now located on the oxygen that was in the C=O bond.

$$\begin{array}{cccc} R_{1} \\ (An oxigen atom & | \\ have pair of electron) & RO-C-O- \\ & & \\ & O-CH_{2}-CH-CH_{2}-O-C=O \\ & & | \\ & O-C=O & R_{3} \\ & & | \\ & R_{2} & & (2.6) \end{array}$$

This pair of electrons then attracted back to the carbon and push off the glycol by forming the alky ester.

Since in the tryglyceride substance contained 3 molecules of glyceride (acylglyceride), this mechanism will continued by two more RO^- groups reacted with other two C=O groups. This completion reaction also has their limitation which the strong nucleophile (RO^-) must fit in the space where there was a slightly positive charged on the carbon atom at double bond structure. So that, only short chain alcohol such as methanol or ethanol required to act as strong nucleophile and reacted with the triglyceride.
The reason of such short chain alcohol used in these process because the present of long alkyl group (-R) on alcohol substance (ex: penthanol, hexanol etc) provided a big structure and affected their nucleophile attacked to the carbon atom located at double bond structure.

2.6.3.2 Acid-Catalyzed Esterification

The esterification occurs through a condensation of carboxylic acid (fatty acid) with alcohol. This reaction required two reactants carboxylic acid (fatty acids) and alcohol. It was showed that the esterification reactions are acidic-catalyzed and proceed slowly in the absence of strong acids such as sulphuric acid (H₂SO₄), phosphoric acid (H₃PO₄), organic sulfonic acids and hydrochloric acid (HCl). The equation 2.8 showed for the esterification reaction.

 (H_2SO_4) $R'COOH + R'OH \longrightarrow R'COOR' + H_2O \qquad (2.8)$ Carboxylic Acid Alohol Catalyst Ester Water

Freedman and Pryde (1986) purposed that alcohol-oil molar ratio used was (30:1) and catalyst used varies from (0.5% to 1%). They claimed that approximated value of catalyst used was 1 mol % but some authors said to use 3.5 mol % of catalyst (Aksoy *et al*, 1988; Zhang *et al*, 2003). The temperature range is 55°C to 80°C but in their studies used 65°C to achive 99% conversion. Unfortunatelly the 50 hours of reaction time is very low in order to give high conversion. Others experimental were carried out by using the buthanolysis and ethanolysis. Buthanolysis need 117°C and ethanolysis need 78°C while the time should be used is 3 hr and 18 hr respectively.

2.6.3.3 Integrated Acid-catalyzed Pre-esterification of FFAs & Based-catalyzed Transesterification

Nowadays, many researchs have been done in transesterification process by using feedstocks or raw materials coming from higher grade vegetable oils such as soybean oil or refine oils which not contain high amount of free fatty acids (FFAs). In spite of that, the conversion of oils will achive at high yield with minimal side effects and reduce the problematic involve separation and purification process and also reduce the production costs. Unfortunately, some operations involving feedstocks coming from waste vegetable oils or waste cooking oils will lead to the present of high amount of free fatty acids (FFAs).

Hence, special process required to transesterified the feedstocks containing high amount of free fatty acids (FFAs) in order to avoid incoming effects of soap formation (saponification) and water residual.

Waste cooking oils usually contain 2-7 % of free fatty acids while the animal fats contain 5-30 % of free fatty acids. Direct transesterification of free fatty acids (FFAs) with alkali catalyst will lead to the water and soap formation. Equation 2.9 provided the reaction between free fatty acids (FFAs) and base-catalyst.



So that, acid-catalyzed pre-esterification is required to converted the FFAs into alkyl ester (biodiesel) and thus reduce the FFA level. Hence, the first process in the transesterification of high FFAs is an acid-catalyzed pre-esterification.



After the pretreatment process, low levels of FFAs pretreated oil were transesterified with an alkali catalyst to convert the triglycerides into alkyl esters. As can be seen above, the water is formed and it can stop the reaction before completion. In another way it is recommended that, alcohol was allowed to separate from pretreated oils and fats. The alcohols and water formed in esterification reaction were removed then second step of esterification or proceeding directly to alkali-catalyzed transesterification was allowed. As the alcohol-water mixture removed, the mixture also contains some dissolved oils and FFAs that should be recovered and reprocessed.

2.6.3.4 Enzyme-catalyzed (Biocatalyst) Transesterification

Biocatalyst that usually used was a lipase-enzyme; however conditions need to be well controlled to maintain the activity of the catalyst. Shuler and Kargi (2002) reported that the enzyme is denatured when exposed to extream temperature or pH environments. Hydrolytic enzymes are generally used as biocatalysts as they are ready available and are easily handled. They are stable, do not require co-enzymes and will often tolerate organic solvent. Recent patents and articles have shown that reaction yields and times are still unfavourable compared to base-catalysed transesterification for commercial application. Table 2.1 provided some information on advantages and disadvantages of using lipase.

Table 2.1 Advantages and disadvantages of lipase enzyme

Advantages of using Lipase

- Possible to regenerate and reuse of the immobilized residue, because it can be left in the reactor.

- High concentaration of lipase-catalyst will provided longer catalyst activation.

- Has bigger thermal stability.

- Immobilization and separation process will be easier.

Disadvantages of using Lipase

- Lose some initial activity due to volume of the oil molecule.

- Number of support enzyme is not uniform.

- Biocatalyst is more expensive than natural enzyme.

- Very sensitives to extream temperature and pH environments.

2.6.3.5 Hydrolysis Process

The hydrolysis of triglycerides form a heterogenous reaction system made up of two liquid phases. The dispersed aqueous phase consists of water and glycerol; the homogenous lipid phase consists of fatty acids and glycerides. The hydrolysis of glycerides takes place in the lipid phase in several stages via partial glycerides (diglycerides and monoglycerides). Acid catalysts are very effective at accelerating the hydrolysis reaction. However, at high temperatures substantial material corrosion occurs. Diabasic metal oxides have a higher activity than more strongly alkaline monobasic metal oxides. Zinc oxide (ZnO) in its soap form has been suggested to be the most active catalyst for hydrolysis reactions. Reaction without a catalyst is not economical below 210°C, thus requiring the implication of high temperature, pressure techniques. Modern continuous plants operated at pressures between 0.6-1.2 MPa at 210-260°C without a catalyst. This increased pressure allows the mutual solubility of the two phases to increases to a point where the formation of continuous phase occurs.

