

**THE EFFECT OF TEMPERATURE AND CATALYST CONCENTRATION
OF ULTRASONIC REACTOR FOR BIODIESEL PRODUCTION FROM
WASTE COOKING OIL**

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I declare that this thesis entitled “The Effect of Temperature and Catalyst Concentration of Ultrasonic Reactor for Biodiesel Production from Waste Cooking Oil” is the results 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 other degree.

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ABSTRACT

Biodiesel fuel is a clean burning alternative fuel that comes from 100% renewable resources. It is considered the fuel of the future because it is biodegradable and non-toxic. A process for the production of the ethyl ester (biodiesel) from waste cooking oil for use as a biodiesel fuel has been studied. Biodiesel production process is the transesterification of the used cooking oil with methanol, in the presence of alkali catalyst, to yield the ethyl ester as a product and glycerine as a by-product. These studies have been performed to determine the best conditions for the preparation of the biodiesel based on temperature effects, catalyst concentration effects and time effect. These processes were using transesterification method with the help of ultrasonic reactor. The experiments were divided into three stages which two variables were fixed and one variable was varied in each stage. For each stage, these procedures were done. They are heating of oil, catalyst preparation, mixing of methanol with catalyst, draining of glycerol, washing of fuel and lastly analyzing the sample. As a result, the best condition that has been determined for maximum biodiesel production were 1.5% catalyst concentration of potassium hydroxides based on weight of waste cooking oil that were used and methanol in ratio 6:1, process were done at temperature 65⁰C and the time is about 60 minutes. These showed that the objective of the experiment has been achieved. Biodiesel yield and moisture content in biodiesel production from waste cooking oil were measured. These processes which using ultrasonic reactor is easy and faster than other biodiesel production process. These were because cavities caused by the ultrasound at the catalyst surface increase the catalyst activity and reduce the activation overpotential loss.

ABSTRAK

Bahanapi biodiesel adalah salah satu bahan bakar alternatif yang dihasilkan daripada 100% bahan buangan terpakai. Ia dipertimbangkan untuk menjadi bahanapi untuk kegunaan pada masa hadapan kerana tidak toksik dan boleh diuraikan. Satu proses penghasilan etil ester (biodiesel) dari minyak goreng terpakai untuk kegunaan sebagai bahanapi biodiesel telah dilakukan. Proses penghasilan biodiesel ialah transesterifikasi minyak masak terpakai dengan metanol, dengan kehadiran pemangkin, untuk menghasilkan etil ester sebagai hasil utama dan gliserina sebagai hasil sampingan. Ujian telah dilakukan untuk mengenalpasti keadaan terbaik untuk menghasilkan biodiesel berdasarkan kesan suhu, kesan pemangkin dan kesan masa. Proses ini menggunakan kaedah transesterifikasi dengan bantuan rektor gelombang sonik. Kajian ini telah dibahagikan kepada tiga peringkat di mana dua pembolehubah ditetapkan dan satu pembolehubah bertindakbalas. Pada setiap peringkat, langkah-langkah ini dilakukan. Ia adalah pemanasan minyak, penyediaan pemangkin, percampuran metanol dengan pemangkin, pengeringan gliserina, pembasuhan minyak dan analisis sampel. Keadaan yang telah dikenalpasti adalah 1.5% pemangkin kalium hidroksida bergantung kepada berat minyak masak terpakai yang digunakan dan metanol dalam nisbah 6:1, proses dilakukan pada suhu 65⁰C dan selama 60 minit. Ini menunjukkan bahawa objektif kajian telah berjaya dicapai. Hasil biodiesel dan kandungan kelembapan di dalam biodiesel daripada minyak goreng terpakai yang dihasilkan telah diukur. Proses menggunakan rektor gelombang sonik ini mudah dan lebih cepat menghasilkan biodiesel daripada proses yang lain. Ini disebabkan oleh proses kaviti yang dihasilkan dari ultrasonik di permukaan pemangkin meningkatkan aktiviti pemangkin dan mengurangkan kehilangan aktiviti pemangkin yang melampau.

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LIST OF SYMBOLS

$^{\circ}\text{C}$	-	Temperature
l	-	Length
ρ	-	Density
s	-	Time (second)
M	-	Mega
Hz	-	Hertz
ml	-	Milimeter
g	-	Gram

INTRODUCTION

Energy is used mainly for transport, and partly for services, industry and commerce. Today most of the worldwide energy demand is fulfilled by fossil fuels, basically by oil, petroleum and natural gas. Petroleum-based fuels are limited reserves concentrated in certain regions of the world. Oil is also currently the major fuel for transport, and there seems to be no alternative in sight for air transport. In future, because of the increased price and reduction in oil availability, increasing interest and needs so it is preferable to focus on other resources. Against this background, new energy sources are needed. If this situation does not change, the conventional oil and gas resources will last for a couple of generations at present levels of consumption. The scarcity of known petroleum reserves will make renewable energy resources more attractive (Sheehan *et al.*, 1998a).

