BIODIESEL PROCESSING USING ULTRASOUND CLAMP ON TUBULAR REACTOR FOR PALM OIL

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ABSTRACT

Biodiesel is defines as monoalkyl fatty acid ester has represents a promising alternative to be substituted as an alternative fuel for the use of diesel engines. The catalyst used in this study was sodium hydroxide (NaOH) and reactant methanol to obtain chemical compound called methyl esters which is known as biodiesel. The approach of this research is to enhance the yield of Fatty Acid Methyl Esters, (FAME). By using ultrasound clamp on tubular reactor, immiscible liquids of vegetable oil and methanol is able to emulsify together in a short period of time based on ultrasound clamp as compared to the conventional stirring method which takes longer period of time to emulsify and to achieve the desired yield of FAME. The use of ultrasonic energy will eventually cause the rapid movement of the mixture molecule hence creating cavities where the liquids will breaks down and cavitation bubbles is produced. Based on the previous research by Achmad, 2011, the optimum result achieve was 98% conversion of esters by using jatropha oil at 5 minutes. The production of biodiesel using palm oil on ultrasound clamp on tubular reactor with selected angle of 15°, 25°, 35° or 45° has been undergone. The obtained results for 1 minute of conversion was 94% ester using Visawit palm vegetable oil, methanol to oil molar ratio 9:1, catalyst concentration 0.75 wt.% with the homogenization temperature at 64.5 °C. The produced biodiesel from this technique has been referred according to the ASTM D-6751 and EN14214.

ABSTRAK

Biodiesel ditakrifkan sebagai monoalkyl asid lemak ester adalah satu alternatif yang berpotensi untuk digantikan sebagai bahan api alternatif untuk penggunaan enjin diesel. Pemangkin yang digunakan pada penyelidikan ini adalah sodium hidroksida (NaOH) dan "reactant" metanol untuk mendapatkan bahan kimia yang dikenali sebagai ester methyl yang dikenali sebagai biodiesel. Pendekatan kajian ini adalah untuk meningkatkan hasil daripada "Fatty Acid Methyl Ester", (FAME) dengan menggunakan pengapit ultrasound pada tiub reaktor. Pengapit ultrasound digunakan bagi meningkatkan pencampuran antara cecair tidak boleh campur seperti minyak sayuran dan metanol untuk ditindakbalas bersama dalam tempoh masa yang singkat dibandingkan dengan kaedah konvensional iaitu dengan menggunakan pengacau mekanikal yang memerlukan emulsifikasi yang lebih lama untuk menghasilkan FAME yang diingini. Penggunaan tenaga ultrasonik akan menyebabkan pergerakan campuran cecair yang lebih tinggi disamping memecahkan rongga diantara molekul cecair. Kajian terdahulu adalah merujuk kepada penyelidikan yang dilakukan oleh Achmad, 2011 telah menghasilkan 98% ester daripada minyak jatropha dalam tempoh 5 minit. Pengeluaran biodiesel daripada minyak sawit dengan bantuan pengapit ultrasound pada susunan tiub reactor bersudut 15°, 25°, 35° atau 45° telah dilakukan. Dapatan bagi penghasilan adalah 1 minit dengan penukaran ester 94% dengan menggunakan minyak masak Visawit, metanol kepada nisbah molar minyak iatu 9:1, kepekatan pemangkin 0.75 wt.% pada suhu pencampuran sekata iatu 64.5°C. Penghasilan biodiesel tersebut melalui kaedah ini telah dirujuk kepada piawaian antarabangsa (ASTM D-6751) dan piawaian Eropah (EN14214).

CONTENTS

CHAPTER 1

INTRODUCTION

1.1   Research background

Biodiesel is of global interest presently due to the limited fossil fuel reserve and supply for the future. Thus researchers are being done to overcome the problems in processing and application locally.

From the hike of fuel prices, Malaysians has to look for an alternative fuel which is environmentally friendly and renewable. Biodiesel is defined as the mono-alkyl esters of vegetable oil or animal fats which is an environment alternative fuel for diesel blended biodiesel. The depletion and unstable price of crude fossil fuel has made biodiesel the best alternative to be substituted in certain percentage of biodiesel during its diesel blending.