Triglycerides + Water \longrightarrow Esters + Glycerol (2.11) Δ (Heat)

2.6.3.6 Supercritical Alcohol Transesterification

The study of the transesterification of rapeseed oil with supercritical methanol was found to be very effect and gave a conversion of >95% within 4 min. A reaction temperature of 350°C, pressure of 30MPa and a ratio of 42:1 of methanol to rapeseed oil for 240s were found to be the best reaction conditions. The rate was substantially high from 300 to 500°C but at temperatures above 400°C it was found that thermal degradation takes place. Supercritical treatment of lipids with a suitable solvent such as methanol relies on the relationship between temperature, pressure and the thermophysical properties such as dielectric constant, viscosity, specific weight and polarity (Kusdiana, 2000). A comparison between of supercritical methanol production and alcoholysis can be seen in table 2.2.

| Parameter | Common Method | Supercritical Methanol |
|--------------------------|--|------------------------|
| | (Alcoholysis) | Method |
| Reaction time | 1-6 hours | 0.067 hour |
| Reaction condition | 0.1 Mpa, 30-65°C | 35 Mpa, 350°C |
| Catalyst | Acid or Alkali | None |
| Free fatty acids (FFAs) | Saponified products | Methyl ester |
| Conversion yield | 97% | 98.5% |
| Removal for purification | Methanol, catalyst and saponified products | Methanol |
| Process | Detailed | Simple |

 Table 2.2 Comparison between productions of biodiesel

It was reported that, there are vary in reaction time of synthesizing the biodiesel depending on the solvent used. Short chain alcohol such as methanol showed lower reaction time which indicated that reaction rate of methanol for fatty acid methyl esters (FAMEs) conversion was faster compared to other solvents used in supercritical treatment of lipids.

The summary of advantages and disadvantages of each technological possibility to produce biodiesel can be found in table 2.3.

| Variable | Alkali | Acid catalysis | Lipase | Supercritical |
|-----------------|---------------|----------------|---------------|---------------|
| | catalysis | | catalysis | Alcohol |
| Reaction | 60-70 | 55-80 | 30-40 | 239-385 |
| temperature | | | | |
| (°C) | | | | |
| Free fatty acid | Saponified | Esters | Methyl esters | Esters |
| in raw | products | | | |
| materials | | | | |
| Water in raw | Interference | Interference | No influence | |
| materials | with reaction | with reaction | | |
| Yield of methyl | Normal | Normal | Higher | Good |
| ester | | | | |
| Recovery of | Difficult | Difficult | Easy | |
| glycerol | | | | |
| Purification of | Repeated | Repeated | None | |
| methyl ester | washing | washing | | |
| Production cost | Cheap | Cheap | Relatively | Medium |
| of catalyst | | | expensive | |

 Table 2.3
 Advantages and disadvantages of technology use

2.7 Catalyst comparison

Since, in this research we can conclude that both homogeneous and heterogeneous catalysts can be carried in the tranesterification reaction. However, there were a lot of differents between them. Both homogeneous and heterogeneous catalysts have their advantages and disadvantages respectively. Table below provide the comparison for both homogeneous and heterogeneous catalyst.

| Homogeneous catalyst | Heterogeneous catalyst | | |
|--|---|--|--|
| Advantages | Advantages | | |
| -Cheaper & faster reaction rate | -Economical & ecological | | |
| -Reaction condition at low temp. & | -Non-corrosive | | |
| pressure | -Present fewer disposal problems | | |
| -Yield high conversion with minimal side | -Easier to separate from mixture | | |
| reaction | -Give higher catalytic activity | | |
| -Soluble in alcohol provide direct | -Higher selectivity & longer catalyst | | |
| conversion to biodiesel yield | lifetime | | |
| -No exotic material of construction are | -Can be reutilized and regenerated | | |
| needed | | | |
| | | | |
| Disadvantages | Disadvantages | | |
| Disadvantages -Base-catalyzed must be neutralized due to | Disadvantages -Some catalyst may easily corrode by | | |
| Disadvantages -Base-catalyzed must be neutralized due to effect on wastewater | Disadvantages-Some catalyst may easily corrode by alcohol | | |
| Disadvantages -Base-catalyzed must be neutralized due to effect on wastewater -Acid-catalyzed provide slow reaction | Disadvantages -Some catalyst may easily corrode by alcohol -Surface of catalyst may be deteriorate | | |
| Disadvantages -Base-catalyzed must be neutralized due to effect on wastewater -Acid-catalyzed provide slow reaction compared to basic-catalyzed | Disadvantages -Some catalyst may easily corrode by alcohol -Surface of catalyst may be deteriorate -Short catalyst lifetime because of low | | |
| Disadvantages -Base-catalyzed must be neutralized due to effect on wastewater -Acid-catalyzed provide slow reaction compared to basic-catalyzed -Catalyst cannot be reutilized | Disadvantages -Some catalyst may easily corrode by alcohol -Surface of catalyst may be deteriorate -Short catalyst lifetime because of low stability | | |
| Disadvantages -Base-catalyzed must be neutralized due to effect on wastewater -Acid-catalyzed provide slow reaction compared to basic-catalyzed -Catalyst cannot be reutilized -Favor to the formation of stable emulsion | Disadvantages -Some catalyst may easily corrode by alcohol -Surface of catalyst may be deteriorate -Short catalyst lifetime because of low stability -Regenerated of catalyst needed higher | | |
| Disadvantages -Base-catalyzed must be neutralized due to effect on wastewater -Acid-catalyzed provide slow reaction compared to basic-catalyzed -Catalyst cannot be reutilized -Favor to the formation of stable emulsion (soap formation) cause to difficult | Disadvantages -Some catalyst may easily corrode by alcohol -Surface of catalyst may be deteriorate -Short catalyst lifetime because of low stability -Regenerated of catalyst needed higher cost | | |
| Disadvantages -Base-catalyzed must be neutralized due to effect on wastewater -Acid-catalyzed provide slow reaction compared to basic-catalyzed -Catalyst cannot be reutilized -Favor to the formation of stable emulsion (soap formation) cause to difficult separation process | Disadvantages -Some catalyst may easily corrode by alcohol -Surface of catalyst may be deteriorate -Short catalyst lifetime because of low stability -Regenerated of catalyst needed higher cost | | |

Table 2.4 Comparison of homogeneous and heterogeneous catalysts

2.8 Reactor Used in Biodiesel

Generally, biodiesel production in industry plant usually used a conventional reactor such as batch and continuous stirrer tank reactor (CSTR). Mostly, the batch and CSTR reactor used to produce a large tons usually thousands tons of biodiesel per month. However, both classical mixing-heating reactors showed the disadvantages due to high production cost in maintenance with large equipment needed and also the longer time of reaction required to synthesize biodiesel.