The world energy demand continues to increase. The growth in energy demand in all forms is expected to continue unabated owing to increasing urbanization, standard of living and expanding population with stabilization not before mid of the current century. The most feasible way to meet this growing demand is by utilizing alternative fuels. One such fuel that exhibits great potential is biofuel, in particular, biodiesel (Fernando *et al.*, 2006). The term biofuel is referred to as liquid or gaseous fuels for the transport sector that are predominantly produced from biomass (Demirbas, 2006). Biofuels are generally considered as offering many priorities, including sustainability, reduction of greenhouse gas emissions, regional development, social structure and agriculture and security of supply (Reijnders,

2006). In developed countries there is a growing trend towards employing modern technologies and efficient bioenergy conversion using a range of biofuels, which are becoming cost-wise competitive with fossil fuels (Puhan *et al.*, 2005). The scarcity of conventional fossil fuels, growing emissions of combustion generated pollutants and their increasing costs will make biomass sources more attractive (Sensoz *et al.*, 2000).

On the other hand, biomass use, in which many people already have an interest, has the properties of being a biomass source and a carbon neutral source (Dowaki *et al.*, 2007). Experts suggest that current oil and gas reserves would suffice to last only a few more decades. To exceed the rising energy demand and reducing petroleum reserves, fuels such as biodiesel and bioethanol are in the forefront of the alternative technologies.

Accordingly, the best alternative for engines is biodiesel. It is well known that transport is almost totally dependent on fossil, particularly, petroleum-based fuels such as gasoline, diesel fuel, liquefied petroleum gas (LPG) and natural gas (NG). An alternative fuel to petrodiesel must be technically feasible, economically competitive, environmentally acceptable and easily available. This current alternative diesel fuel can be termed as biodiesel. Renewable resources are more evenly distributed than fossil and nuclear resources, and energy flows from renewable resources are more than three orders of magnitude higher than current global energy use. Today's energy system is unsustainable because of equity issues as well as environmental, economic, and geopolitical concerns that have implications far into the future (UNDP (United Nations Development Programme) Energy and the challenge of sustainability. World energy assessment, 2000).

1 Background of study

There are a lot of researches that have been done previously on biodiesel production. Biodiesel production is the process of synthesizing biodiesel. Biodiesel is a liquid fuel source largely compatible with petroleum based diesel fuel. Biodiesel contains no petroleum diesel, but it can be blended with petroleum diesel. Since the oil embargo of 1973 by the OPEC a lot of research was done on biodiesel in various universities and government agencies in the USA. Based on research done, biodiesel can be produced by palm oil, cassava, jatropha, safflower, yam, cottonseed, rapeseed, sunflower, canola, soybean, sugarcane, corn, and peanut oil. Modifying these oils to produce the methyl or ethyl esters has been shown to be essential for successful engine operation over the long term. Development of vegetable oil as an alternative fuel would make it possible to provide energy from renewable sources so it could be used.

One of the alternative way biodiesel productions is produce from jatropha. Jatropha is one of such non-edible oils, which has an estimated annual production potential of 200 thousand metric tonnes in India and it can be grown in waste land (Srivastava *et al.*, 2004). Jatropha oil contains about 14% free fatty acid (FFA), which is far beyond the limit of 1% FFA level that can be converted into biodiesel by transesterification using an alkaline catalyst. Hence, an integrated optimized procedure for converting jatropha oil, which contains high FFA% into biodiesel, is very much required. Few researchers have worked with feedstocks having higher FFA% levels using alternative processes, which include a pretreatment step to reduce the FFA of these feedstocks to less than 1% followed by transesterification reaction with an alkaline catalyst (Canakci *et al.*, 2001). This procedure yielded more than 95% biodiesel.

On the other hand, tobacco seed also can be used for biodiesel production. With tobacco seed oil, the free fatty acid level was reduced from about 17wt% to less than 2wt% in 25 min at reaction temperature of 60⁰C and molar ratio of 18:1 of methanol to oil in the first step. In the second step, the maximum yield of 91% FAME (fatty acid methyl ester) was obtained in 30 min at molar ratio of methanol to triglycerides of 6:1, KOH (potassium hydroxide) amount of 1 wt% and a reaction temperature of 60⁰C (Veljkovic *et al.*, 2006).

Soy biodiesel is fuel alternative produced from soybean oil. Since the oil embargo of 1973 by the OPEC a lot of research was done on biodiesel in various universities and government agencies in the USA (available from <http://www.soya.be/review-soy-products.php>.) Soy biodiesel can be used in diesel engines with little or no modifications. Soy biodiesel is made through a chemical process called transesterification whereby the glycerin is separated from the soybean oil. The process gives two products: methyl esters and glycerin.