In South East Asia, Malaysia is one of the country that actively produce oil for commercialization and the usage of biodiesel as fossil fuel replacement due to its palm agricultural where the oil palm planted area in 2011 reaches to 5 million hectares, an increase of 3 % against 4.85 million hectares recorded the previous year. The current approved installed capacity of biodiesel production is about 10.2 million tons in Malaysia (Phuah & Choo, 2008) but the major concern for biodiesel production is the current economic feasibility where the biodiesel production will not be favored without its tax exemption and subsidy from the government due to its high production cost compared to fossil derived diesel (Demirbras & Balat, 2006). Besides that, Malaysia may also need to compete to the latecomers like Indonesia, Thailand and Cambodia which in turn are competitive players in the market although Malaysia was a leading palm based biodiesel or palm methyl ester (PME) back in year 2006 and are now losing out to the country mentioned (Hanim, 2012). Biodiesel

is commonly produced by many countries such as Malaysia, Germany, United States of America, Italy and also in Australia, Brazil and Argentina where it is a positive response on the important of reducing the greenhouse gases which contributes to global warming.

The overall production of biodiesel mainly consists of the production and processing where in order to produce biodiesel, proper measurements in the sense of raw material such as the catalyst and the feedstock has to be taken into account and the energy consumption, consumables, transportation, taxes and labor which also affects the cost of biodiesel production (Haas *et al.*,2006). The present production of biodiesel uses refined vegetable oils which contributed nearly 80% of the overall biodiesel production cost (Lam *et al.*, 2009). It is acknowledge that the major economic factor to consider for the input costs of biodiesel production is the feedstock where 90% of the total cost of biodiesel production is the resource of the feedstock by using other alternative oil in the production (Haas & Scott, 1996).With the increase demand of biodiesel, new novel methods in biodiesel production is being researched in the context of enhancing and increasing the biodiesel production as the present method in biodiesel production is time and energy consuming which leads higher cost of production. Conventional process of biodiesel requires maintaining the reactants at a temperature of 60 °C for 1-2 hours and the yield of 97-98% (Chand, 2008).

1.2   Problem statements

The conventional stirring method which is being used in biodiesel production takes long time as the rate of chemical reaction needed is higher because during the transesterification process, the mixing of oil and alcohol is considered immiscible due to the interfacial regions between the liquids. Hence, vigorous mixing is needed so that the methyl ester could be achieved in a percentage range of 90-95%. A vigorous mixing from the conventional method helps both liquids to emulsify and to achieve the targeted yield of esters during the transesterification process.

With the current technologies in biodiesel production, the use of ultrasonic can be an approach to increase the rates of reaction in the process. This is because ultrasonic waves are energy application of sound waves which vibrated more than 20000 per second. It is reported by many researchers that the use of ultrasonic

enhance the emulsification process which leads to excellent biodiesel yield (Stavarache *et al.*, 2007).

1.3   Objectives

The objectives of this research are:

a) To evaluate the batch application of ultrasound clamp on tubular reactor in a continuous biodiesel process using vegetable oil as input.

b) To acquire an ultrasonic inclination angle of 15°, 25°, 35° or 45° for biodiesel process using ultrasound clamp on tubular reactor using vegetable oil as input

1.4   Research scope

The scope of this study is on the inclination angle of biodiesel process using vegetable oil as input which is carried out using a fabricated test rig from the research grant. This is a small test rig using ultrasound clamp on tubular reactor. The study will evaluate the output and determine the optimum parameter that can be implemented on the test rig.

1.5   Research aim

The aim of this research is to study the benefits of using ultrasound clamp on tubular reactor in biodiesel production especially in term of process time and yield.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The increase demand of global energy and limited fossil fuel reserves is the driving force to use biodiesel is being used as an alternative diesel fuel. Biodiesel is defined as the mono-alkyl esters of vegetable oils or animal fats and it is being derived from the feedstocks by a process called the transesterification process (Mittelbach & Remschnidt, 2004; Knothe *et al.*, 2005). Biodiesel has been obtained from commodity vegetable oils such as palm oil, soybean and sunflower oils as a form of feedstock to be derived into esters. Biodiesel is sustainable and it has become a prime priority for many countries to reduce the use of fossil fuel as biodiesel has the potential to reduce the level of pollutants and carcinogens (Krawczyk, 1996).