Hence, in this study, some authors recommended a new succesful way of biodiesel production by using the ultrasonic reactor (Stavarache *et al*, 2004). The ultrasonic reactor is suitable to replace the classical reactor since it was proved to perform the transesterification reaction. The author claimed that, an ultarasonic irradiation proved and suitable for large-scale processing of biodiesel. The highest conversion was achieved when short residence time was employed while compared to the batch and CSTR reactor which required long reaction time to achive the same yield of production. Some other benefits were discussed here.

Ultrasonication benefits:

- i) Reduction of reaction time by up 97.5% (10 min using ultrasonic while 5-10 hr using conventional reactor)
- ii) Reduction of static separation time by up to 98%
- iii) Increase in biodiesel yield by up 99%
- iv) Reduce in catalyst requirement up to 66%

2.9 Product of Analysis

Various methods were introduced to investigate the analysis of biodiesel, its impurities and by-product. There are currently limits on the levels of these compounds in biodiesel that are provide in guidelines such as American Society for Testing and Materials (ASTM) which can be seen in table 2.5.

| Property test | Limits | Units |
|-------------------------|--------------|----------|
| Flash point | 100 minimum | °C |
| Water sediment | 0.05 maximum | % vol |
| Kinematic and viscosity | 1.9-1.6 | mm³/g |
| Sulphated ash | 0.02 maximum | % mass |
| Copper strip corrosion | No.3 maximum | |
| Cetane number | 40 minimum | |
| Cloud point | RTC | °C |
| Carbon residue | 0.05 maximum | % mass |
| Acid number | 0.8 maximum | mg KOH/g |
| Free glycerol | 0.02 | % mass |
| Total glycerine | 0.24 | % mass |
| Sulphur | 0.05 maximum | % mass |

Table 2.5Detailed requirement for biodiesel fuel

There are several methods of analysis which can be used to determine the property of biodiesel and composition of impurities and by-products such as GC Gas chromatography, solid phase separation, thin film liquid chromatography (TLC), High Precision Liquid Chromatography (HPLC), Refractometry, Near Infrared Spectroscopy with a Fibre-Optic Probe (NIR) and Thin Layer Chromatography/Flame-Ionization Detection (TLC/FID) (Freedman et al, 1984).

CHAPTER 3

METHODOLOGY

3.1 Introduction

In order to study the performance of Sodium Methoxide (NaOCH₃) as homogeneous basic-catalyzed towards yield and selectivity on biodiesel production, several important variables will be test-out such as reaction temperature, time and catalyst concentration. In this experiment, three major stages will be introduced in order to choose the condition of catalyst which shows their best amount of concentration, temperature and reaction time that will be undergoes as optimum condition for biodiesel production. Other four major methods including raw material and catalyst preparation, equipment uses, experimental and analysis procedures will be discuss here. Figure 3.1 showed the flow process for all method procedures.



Figure 3.1 Process flow diagram

3.2 Material and Catalyst Preparation

The raw material that will be use in this experiment is waste cooking oils (WCOs). Waste cooking oils are the good sources of triglycerides and less expensive compared to edible oils or high grade oils. The waste cooking oils were provided by local area which collected from restaurants and canteens. Prior to be used direct toward transesterification process, the raw material (WCOs) must be treated and filtered-out by using filter press in order to remove any food residual and other impurities which can contaminate the production process.

Methanol was used as a solvent and the molar ratio of methanol to waste cooking oils (WCOs) is fixed to (6:1) in transesterification process for biodiesel production. In this experiment, the amount of WCOs used as raw material for each sample preparation is 200g while the methanol is 38.448g. The calculation for required amount of waste cooking oils and methanol were shown in the table below.

| Component | Methanol | Waste cooking oils (WCOs) |
|------------------------|-------------------------|---------------------------|
| Molar Ratio | 6 | 1 |
| Density | 0.791 g/cm ³ | 0.92 g/cm ³ |
| Molecular Weight | 32.049 g/mol | 1000 g/mol |
| Mass Ratio | 6 mole x 32.049 g/mol | 1mole x 1000 g/mol |
| Total Mass | 192.24g | 1000g |
| Required Amount | 38.448g | 200g |

Table 3.1Methanol and WCOs preparation

The mass ratio (wt/wt %) of catalyst (NaOCH₃) used to waste cooking oils is fixed to (1:1).

3.3 Equipment/Apparatus

Actually, the equipment used can be divided into two parts which equipments that involved during experimental procedure and the other involved during analysis procedure. There are several equipments that will be used during experimental procedures such as ultrasonic cleaner, mechanical stirrer, stirring hotplate, high speed centrifugal and rotary evaporator. The equipment that will be involved during analysis procedure only Karl Fischer Analyzer which used to obtain the percentage of moisture content in biodiesel sample. Other apparatus such as beaker 500 mL, connical flask (250 to 500 mL), filter paper (125 mm diameter) and separator funnel (500 mL) also involved in this experiment.

3.3.1 Experimental Equipment/Apparatus

Ultrasonic cleaner is the main equipment because the transesterification process will be conducted in this reactor. The mixture of waste cooking oils and methanol will be reacted together in the presence of catalyst and the reaction will took place in this reactor. All the components will be mixed together by using agitator (mechanical stirrer) at 150 of rotation per minute (rpm).



Figure 3.2 Ultrasonic cleaner

Filterification or purification process is needed to remove dirt and any residual of food particle (non-oil material). The filterification can be carried out whether using the conventional way of filtered paper or using the fastest way with high speed centrifugal.



Figure 3.3 High speed centrifugal

In order to remove dissolved or any suspended water from filtered oils, the conventional way such using the stirring hotplate will be used. The sample of filtered oils or cleaned oils will be placed in the beaker and heating up approximately to above the boiling point of water by using the stirring hotplate. However, there had an easy way to remove the suspended water using the rotational evaporator. Rotational evaporator also will be performed to recover an excess methanol for further reused.



Figure 3.4 Rotary evaporator



Figure 3.5 Stirring hotplate

The separator funnel is used once the reaction was completed to separate final product into two layers. The mixture of final product was left to settle down which the top oils layer contained biodiesel and unreacted triglyceride while the bottom layer contains glycerine and insoluble catalyst that will be recovered for further used. In addition, the separator funnel also was used during washing step in order to separate water from biodiesel sample.