In Southeast Asia, Malaysia has a rich oil palm industry that generates excess crude palm oil (CPO), in vast quantities for consumption. CPO is one of the four leading vegetable oils traded on the world market. It is also cheaper than canola, rapeseed or soybean oil and would reduce the overhead cost of biodiesel production and generate a ready supply of diesel fuel substitute or blend. In a preceding investigation we reported that CPO–FAME or crude palm oil methyl ester (CPOE) is biocompatible with the process organism, selectively extracted butanol and increased both butanol productivity and production in ABE (acetone butanol ethanol) fermentation (Ishizaki *et al.*, 1999).

2 Problem statements

One of the sources to produce biodiesel is vegetable. Vegetable oil is a fuel alternative. As compared to normal diesel, vegetable oil has two advantages. First, vegetable oil is better for the environment because it is made from renewable resources and has lower emissions compared to petroleum diesel. Second, vegetable oil is a better lubricant. But vegetable oil is a limited feedstock because the production is widely used such in food industry and manufacturing industry. As the other alternative that are more preferable for biodiesel production is using waste cooking oil (WCO). Waste cooking oil is preferable used to produce biodiesel because environmental conservation. Moreover this method used recycling technology, low price of feedstock, unlimited feedstock, and low cost operation. Biodiesel produced by transesterification reactions can be alkali catalyzed, acid catalyzed or enzyme catalyzed, but the first two types have received more attention because of the short reaction times and low cost compared with the third method. When waste cooking oil was used as the reactant, the conversion of the oil was only 90.4% by a three step catalyzed process in 48 h (Watanabe *et al.*, 2001). Chemically catalyzed processes, including alkali catalyzed.

Maximum production of biodiesel with low operating cost, high yield of biofuel and low yield of glycerin is very important for the industry. An alternative way to produce biodiesel is using ultrasonic reactor to process waste cooking oil. When ultrasonic reactor with high wave with certain temperature is applied to a combination of a triglyceride with a monohydroxy alcohol with catalyst, the amount of liquid sampled for concentration determination can have a high effect on the rate of a chemical reaction (Ostroski and Stambaugh, 1950; Weissler *et al.*, 1950; Chen and Kalback, 1967).

1.3 Objective of the Study

The main objective of this study is to identify the value of temperature and catalyst concentration that can produce maximum biodiesel from waste cooking oil by ultrasonic reactor.

4 Scopes of research work

The work will be carried out for this project is divided into three stages.

1) Firstly is preparation of catalyst to react with alcohol. In this step, mixing process will be done.

2) Secondly, transesterification process with waste cooking oil will be conducted using ultrasonic reactor at different temperature, operating time and catalyst ratio.

3) Thirdly, product analysis via yield production, moisture content and thin layer chromatography (TLC).

CHAPTER 2

LITERATURE REVIEW

1 Biodiesel

Biodiesel is methyl or ethyl ester of fatty acid made from used vegetable oils (both edible and non edible) and animal fats. Biodiesel is an alternative fuel for diesel engines that is produced by chemically reacting a vegetable oil or animal fat with an alcohol such as methanol. Biodiesel contains no petroleum, but it can be blended at any level with petroleum diesel to create a biodiesel blend or can be used in its pure form. Biodiesel is a liquid which varies in color between golden and dark brown depending on the production feedstock. It is practically immiscible with water, has a high boiling point and low vapor pressure. Typical methyl ester biodiesel has a flash point of 150 °C (300 °F), making it rather non-flammable. Biodiesel has a density of 0.88 g/cm³, less than water. Figure 2.1 below shows an example of biodiesel.



Figure 2.1: Example of biodiesel

Biodiesel fuel can be blended with other diesel fuels so no changes are needed in the fuel injection system. Furthermore, biodiesel has been demonstrated to yield a reduction in emissions relative to petroleum diesel (Mike Osenga, 1993). Just like petroleum diesel, biodiesel operates in compression ignition (diesel) engine, which essentially require very little or no engine modifications because biodiesel has properties similar to petroleum diesel fuels. Biodiesel produces lower carbon monoxide (CO) and hydrocarbon (HC) emissions than conventional diesel. Biodiesel is considered clean fuel since it has almost no sulphur, no aromatics and has about 10% built-in oxygen, which helps it to burn fully (Chris Tollefson, 1993). Selected economic and environmental implications of developing and using biofuels have been analyzed. Countries which have shown great interest in biofuels often subsidize their development at the expense of other alternate fuels such as the chemical ethanol, MTBE (methyl tertiary butyl ether), and ETBE (ethyl tertiary butyl ether), or byproducts such as glycerine (Mary Heathcote, 1993).