2.2 Biodiesel production from vegetable oil via transesterification process

Vegetable oil as a possible alternative to be used in diesel engines has long been recognized since the beginning of diesel engines where Rudolf Diesel runs its first diesel engine with peanut oil. Due to the high viscosity of vegetable oil, problem has been identified where high viscosity in vegetable oil will cause deposits in engine (Knothe & Dunn, 2001). Hence various methods have been used to reduce the level of viscosity in vegetable oil. The few methods being use are dilution, microemulsification, pyrolysis and transesterification to solve the problems of high fuel viscosity.

Transesterification is the most common method used to reduce oil viscosity in biodiesel industry where by this method, the chemical and the vegetable oil is converted into corresponding fatty ester (Bala, 2005). Transesterification or alcoholysis is the reaction of a fat or oil triglyceride with an alcohol to form esters and glycerol where the presence of catalyst is usually used to improve the reaction rate and its yield of the esters. In the transesterification reaction, sodium hydroxide as catalyst is used to split the oil molecules and alcohol such as methanol or ethanol is used to combine with the separated esters. From this chemical reaction, ester is formed leaving behind its byproduct glycerin. From this widely used method, the process has reduces the viscosity of the end product (Pinto et $al.$, 2005). The stoichiometric ratio states that the transesterification reaction requires three moles of alcohol and one mole of triglyceride to yield three moles of fatty acid ester and one mole of glycerol.
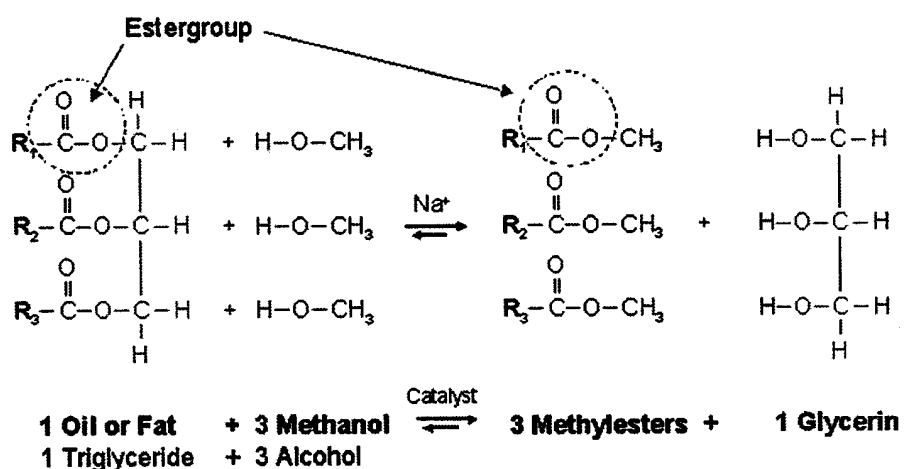
Figure 2.1: Transesterification of triglycerides with alcohol (Ayahan & Demibras, 2008).

Transesterification reaction will proceed well with the presence of homogeneous catalysts such as potassium hydroxide (KOH), sodium hydroxide (NaOH) and sulfuric acid (H_2SO_4) or with heterogeneous catalyst such as metal oxides or carbonates. In the industry, the well accepted catalyst in the production of biodiesel will be the sodium hydroxide or commonly called lye. This is because sodium hydroxide is low in cost and the reaction by using it as catalyst produces

higher yield (Demibras, 2003). Figure 2.1 shows the transesterification of triglycerides with alcohol to produce methyl esters and glycerol.

The general term of "transesterification" is an important organic reaction where esters are transformed into another through the interchange of the alkoxy moiety. Transesterification is regarded as an equilibrium reaction and with the catalyst presence, the reaction is being accelerated and can be considerably adjusted to its equilibrium. Achieving high yield of ester is increased by using alcohol in excess hence exchanging the alkoxy group of an ester compound by another alcohol.

2.2.1 Alcohol in transesterification reaction and its effect

Alcohol an organic compound which is in the hydroxyl functional group is important in the transesterification process. Types of alcohol and its effect have been studied beyond the use of methanol and ethanol which is widely used for biodiesel production (Demibras, 2003). Many choices of alcohol are possible for transesterification reaction, including methanol, ethanol, isopropanol, butanol and pentanol (Lang et al., 2001). However in some country, ethanol is in primary interest as it is less expensive than methanol in some regions of the world and the preparation of biodiesel will be prepared from bio-ethanol which is completely in bio-based (Qureshi et al., 2008). Methanol, propanol and iso-propanol are normally produced from petrochemical materials such as methane which is obtained from natural gas in the case of methanol.