Figure 3.6 Separator funnel

3.3.2 Analysis Equipment

Method for analysis is required to find out whether the biodisel produced meet the biodiesel specification measured by ASTM standard. However, in this experiment the only equipment used for analysis is Karl Fischer Analyzer which to determine the moisture content contained in the sample product. Figure 3.7 showed the Karl Fischer Analyzer that has been used for analysis in moisture content.



Figure 3.7 Karl Fischer Analyzer

3.4 Experimental Procedure

In order to obtain the best condition for biodiesel production, all the samples will be transesterified accordingly to the data provided by three stages of experiment in which three respons variable for each stage must be determined such as biodiesel yield, moisture and methyl ester content.

In the first stage, temperature and reaction time will be fixed while varying the catalyst concentration within 0.5 to 2.5 wt %. In this case, the best catalyst concentration which shows the best condition for biodiesel yield, moisture and methyl ester content will be chosen for the next stage of experiment. Second stage of experiment will be done in order to determine the best temperature condition within 40°C to 80°C by fixing the catalyst concentration and reaction time. In this stage, the sample which shows the best temperature condition for an optimum production will be chosen in the final stage. For the final stage, catalyst concentration and temperature condition that have been chosen from previous stage will be fixed while varying the reaction time within range of 20 min to 60 min.

3.4.1 Method of Purification

Initially, the sample of waste cooking oils will be filtered out in order to remove dirt and residual of food particle (non-oil material). The waste cooking oils will be filtered or centrifuged by using high speed centrifugal. However, in this experiment the raw material (WCOs) were provided by the local restaurants and canteens have been filtered-out by using filter press of the pilot plant. In order to remove dissolved or suspended water content, the filtered or cleaned oils will be placed in the beaker and heating up approximately about 100°C to 120°C by using stirring hot-plate.

3.4.2 Transesterification Process

Transesterification process of waste cooking oils with methanol-catalyst mixture will be done in the ultrasonic-bath cleaner. The molar ratio of methanol to waste cooking oils is fixed to (6:1). Initially, the 200 gram of raw material (WCOs) will be placed in a beaker 500 mL. The waste cooking oils then will be heated-up to 60°C for a few minutes in order to drive the kinetic reaction of WCOs. As being part of experiment, the required amount of methanol (CH₃OH) and catalyst, sodium methoxide (NaOCH₃) will be prepared and mixed together by using magnetic stirrer before taking placed into reaction process. In the meantime, the temperature condition and reaction time for ultrasonic-bath cleaner will be set-up accordingly to the data provided by three stages of experiment. It should be noticed that, the transesterification process can be started if the temperature setting of an ultrasonic reached at desired temperature. Once the temperature reached at desired condition, the transesterification reaction will be started by mixing together the portion of waste cooking oils and methanol-catalyst in a beaker using the agitator (mechanical sitirrer) with the presence of ultrasonic radiation. The rotation of agitator is maintained to 150 (rpm) for all samples preparation. The ultrasonic radiation provides the kinetic reaction faster between molecules thus produced the biodiesel product in short time period compared to other reactor. After reaction completed, the sample will be settled-out over one night in order to get two layers which can be more easiers for separation process.

3.4.3 Separation Process

After reaction completed, the sample prepared will be settled-out over one night for gravitational settling by using separator funnel. This process indicated that the prepared sample will be formed into two layers component. Glycerine and catalyst residue will be settled down at the bottom while the top layer consist biodiesel and residue of methanol. Top layer consist of biodiesel will be separated from the glycerine content by filteration using filter-paper. Biodiesel collected from this separation process will undergo for methanol recovery and washing-step.

3.4.4 Methanol Recovery and Washing Process

Biodiesel sample which have been separated from glycerine layer might contained residue catalyst, excess methanol and suspended water (moisture content). Methanol recovery was done in order to recover back the methanol which can be reuse in the transesterification process and it can be done by using rotary evaporator. Since the boiling point of methanol is quite lower which 65°C, temperature setting for rotary evaporator was conducted between 60°C to 70°C for half an hour in order to remove methanol from biodiesel sample. However, there was an easy way to remove excess methanol from biodiesel by heating-up the sample to 70°C about half an hour using the stirring hot-plate.

Washing process is the method to remove suspended water (moisture) contained in the sample. Moisture contained in the sample might cause a problem toward separation process which is favorable to form an emulsion. Washing-step also gave a better appearance to biodiesel product in which the particles contained in the sample would be clarified through this process. In this process, water is boiled to 80°C and will be used to wash the sample about half to one hour. This process will be repeated twice in order to get the better result for moisture content and to clarify the biodiesel. Water is used as washing reagent in order to attract the water molecules contained in the sample. This statement was indicated that water is the hydrophilic (polar) while biodiesel (organic compounds) is hydrophobic (non-polar). However, some authors stated that, warm water (not to cold or hot) was efficiently to be used during washing process.

There should be noticed that, the sample (biodiesel) will be separated from wash-water by using separator funnel. It was an easy way to separate the biodiesel and water using this method. The sample that have been separated will be heated-up approximately from 100°C to 110°C by using stirring hot-plate in order to remove any residual of moisture content. This heating process will take placed about half to one hour in order to make sure that there has no bubble (moisture) contained in biodiesel sample. Continuing from heating process, sample will be stored tightly in the sample bottle in order to prevent any residue or particulate moisture from surrounding environment.

3.4.5 Method of Analysis

After methanol recovery and washing process, all the samples are ready to be analyzed. In this method there were three analyses that should be test-out in order to examine the performance of catalyst towards biodiesel production such as biodiesel yield, moisture content and methyl ester content. All these methods for analysis will be discuss later in this chapter.

3.4.5.1 Biodiesel Yield

Actually, the biodiesel yield will be analyzed using standard provided by gas chromatography (GC). However, there was another way that could be easy to determine the biodiesel yield by using simple calculation. After all the process completed, each sample of biodiesel will be calculated in order to get their yield. Calculation for biodiesel yield will be simply expressed according to the following equation:

Biodiesel Yield =
$$\frac{Mass of Biodiesel Sample}{Mass of Raw Material (WCOs)} \times 100\%$$
(3.1)

3.4.5.2 Moisture Content

Moisture content analysis was done in order to determine the water suspended (moisture) contained in biodiesel sample. This is an important part because the data provided from this analysis must fulfill the requirement standard of ASTM for biodiesel production. The requirement standard for moisture content in biodiesel production must less than 0.05%. This statement was indicated that, excessed moisture (more than 0.05%) contained in the sample biodiesel will cause a problem to the engine performance thus some modification and purification towards biodiesel must aquire the ASTM standard. However, in this experiment the moisture analysis was not critical part and important as methyl ester content towards selectivity in biodiesel production.