Biodiesel uncontaminated with starting material can be regarded as non-toxic. The reaction requires a catalyst, usually a strong base, such as sodium or potassium hydroxide, and produces new chemical compounds called methyl esters. It is these esters that have come to be known as biodiesel. Because its primary feedstock is a vegetable oil or animal fat, biodiesel is generally considered to be renewable. Since the carbon in the oil or fat originated mostly from carbon dioxide in the air, biodiesel is considered to contribute much less to global warming than fossil fuels which is that is not harmful to the environment like traditional fuels. Biodiesel is made from renewable resources which mean it is safe for the environment. It can help reduce greenhouse gas emissions, as well as public health risks associated with air pollution. It does not produce the high emissions like traditional fuels. Biodiesel does not cause harmful effects to the environment that will produce lasting effects on generations to come. Most biodiesel is produced by reacting vegetable oil with methanol.

Biodiesel is an innovative fuel that is rapidly becoming more available to the general public. Biodiesel can help dependence on foreign oil and help leverage fossil fuel supplies. Biodiesel can be found around the country in select places or it can be bought directly from producers. It costs a little more than traditional fuels at the current time because the demand is not as great. Table 2.1 and 2.2 below shows physical and chemical properties of biodiesel.

Table 2.1 Physical properties of biodiesel

1. Density at 15 ⁰ C	860 – 900 kg/m ³
2. Kinematics viscosity at 40	3.5 – 5.0, mm ² /s. Lower than petrodiesel. Depends on the degree of unsaturation. Injector efficiency
3. Flash point	120 min. Limits unreacted alcohol. Higher than petrodiesel
4. Cold Filter Plugging Point (CFPP)	Winter, -4 .max. Summer, +3 .max
5. Diesel Engine Suitability Cetane Number	51.0 min. Saturated FAMEs has higher cetane number than unsaturated.

Table 2.2 Chemical properties of biodiesel

Deposition Material 1. Carbon residue 2. Sulfated content 3. Total contamination	0.3 mass fraction max 0.2 % mass fraction max. 24 mg/kg max. Insoluble material on 8µm filter
Water content	0.5 % mass fraction max. Promotes biological growth, hydrolysis, corrosion
Inorganic Compound 1. Group I metals (total Na and K) 2. Group II metals (total Ca and Mg) 3. Phosphorus content 4. Sulfur content	5.0 mg/kg max 5.0 mg/kg max 10.0 mg/kg max. 10.0 mg/kg max. Biodiesel is naturally sulfur free
Corrosiveness 1. Copper strip corrosion 2. Acid value	rating max Class 1 (3 h at 50) 0.5 mg KOH/g max
Stability -Oxidative stability	min 6 h at 110
Methanol content	0.2 % mass fraction max
Fuel Content -Ester contents	96.5 % mass fraction, min. GC method.
Free Glycerol	0.02% mass fraction max. GC of aqueous extract. Separate Phase: attracts

	water, soaps, injector deposits. Collects in tanks
Total Glycerol -Monoglyceride content	0.8 % mass fraction max
Diglyceride content	0.2 % mass fraction max
Total glycerol	0.25 % mass fraction max.
Degree of Saturation <ol style="list-style-type: none"> 1. Iodine value 2. Linolenic acid methyl ester 3. Polyunsaturated methyl esters 	<p>140 g of iodine/100 g of FAME max</p> <p>12 % mass fraction max. Three conjugated double bonds</p> <p>1% mass fraction max. Four or more double bonds.</p>

2.2 Process

Biodiesel production is the process of synthesizing biodiesel. Biodiesel is a liquid fuel source largely compatible with petroleum based diesel fuel. Development of vegetable oil as an alternative fuel would make it possible to provide energy for agriculture from renewable sources located in the area close to where it could be used. The most common way to produce biodiesel is by transesterification, which refers to a catalyzed chemical reaction involving vegetable oil and an alcohol to yield fatty acid alkyl esters (i.e., biodiesel) and glycerol.

Triacylglycerols (triglycerides), as the main component of vegetable oil, consist of three long chain fatty acids esterified to a glycerol backbone. When triacylglycerols react with an alcohol (e.g., methanol), the three fatty acid chains are released from the glycerol skeleton and combine with the alcohol to yield fatty acid alkyl esters (e.g., fatty acid methyl esters or FAME). Glycerol is produced as a by-product. Methanol is the most commonly used alcohol because of its low cost and is the alcohol of choice in the processes developed in this. Fatty acid methyl esters show large potential applications as diesel substitutes, also known as biodiesel fuel. Biodiesel fuel as renewable energy is an alternative that can reduce energy dependence on petroleum and reduce air pollution. Several processes for the production of biodiesel fuel have been developed. Transesterification processes of the domestic waste cooking oil with methanol to produce biodiesel and glycerin under alkali-catalyst with short-chain alcohols give high yields of methyl esters in short reaction times. The ratio of fatty acid methyl esters in mixed biodiesel fuel ranges between 5 to 30 wt%. Biodiesel is compatible with petrodiesel in compression-ignition engines, and mixtures of biodiesel and petro-diesel have been used without any need for engine modification. (Jeromin *et al.*, 1987)The general process flow for biodiesel production is shown in figure 2.2.