In this method, moisture content was analyzed by using Karl Fischer Analyzer. All the method procedures for moisture content analysis will be showed in figure 3.8.



Figure 3.8 Standardization of Karl Fishcer Titration

3.4.5.3 Metyl Ester Content (TLC)

The most important part of biodiesel production is methyl ester content. Methyl ester content was measured in order to determine the relationship between performances of catalyst used and other parameters setting such as temperature and reaction time towards methyl ester conversion in biodiesel production. Methyl ester conversion also difference for each sample which indicated that the amount of triglyceride converted into methyl ester also different either proceed in complete or incomplete reaction.

In order to obtain the methyl ester contained in biodiesel sample, thin layer chromatography (TLC) analysis was conducted. In this analysis, 10 cm of TLC plate was used. The chemical reagent used in this analysis was chloroform and hexane with molar ratio (1:1) while iodine pellet was used as color indicator to exhibit the image of methyl ester content. 10 mL of each chloroform and hexane will be mixed together in the beaker 500 mL and sample of biodiesel will be dropped onto the TLC plate. The TLC plate with biodiesel spot will be placed into a beaker containing chloroform-hexane mixture. This process took about 15 to 20 min in order to let the solution of chloroform-hexane mixture dispersed the sample and reach-up the top of TLC plate. Calculation for metyl ester conversion can be determined by using equation 3.2.

$$\therefore \% of Metyl Ester conversion = \frac{Length of ME conversion}{Length of TLC plate} \times 100\%$$
(3.2)

CHAPTER 4

RESULT AND DISCUSSION

Homogeneous catalyzed reaction is the conventional way in biodiesel production. In this experiment, the catalyst used was sodium methoxide (NaOCH₃) in order to study their performance towards biodiesel production compared to other strong alkaline-catalyzed such as potassium hydroxide (KOH) and sodium hydroxide (NaOH). In this experiment, all of these parameters such as catalyst concentration, temperature and reaction time were studied in order to obtain the optimum condition for biodiesel production. As previously mentioned, the catalyst concentration used in the range within 0.5 to 2.5 wt%, temperature condition range from 40°C to 80°C and the reaction time conducted from 20 to 60 min. In transesterification process using ultrasonic-bath cleaner, the molar ratio of methanol to waste cooking oils (WCOs) is fixed to (6:1) while mass ratio of catalyst used to raw material (WCOs) is fixed to (1:1). After all reaction were completed, resulted was obtained from analysis data and the effect of catalyst concentration, temperature condition and reaction time towards biodiesel yield, moisture content and methyl ester conversion were studied in this chapter.

4.1 Effect of Catalyst Concentration

The first parameter was studied in transesterification process is catalyst concentration. Concentration of sodium methoxide used in the first stage of experiment range within 0.5 to 2.5 wt% while other parameter such as temperature condition and reaction time were fixed to 40°C and 60 min respectively. Table 4.1 shows result for the first stage of experiment. All the data was repeated in three times in order to get the better resulted.

| Sample | Mass of Sample | Biodiesel Yield | Moisture (%) | Methyl Ester (%) |
|---------|----------------|-----------------|--------------|------------------|
| 0.5 wt% | 164.223 g | 82. 1115 % | 0.05 % | 63.5556 % |
| 1.0 wt% | 135.24 g | 67.62 % | 0.04 % | 71.4444 % |
| 1.5 wt% | 103.954 g | 48.977 % | 0.03 % | 70.3333 % |
| 2.0 wt% | 54.08 g | 27.04 % | 0.02 % | 65.6667 % |
| 2.5 wt% | 38.335 g | 19.1675 % | 0.02 % | 65.0 % |

Table 4.1Effect of catalyst concentration

Result for effect of catalyst concentration on biodiesel yield, moisture content and methyl ester conversion will be plotted on the graph. Figure 4.1, 4.2 and 4.3 showed the resulted for effect of catalyst concentration on biodiesel yield, moisture content and methyl ester conversion respectively.



Figure 4.1 Effect of NaOCH₃ concentration on biodiesel yield



Figure 4.2 Effect of NaOCH₃ concentration on moisture content



Figure 4.3 Effect of NaOCH₃ concentration on methyl ester conversion

In the first stage experiment, the effect of catalyst concentration was studied towards biodiesel yield, moisture content and methyl ester conversion. Experiment results (figure 4.1) showed that, when the catalyst concentration was increased from 0.5 to 2.5 wt%, the product of biodiesel yield will be decreased linearly from about 82% to almost 20%. This was indicated that, the increasing NaOCH₃ concentration towards transesterification process of waste cooking oils is unfavorable due to glycerine and soap formation. It can be seen that, the raw material (WCOs) used might contained large amount of free fatty acids (FFAs) which indicated an excess of alkaline catalyst (NaOCH₃) presence in the reaction caused more selectivity of triglycerides in the saponification process rather than selectivity towards methyl ester yield (Leung *et al*, 2006).

Results (figure 4.2) for moisture content showed that, the increasing in catalyst concentration from 0.5 to 2.5 wt% cause to decrease linearly in moisture from 0.04 to 0.02%. However, there has no evidence which can be used to prove this statement but it should be noticed that, general handling and care taken during washing process is the important thing to make sure the biodiesel product contained less moisture content.

Since, parameter such as moisture content is one of the properties included in biodiesel standard. In addition, it was an acceptable if moisture content of the sample is below than 0.05 % which meant that this amount followed the biodiesel standard and can be used in engine fuel.

Rather than biodiesel yield and moisture content, methyl ester conversion is the most important response that should be studied and will be chosen for the next stage of experiment. Results (figure 4.3) showed that, the increasing in catalyst concentration as well also increase the methyl ester conversion. However, since an excess of catalyst added to the reaction the product yield as well as methyl ester content will decreased because more catalyst added will reacted with high FFAs contained in waste cooking oils (WCOs) and favored to soap formation rather than triglycerides conversion towards esters content. It also can be seen that, the optimum value of methyl ester occurred when NaOCH₃ reached a certain level and decreased if an excess catalyst was added. The optimum value of methyl ester content reached at 71 % which can be used for the next stage experiment.

4.2 Effect of Reaction Temperature

Effect of reaction temperature will be studied in the second stage of experiment. Reaction temperature was conducted within range from 40°C to 80°C. In this experiment, other parameters setting such as catalyst concentration and reaction time will be fixed to 1.0 wt% and 60 min respectively. Table 4.2 shows the result for second stage of experiment.

| Sample | Mass of Sample | Biodiesel Yield | Moisture (%) | Methyl Ester (%) |
|--------|----------------|-----------------|--------------|------------------|
| 40°C | 152.34 g | 76.17 % | 0.04 % | 70.18 % |
| 50°C | 152.965 g | 76.4825 % | 0.04 % | 70.37 % |
| 60°C | 141.72 g | 70.86 % | 0.06 % | 71.85 % |
| 70°C | 145.335 g | 72.6675 % | 0.08 % | 69.26 % |
| 80°C | 142.65 g | 71.325 % | 0.12 % | 69.81 % |

Table 4.2Effect of reaction temperature

Result for effect of reaction temperature on biodiesel yield, moisture content and methyl ester conversion will be plotted on the graph. Figure 4.4, 4.5 and 4.6 showed the resulted for effect of reaction temperature on biodiesel yield, moisture content and methyl ester conversion respectively.



Figure 4.4 Effect of temperature on biodiesel yield



Figure 4.5 Effect of temperature on moisture content



Figure 4.6 Effect of temperature on methyl ester conversion

To determine the effect of temperature on biodiesel yield, moisture content and methyl ester conversion, the transesterification reaction was carried out at fixed catalyst concentration and reaction time. Catalyst concentration 1.0 wt % and 60 min of reaction time will be fixed in this reaction process.

The results (figure 4.4) showed that the effect of temperture on biodiesel yield. The maximum product yield (76.5%) was achieved at temperature 50°C. However, it can be stated that, the pattern of graph seems to be flatted or just have a little decreased among the samples from reaction temperature of 40 to 80°C due to amount of catalyst used is the same for all sample preparation in these second stage. In addition, general handling during separation and washing process are the main factor to be taken in order to obtain the best result for samples collection. The conversion of metyl ester achieved the maximum value almost 72% at temperature of 60°C. It was indicated that, the high temperature could accelerate the reaction towards biodiesel yield as well as methyl ester conversion due to the effect of temperature on viscosity of waste cooking oils (Leung *et al*, 2006). In addition, (figure 4.6) higher temperature could lead to a decreasing in product yield as well as methyl ester content because impact of this high temperature will accelerate the selectivity of triglyceride towards saponification process which leading to the negative effect on product yield. Since the methyl ester conversion is an important part that should be studied in this experiment therefore, for the transesterification of waste cooking oils (WCOs), an optimal reaction temperature of 60°C was chosen in this process and will undergo for the next reaction stage.

4.3 Effect of Reaction Time

The last parameter that would be studied in the last stage of experiment was the effect of reaction time. Reaction time will be conducted within range from 20 to 60 min while other parameters setting such as catalyst concentration and reaction temperature will be fixed at 1.0 wt % and 60°C respectively. Table 4.3 shows the result for the last stage of experiment.

| Sample | Mass of Sample | Biodiesel Yield | Moisture (%) | Methyl Ester (%) |
|--------|----------------|-----------------|--------------|------------------|
| 20 min | 147.2 g | 73.6 % | 0.05 % | 88.71 % |
| 30 min | 150.235 g | 75.1111 % | 0.06 % | 85.93 % |
| 40 min | 156.23 g | 78.115 % | 0.05 % | 88.8889 % |
| 50 min | 154.54 g | 77.27 % | 0.07 % | 87.08 % |
| 60 min | 149.735 g | 74.8675 % | 0.12 % | 85.8889 % |

Table 4.3Effect of reaction time

Results for effect of reaction time on biodiesel yield, moisture content and metyl ester content will be plotted on the graph as shown in figure 4.7, 4.8 and 4.9 respectively.



Figure 4.7Effect of reaction time on biodiesel yield






Figure 4.9 Effect of reaction time on methyl ester conversion

Last but not least is the final stage of experiment which to investigate the effect of reaction time against biodiesel yield, moisture and metyl ester conversion. In this experiment, catalyst concentration (1.0 wt %) and reaction temperature (60° C) chosen from initial and secondary stage respectively will be fixed. It has been proved that, reaction time required for completion of the alkaline-catalyzed transesterification process depended not only on temperature but also on the degree of mixing of mechanical stirrer (Leung *et al*, 2006). In addition, in this experiment the reaction rate of transesterification was also influenced with irradiation wave provided by the ultrasonic bath-cleaner.

From figure 4.7, it can be observed that increasing in reaction time from 20 to 40 min at fixed catalyst concentration (1.0 wt%) and temperature (60°C) will increase the reaction rate as well as product yield (biodiesel yield). The product yield reached an optimal value about 78 % at certain time (40 min). It also indicated that, the completion of transesterification process occurred at 40 minutes of reaction, however slightly reduction in biodiesel yield occurred due to longer reaction time enhanced the

hydrolysis of ester (reverse reaction of transesterification) which could result in loss production.

Figure 4.8 showed the resulted of reaction time on moisture content. It can be stated that, the increasing in reaction time towards transesterification process will affected the purity product with high moisture content. In addition, the value of moisture content in the sample differs from one to another due to handling procedure during washing-step which indicated that the sample might contain even small quantities of sediment or water residual. However, it was reasonable to accept the value of moisture content below than 0.05 % as indicated under standard of biodiesel production.

Instead of biodiesel yield and moisture content, metyl ester conversion was an important part to be investigated during experiment. Result from figure 4.9 indicated that, an extension of reaction time had no significant effect on conversion of triglycerides towards metyl ester but led to slightly decreased due to soap formation resulted from high amount of free fatty acids (FFAs) contained in waste cooking oils (WCOs). It can be showed that, the value of metyl ester content achieved at high conversion about 88.9 % at 40 min as same condition as optimal value of product yield (biodiesel yield) for the same reaction time.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The homogeneous catalyzed reaction showed an excellent result in transesterification process of biodiesel production. In this research work, alkaline-catalyzed such as sodium methoxide was studied in order to obtain the optimum condition for biodiesel production. Sodium methoxide showed an excellent result as well as other strong base such as NaOH and KOH in transesterification reaction.