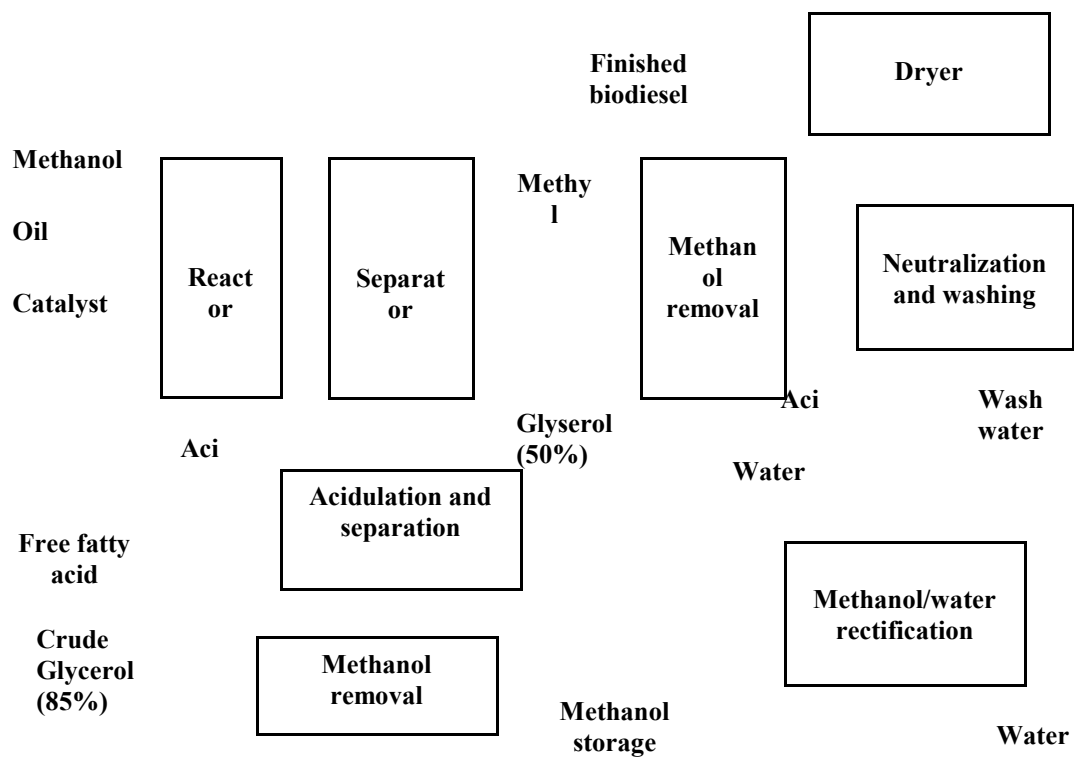


Figure 2.2: Process flow schematic for biodiesel production

1 Pretreatment

Pretreatment process is done to filter to remove dirt, charred food, and other non-oil material often found in waste cooking oil. Water is removed because its presence causes the triglycerides to hydrolyze to give salts of the fatty acids instead of undergoing transesterification to give biodiesel. This is often accomplished by heating the filtered oil to approximately 120 °C. At this point, dissolved or suspended water will boil off. When the water boils, it spatters. To prevent injury, this operation should be done in a sufficiently large container which is closed but not sealed. In the laboratory, the crude oil may be stirred with a drying agent such as magnesium sulfate to remove the water in the form of water of crystallization. The drying agent can be separated by decanting or by filtration. However, the viscosity of the oil may not allow the drying agent to mix thoroughly (Gerpen *et al.*, 2005)

2 Neutralization of free fatty acids

A sample of the cleaned oil is titrated against a standard solution of base in order to determine the concentration of free fatty acids (RCOOH) present in the waste vegetable oil sample. The quantity (in moles) of base required to neutralize the acid is then calculated (Gerpen *et al.*, 2005)

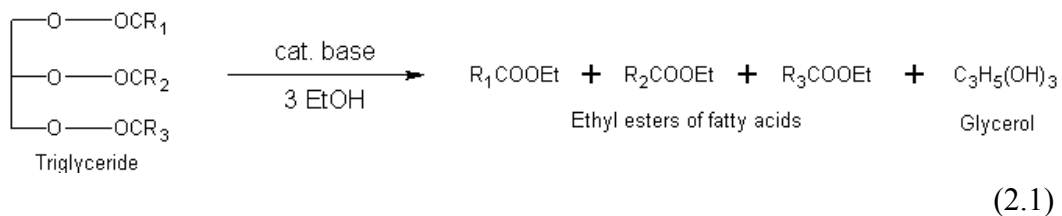
3 Transesterification Process

Biodiesel is made from the combination of a triglyceride with a monohydroxy alcohol (i.e. methanol, ethanol). Triglyceride is made from a combination of glycerol and three fatty acids. Animal and plant fats and oils are typically made of triglycerides which are esters of free fatty acids with the trihydric alcohol, glycerol. In the transesterification, the alcohol is deprotonated with a base to make it a stronger

nucleophile. As can be seen, the reaction has no other inputs than the triglyceride and the alcohol.