It can be seen that, the type and amount of catalyst, molar ratio of methanol to feedstocks used, effect of temperature and reaction time were the main factors affecting the reaction process. Since, the waste cooking oils (WCOs) used might contain high value of free fatty acids (FFAs) thus, the optimal values of these parameters for achieving best conversion of triglycerides towards biodiesel yield and methyl ester depended on the chemical and physical properties of the feedstock oils.

The higher amount of catalyst used during transesterification might cause to soap formation thus decreased in biodiesel yield and methyl ester conversion. As the temperature increased will accelerated the reaction rate towards product yield and methyl ester conversion. However, increasing the reaction temperature was unfavored due to saponification of triglyceride rather than desired conversion. The last parameter studied is the reaction time which indicated that an extension of reaction time had negative effect on product (biodiesel yield) and metyl ester conversion due to reversible reaction (hydrolysis) of transesterification process also led to the soap formation. Since, an ultrasonic irradiation was proved and suitable for processing of biodiesel. The highest conversion can be achieved with short residence time employed while compared to the batch and CSTR reactor which required long reaction time in order to reach the same product yield. Hence, the optimum condition for biodiesel production from waste cooking oils (WCOs) with sodium methoxide (NaOCH₃) as alkaline-catalyzed can be achieved at catalyst concentration of 1.0 wt % while the effect of temperature and reaction time were conducted at 60°C and 40 min respectively.

The resulted also indicated that the high conversion of product (biodiesel yield) and methyl ester content can be achieved approximately about (75 to 80 %) and (88 to 90 %) respectively. Hence, it can be stated that, the performance of this catalyst showed the promissing resulted as other strong alkaline-catalyst such as sodium hydroxide (NaOH) and potassium hydroxide (KOH) in biodiesel production of waste cooking oils.

5.2 Recommendation

Instead of using high grade or edible oils in synthesizing of biodiesel waste cooking oils also can be used as raw material but in order to achieve high product yield as well as methyl ester conversion, the waste cooking oils must be treated well or purify to remove any residual of food particle or other impurities. High amount of free fatty acids (FFAs) contained in waste cooking oils (WCOs) is the major problem towards tranesterification reaction because it was favored to soap formation rather than selectivity of triglycerides on methyl ester conversion. Hence, it was recommended to treat or analyzed the amount of free fatty acids contained in the raw material before it can be used further in transesterification reaction.

Homogeneous alkaline-catalyzed also favored to soap formation when reacting with high amount of FFAs. However, there was an alternative way that can be used to replace the homogeneous base-catalyzed which is to use the heterogeneous alkalinecatalyzed. Heterogeneous alkaline-catalyzed also showed convincing result as good as homogeneous catalyzed and favorable because this type of catalyst presence fewer disposal problems and also easier to separate from liquid product. In addition, using this heterogeneous catalyst provided many advantages such as give the higher activity and selectivity, more economical and ecological thus contributed to the environmental friendly also give longer catalyst lifetime which can be regenerated or recovered after reaction processed.

In order to improve the purity of product yield as well as methyl ester conversion, some precautions and cares should be taken such as general handling during separation and washing process. Separation and washing process are the critical part in experimental procedure because any water sediment or other impurities such as catalyst residual will affected the moisture problems thus decreasing in product yield as well as purity of methyl ester conversion.

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APPENDIX A

EFFECT OF CATALYST CONCENTRATION

A.) Calculation for biodiesel yield (%):

The value of biodiesel yield for each sample prepared from stage 1 through stage 3 will be calculated using equation 3.1.

i) Sample 1 (0.5 wt %): Mass of Sample = 164.223 g Mass of Raw Material = 200g $\therefore Biodiesel Yield : \frac{Mass of Sample}{Mass of Raw Material} \times 100\%$ $= \frac{164.223 g}{200 g} \times 100\%$ = 82.1115 %ii) Sample 2 (1.0 wt %): Mass of Sample = 135.24g Mass of Raw Material = 200 g $\therefore Biodiesel Yield : \frac{Mass of Sample}{Mass of Raw Material} \times 100\%$ $= \frac{135.24 g}{200 g} \times 100\%$ $= \frac{135.24 g}{200 g} \times 100\%$ = 67.62 % iii) Sample 3 (1.5 wt %):

Mass of Sample = 103.954 g

Mass of Raw Material = 200 g

 $\therefore Biodiesel Yield : \frac{Mass of Sample}{Mass of Raw Material} \times 100\%$

$$= \frac{103.954 \,g}{200 \,g} \times 100\%$$
$$= 48.977 \,\%$$

iv) Sample 4 (2.0 wt %): Mass of Sample = 54.08 g

Mass of Raw Material = 200 g

:. Biodiesel Yield :
$$\frac{Mass of Sample}{Mass of Raw Material} \times 100\%$$

$$= \frac{54.08 \, g}{200 \, g} \times 100\%$$
$$= 27.04 \ \%$$

v) Sample 5 (2.5 wt %):
Mass of Sample = 38.335 g
Mass of Raw Material = 200 g

$$\therefore$$
 Biodiesel Yield : $\frac{Mass of Sample}{Mass of Raw Material} \times 100\%$
 $= \frac{38.335 g}{200 g} \times 100\%$
 $= 19.1675 \%$

B.) Calculation for metyl ester (ME) content:

In order to determine an optimum conversion for metyl ester content, each sample analysis in stage 1 till stage 3 will be repeated three times to obtain the averaged value. Calculation for metyl ester content can be determined using equation 3.2.

i) Sample 1 (0.5 wt %): Length of ME conversion = 5.72 cm Length of TLC plate = 9.0 cm $\therefore \%$ of Metyl Ester conversion = $\frac{Length of ME conversion}{Length of TLC plate} \times 100\%$ 5.72 cm

$$=\frac{3.72\,cm}{9.0\,cm}\times 100\%$$

ii) Sample 2 (1.0 wt %):Length of ME conversion = 6.43 cmLength of TLC plate = 9.0 cm

:.% of Metyl Ester conversion = $\frac{\text{Length of ME conversion}}{\text{Length of TLC plate}} \times 100\%$

$$=\frac{6.43\,cm}{9.0\,cm}$$
 ×100%

iii) Sample 3 (1.5 wt %):Length of ME conversion = 6.33 cmLength of TLC plate = 9.0 cm

:.% of Metyl Ester conversion = $\frac{\text{Length of ME conversion}}{\text{Length of TLC plate}} \times 100\%$

$$= \frac{6.33 \, cm}{9.0 \, cm} \times 100\%$$
$$= 70.3333 \, \%$$

iv) Sample 4 (2.0 wt %):