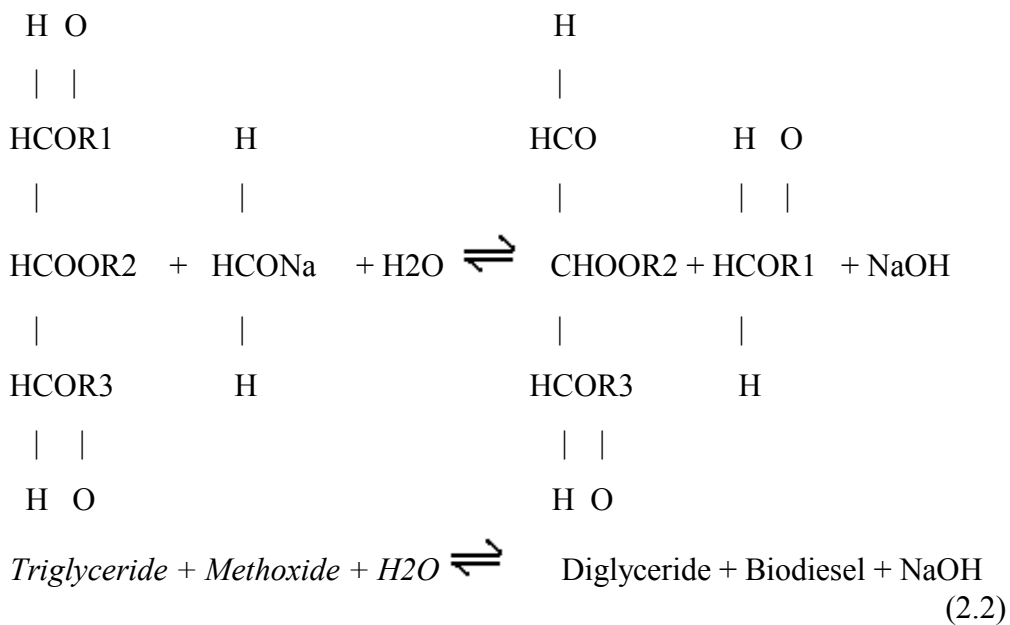
Normally, this reaction will continue either slowly or not at all. Heat, as well as an acid or base are used to help the reaction proceed more quickly approximately at temperature 60-70⁰C. It is important to note that the acid or base are not consumed by the transesterification reaction, thus they are not reactants but catalysts (Gerpen *et al.*, 2005). The mixture at the end of the reaction is allowed to settle. The lower glycerine layer is drawn off while the upper methyl ester layer is washed to remove entrained glycerine and is then processed further. The excess acid or base is recovered by distillation. The transesterification process works well when the starting oil is high quality.

Transesterification reaction scheme is as follows:



Based on equation 2.1, R1, R2, and R3 are fatty acid alkyl groups (could be different, or the same), and depend on the type of oil. The fatty acids involved determine the final properties of the biodiesel (cetane number, cold flow properties).

Steps of transesterification are shown in equation 2.2. First step triglyceride turned into diglyceride. Second step methoxide (minus Na) joins freed FA to make biodiesel. Then, Na joins OH from water (from methoxide formation) to make NaOH. Lastly, other H joins the diglyceride



2.2.4 Glycerine Washing and Methanol Recovery Process

Most biodiesel in the USA is made by reacting vegetable oils with methanol in the presence of a catalyst by a chemical process known as transesterification. The reaction process forms two products: methyl ester and glycerol. To force the reaction to completion, an excess amount of methanol is used. The two products are separated by decanting, and the unreacted methanol is divided between the two products: approximately 40% with the biodiesel, and 60% with the glycerol (available at <http://www.wintekcorp.com/biodiesel/methanol-recovery.html>). Methanol recovery from both the biodiesel and glycerol products is imperative to the economics of any

biodiesel production facility. The preferred result is to recover the methanol in a form for reuse in production to reduce the overall methanol costs. There are actually a couple steps involved: methanol removal from biodiesel (or glycerol), and recovery of the methanol.

There are several different methods of removing methanol from the biodiesel: vacuum evaporation (or stripping), distillation, and water washing. Water washing to remove the total amount of methanol from biodiesel generally is a lower equipment cost method of removal.

However, the recovery of methanol from the resulting methanol-water mix becomes very expensive. Distillation of methanol from biodiesel can be performed in a single column or rectifying column for purification and recycled. However the column is relatively complex in design, control and operation (Friesenhagen 1986; Watanabe *et al.*, 2001). Lepper and Friesenhagen (1986) recommended a pretreatment step to reduce the free fatty acid content via an esterification reaction with methanol in the presence of sulfuric acid catalyst.

Glycerine was employed as a liquid entraining agent to purify the refined oil. After such a treatment, the oil phase, having a low level of free fatty acids (less than 0.5 wt. %), was subjected to the alkali-catalyzed transesterification. Such a pretreatment step was applied to the alkali-catalyzed process using waste cooking oil in the present study.

2.3 Glycerine

Glycerine is the main by-product of making biodiesel. It is a colorless, odorless, viscous, nontoxic liquid with a very sweet taste and has literally thousands of uses. The glycerine burns well, but unless it's properly combusted at high temperature it will release acrolein, which is toxic. Glycerine can be used as a source

of lecithin (used in foods as a fat emulsifier and a vital component of all the cell membrane in the body) and for tocopherols (vitamin E). It is used in skin moisturizer, lotions, makeup and pharmaceutical.

2.4 Catalyst

The production of biodiesel, or alkyl esters, is well known. There are three basic routes to ester production from oils and fats. First, base catalyzed transesterification of the oil with alcohol. Second, direct acid catalyzed esterification of the oil with methanol. Third, conversion of oil to fatty acids and then to alkyl esters with acid catalysis. Almost all biodiesel is produced using the base catalyzed technique as it is the most economical process requiring only low temperatures (150 F) and pressure (20 psi) processing, high conversion (98%) with minimal side reactions and reaction time, direct conversion to methyl ester with no intermediate steps which producing over 98% conversion yield (provided the starting oil is low in moisture and free fatty acids) and exotic materials of construction are not necessary (Mittelbach *et al.*, 1998).

2.4.1 Alkali-catalyzed

Many studies of alkali-catalyzed transesterification on the laboratory scale have been carried out. A reaction temperature near the boiling point of the alcohol (e.g., 60⁰C for methanol) and a 6:1 molar ratio of alcohol to soybean oil were recommended. The molar ratio is normally used in industrial processes to obtain methyl ester yields higher than 98% by weight (Freedman *et al.*, 1984; Nouredini and Zhu, 1997). The kinetics of the alkali-catalyzed system was also studied by Freedman *et al.*, (1986), Nouredini and Zhu (1997) and Darnoko and Cheryan

(2000). Based on their results, approximately 90–98% oil conversion to methyl esters was observed within 90 min.

In order to speed up the reaction, Boocock and Koner (1998) suggested the addition of tetrahydrofuran (THF) as a co-solvent to minimize mass transfer resistance. After the reaction, different separation techniques to purify the biodiesel product from the other products were investigated by (Karaosmanoglu *et al.*, 1996).

In terms of the purity and yield of the biodiesel product, they concluded that the use of hot water washing at 50⁰C was the best way to obtain a high purity (99%) and yield (86%) of the biodiesel product. Apart from the bench-scale research, the alkali-catalyzed process for biodiesel production has been applied industrially.

A commercial continuous alkali-catalyzed transesterification process to produce methyl esters on the industrial scale under high pressure (90 bar) and at high temperature (240⁰C) was demonstrated (Kreutzer, 1984). However, high energy consumption, a significant increase in equipment cost and process safety issues related to, for example, high pressure and high temperature could make this process prohibitive. Krawczyk (1996) presented a flow diagram for producing biodiesel via transesterification on the industrial scale. The process mainly consisted of a transesterification reactor, a methanol/glycerol distillation column and a methyl ester distillation column. Aside from the flowsheet, no detailed description of the process was provided. A continuous deglycerolization process to produce biodiesel from refined rapeseed oil by alkali catalyzed transesterification at ambient pressure and 65–70⁰C was introduced by Connemann and Fischer (1998). They noted successful commercial applications of this process in Europe. In this process, a distillation column was also used to separate methanol from biodiesel and glycerol. The methanol was recycled to the transesterification reactor and multi-stage water washing was employed to purify the biodiesel product.

The above industrial manufacturing information on biodiesel production defined the design of the alkali-catalyzed processes in this study. One limitation to the alkali-catalyzed process is its sensitivity to the purity of reactants which the alkali-catalyzed system is very sensitive to both water and free fatty acids. The presence of water may cause ester saponification under alkaline conditions (Liu, 1994; Basu and Norris, 1996). Also, free fatty acids can react with an alkali catalyst to produce soaps and water. Saponification not only consumes the alkali catalyst, but also the resulting soaps can cause the formation of emulsions.

Emulsion formation creates difficulties in downstream recovery and purification of the biodiesel. Thus, dehydrated vegetable oil with less than 0.5 wt% free fatty acids, an anhydrous alkali catalyst and anhydrous alcohol are necessary for commercially viable alkali-catalyzed systems (Freedman *et al.*, 1984; Jeromin *et al.*, 1987).