Length of ME conversion = 5.91 cm

Length of TLC plate = 9.0 cm

:.% of Metyl Ester conversion = $\frac{\text{Length of ME conversion}}{\text{Length of TLC plate}} \times 100\%$

$$=\frac{5.91 cm}{9.0 cm} \times 100\%$$

 v) Sample 5 (2.5 wt %): Length of ME conversion = 5.85 cm Length of TLC plate = 9.0 cm

:.% of Metyl Ester conversion = $\frac{\text{Length of ME conversion}}{\text{Length of TLC plate}} \times 100\%$

$$=\frac{5.85\,cm}{9.0\,cm}\times100\%$$

APPENDIX B

EFFECT OF REACTION TEMPERATURE

A.) Calculation for biodiesel yield (%):

i) Sample 1 (T = 40°C):
Mass of Sample = 152.34 g
Mass of Raw Material = 200 g

$$\therefore$$
 Biodiesel Yield : $\frac{Mass of Sample}{Mass of Raw Material} \times 100\%$
 $= \frac{152.34 g}{200 g} \times 100\%$
 $= 76.17 \%$
ii) Sample 2 (T = 50°C):
Mass of Sample = 152.965 g
Mass of Raw Material = 200 g
 \therefore Biodiesel Yield : $\frac{Mass of Sample}{Mass of Raw Material} \times 100\%$
 $= \frac{152.965 g}{200 g} \times 100\%$
 $= \frac{152.965 g}{200 g} \times 100\%$
 $= 76.4825 \%$

iii) Sample 3 (T = 60° C): Mass of Sample = 141.72 g

Mass of Raw Material = 200 g

$$\therefore Biodiesel Yield : \frac{Mass of Sample}{Mass of Raw Material} \times 100\%$$

$$= \frac{141.72 g}{200 g} \times 100\%$$

$$= 70.86 \%$$
iv) Sample 4 (T = 70°C):
Mass of Sample = 145.335 g
Mass of Raw Material = 200 g
$$\therefore Biodiesel Yield : \frac{Mass of Sample}{Mass of Raw Material} \times 100\%$$

$$= \frac{145.335 g}{200 g} \times 100\%$$

v) Sample 5 (T = 80° C)

Mass of Sample = 142.65 g

Mass of Raw Material = 200 g

 $\therefore Biodiesel Yield : \frac{Mass of Sample}{Mass of Raw Material} \times 100\%$

$$=\frac{142.65\,g}{200\,g}\times100\%$$

B.) Calculation for metyl ester (ME) content:

Since the calculation method for metyl esters conversion can be determined by repeating three times of valued. Each trial for each sample will be calculated using same equation (eq: 3.2) as the first satge of experiment.

:.% of Metyl Ester conversion = $\frac{\text{Length of ME conversion}}{\text{Length of TLC plate}} \times 100\%$

| Sample | Trial 1 | Trial 2 | Trial 3 | Average Value |
|----------|-----------|-----------|-----------|---------------|
| Sample 1 | 72.22 % | 68.8889 % | 69.4444 % | 70.18 % |
| (40°C) | | | | |
| Sample 2 | 73.33 % | 68.8889 % | 68.8889 % | 70.37 % |
| (50°C) | | | | |
| Sample 3 | 75.5556 % | 70.0 % | 70.0 % | 71.85 % |
| (60°C) | | | | |
| Sample 4 | 69.449 % | 68.33 % | 70.0 % | 69.26 % |
| (70°C) | | | | |
| Sample 5 | 70.0 % | 69.4444 % | 70.0 % | 69.81 % |
| (80°C) | | | | |

Table B.1Trial result of methyl ester conversion (Exp: 2)

APPENDIX C

EFFECT OF REACTION TIME

A.) Calculation for biodiesel yield (%):

i) Sample 1 (20 min):
Mass of Sample = 147.2 g
Mass of Raw Material = 200 g

$$\therefore$$
 Biodiesel Yield : $\frac{Mass of Sample}{Mass of Raw Material} \times 100\%$
 $= \frac{147.2 g}{200 g} \times 100\%$
 $= 73.6 \%$
ii) Sample 2 (30 min):
Mass of Sample = 150.235 g
Mass of Raw Material = 200 g
 \therefore Biodiesel Yield : $\frac{Mass of Sample}{Mass of Raw Material} \times 100\%$
 $= \frac{150.235 g}{200 g} \times 100\%$

= 75.1175 %

iii) Sample 3 (40 min):

Mass of Sample = 156.23 g

Mass of Raw Material = 200 g

:. Biodiesel Yield : $\frac{Mass of Sample}{Mass of Raw Material} \times 100\%$

$$=\frac{156.23\,g}{200\,g}\times100\%$$

= 78.115 %

iv) Sample 4 (50 min):

Mass of Sample = 154.54 g

Mass of Raw Material = 200 g

:. Biodiesel Yield :
$$\frac{Mass of Sample}{Mass of Raw Material} \times 100\%$$

$$= \frac{154.54 \,g}{200 \,g} \times 100\%$$

Mass of Sample = 149.735 g

Mass of Raw Material = 200 g

 $\therefore Biodiesel Yield : \frac{Mass of Sample}{Mass of Raw Material} \times 100\%$

$$=\frac{149.735\,g}{200\,g}\times100\%$$

= 74.8675 %

| Sample | Trial 1 | Trial 2 | Trial 3 | Average Value |
|------------------|-----------|-----------|-----------|---------------|
| Sample 1 | 91.1111 % | 84.4444 % | 90.566 % | 88.71 % |
| (20 min) | | | | |
| Sample 2 | 88.3333 % | 82.2222 % | 87.2222 % | 85.93 % |
| (30 min) | | | | |
| Sample 3 | 90.0 % | 86.6667 % | 90.0 % | 88.8889 % |
| (40 min) | | | | |
| Sample 4 | 88.3333 % | 85.5556 % | 87.35 % | 87.08 % |
| (50 min) | | | | |
| Sample 5 | 87.2222 % | 84.4444 % | 86.0 % | 85.8889 % |
| (60 min) | | | | |

Table C.1Trial result of metyl ester conversion (Exp: 3)

APPENDIX D

RESULT OF METHYL ESTER CONVERSION

The result of methyl ester conversion for each stage of experiment also showed in figure D.1, D.2 and D.3.



Figure D.1 Effect of catalyst concentration on methyl ester conversion



Figure D.2 Effect of reaction temperature on methyl ester conversion



Figure D.3 Effect of reaction time on methyl ester conversion