2.4.2 Acid-catalyzed

Acid-catalyzed transesterification has been largely ignored mainly because of its relatively slower reaction rate. Freedman *et al.* (1984) investigated the transesterification of soybean oil with methanol using 1 wt% concentrated sulfuric acid. They found that at 65⁰C and a molar ratio of 30:1 methanol to oil, it took 69 h to obtain more than 90% oil conversion to methyl esters. Canakci and Gerpen (1999) studied the effects of the molar ratio of alcohol to soybean oil, the reaction temperature, the amount of catalyst, and the reaction time on the ester conversion by acid-catalyzed transesterification. Each effect was studied independently of the other effects. They found that increased ester conversions could be obtained at increased molar ratios of alcohol to oil, increased reaction temperatures, increased concentrations of sulfuric acid, and longer reaction times.

The kinetics of the acid-catalyzed transesterification with butanol was also investigated (Freedman *et al.*, 1986). They stated that the forward and reverse reactions followed pseudo first-order and second-order kinetics, respectively. This conclusion of pseudo first-order forward reaction is consistent with preliminary results in laboratory (Ripmeester, 1998; McBride, 1999). Studies of the acid-catalyzed system have been very limited in number. Despite its relatively slow reaction rate, the acid catalyzed process offers benefits with respect to its independence from free fatty acid content and the consequent absence of a pretreatment step. These advantages favour the use of the acid-catalyzed process when using waste cooking oil as the raw material.

2.5 Reactor

Reactors are vessels designed to contain chemical reactions. Reactor is known as the 'heart' of chemical plant. All form of chemical reaction occurs here. There are many types of reactors such as batch reactor, plug flow reactor (PFR), continuous stirred tank reactor (CSTR) and ultrasonic reactor. In this study, ultrasonic reactor is used for the production of biodiesel.

1 Ultrasonic reactor

Biodiesel is a renewable and biodegradable fuel. Biodiesel has several advantages. It requires no engine conversion or fuel system modification to run biodiesel on diesel engines. Biodiesel is commonly added to the petrodiesel sold at pumps today to increase the lubricity of pure Ultra-Low Sulfur Diesel (ULSD), which is advantageous since biodiesel has almost no sulfur content. Biodiesel is commonly produced in batch reactors using heat and mechanical mixing as energy input.

Using an ultrasonic reactor for biodiesel production drastically reduces the reaction time. Hence the process of transesterification can run inline rather than using the time consuming batch processing. Industrial scale ultrasonic devices allow for the industrial scale processing of several thousand barrels per day. Cavitation has also been shown to have a similar effect. The benefits using ultrasonic reactors are reduction of reaction time by up to 97.5%: 5–10 h (using conventional agitation) and 15 min (using ultrasound irradiation), reduction of static separation time by up to 98%: 5–10 h (using conventional agitation) and 10 min (using ultrasound irradiation), increase of biodiesel yield to up to 99% (available from <http://asae.frymulti.com/abstract.asp>) and reduction of catalyst requirement by up to 66%. The use of ultrasonic processing not only can provide energy for the reaction, but can achieved better mixing and more rapid separation. Figure 2.3 shows an example of ultrasonic reactor diagram.



Figure 2.3: Ultrasonic reactor diagram

Ultrasonic measurement is an established technique for many industrial applications, for example medical imaging, materials testing, flow detections, and level measurements (Straus *et al.*, 1984). The ultrasonic techniques have many

advantages over many existing method because it is non-invasive and non-destructive in systems which are concentrated and electrically non-conducting (MaClement, 1991).

Ultrasonic cavitation mixing is an effective alternative means to achieve a better mixing in commercial processing. Ultrasonic cavitation provides the necessary activation energy for the industrial transesterification process. Ultrasound allows for the continuous inline processing. In the present work, power ultrasonic reactors were applied to prepare biodiesel through sodium hydroxide-catalyzed methanolysis of soybean oil. Finally, energy consumption of mechanical stirring (MS) and power ultrasonic (PU) was estimated (Ruo Feng, 1999).

5 Waste Cooking Oil

Waste cooking oils (WCO), which contain large amounts of free fatty acids. Waste cooking oil is preferable used to produce biodiesel because environmental conservation. Moreover this method used recycling technology, low price of feedstock, unlimited feedstock, and low cost operation and as other alternative fuel source. Waste cooking oil (WCO), if no suitable treatment is available, would be discharged and cause environmental pollution. Now, WCO is collected currently by the environmental protection agency authorized by the local government in the main cities of China. It is estimated that the WCO collected in Guangzhou, the third largest city in China, is over 20 thousand tons every year (Durbin, *et al.*, 2000).

This collected material is a good commercial choice to produce biodiesel due to its low cost. Biodiesel produced by transesterification reactions can be alkali