Higher conversion of fatty acid methyl ester (FAME) or biodiesel can be obtain by adding extra alcohol this is because molar ratio of alcohol plays a vital role in biodiesel yield. In the transesterification reaction, it requires 3 mol of alcohol for one mole of triglycerides to 3 mols of fatty acid esters and one mol of glycerol. With the excess amount of alcohol, the conversion of fats into esters will be converted in a very short time (Leung & Guo, 2006).

The yield of the biodiesel increases with the increase of alcohol concentration, however further increase of alcohol content does not increase the yield of biodiesel but will eventually lead to the increase of cost of biodiesel production and the ratio of alcohol may vary with the type of catalyst being used and the percentage of catalyst concentration (Leung & Guo, 2006). The ratio of alcohol to oil will be determined by its molecular weight of both the alcohol and vegetable oil.

Lower molecular weights of fatty acid comprise a smaller portion of an ester product than higher molecular weight substance. Biodiesel which is made from oil rich palmitic acid will require more alcohol than biodiesel which is being produced form rich oleic (Reaney, 2005).

Table 2.1: Impact of oil type on alcohol required for transesterification in biodiesel production

Oil Type	Oil moles/kg	Methanol (kg/kg oil)
Palm oil	1.17	0.112
Canola oil*	1.13	0.108
Rapeseed oil	1.04	0.100

*Moles/ kilogram are similar to canola, soy, corn, sunflower and flax.

From the studies by (Canakci and Van Gerpen, 1999), the increasing of molar ratios of alcohol to triglycerides (TAG) ratio of 30:1 will have a conversion as high as 98.4 % but the effects decreased sharply beyond 6:1 ratios that resulted in nearly 90 % conversion. The longer chain the alcohol has will lead to higher reaction rates for acid-catalyzed reactions. However, opposite effects was observed for base-catalyst reaction. Table 2.1 shows the alcohol required for the transesterification reaction from different oil feedstock. According to (Demirbras, 2002) higher molar ratios between alcohol and oil will results in greater ester production in a shorter time where in one studies, the vegetable oil were transesterified at 6:1 to 40:1 alcohol-vegetable oil molar ratios conditions this has also been mentioned by (Achmad, 2011). Excess amount of methanol for example also accelerated the shift of reaction towards the methyl ester formation (Achmad, 2011).

2.3 Different types of oil for biodiesel production

Oils have different properties that make them suitable to use as biofuel thus it has been chosen as an alternative diesel engine fuel which has receives modest interest for several decades. The first use of vegetable oil in diesel engine is attributing to Rudolf Diesel himself where Rudolf has shown the use of peanut oil to be use in diesel engine.

2.3.1 Vegetable oil as feedstock for biodiesel production

Vegetable oil comes in various different thicknesses which are from solid vegetable lard to very light linseed oil. Most vegetable oil has promising fatty acid esters that can be produce by transesterification reaction.

The advantage of using vegetable oil includes in bypassing the processing of oils to biodiesel esters substantially reducing the cost of fossil fuel. Disadvantage may be included where several drawbacks limit the use of biodiesel, which is the requirement of the modification of engine in order to use biodiesel. Besides that, vegetable oils as biodiesel have relative low energy content (8 percent less than petroleum diesel) and potential of glycerol presence from the unreacted glycerol (Demibras, 2003).

The basic constituent of vegetable oils is triglyceride where vegetable oils comprise of 90 % to 98 % triglycerides and some amounts of mono and diglycerides. Triglyceride is a compound where the molecule glycerin a trivalent alcohol is estered with three fatty acid molecule (Srivastva & Prasad, 2000). Figure 2.2 shows a typical triglyceride molecule.

$$
\begin{array}{l}
\quad\quad\overset{\displaystyle O}{\underset{\displaystyle \|}{}} \\
H_2C\text{-}O\text{-}C\text{-}(CH_2)_{ses}CH_a \\
\quad\quad\overset{\displaystyle O}{\underset{\displaystyle \|}{}} \\
HC\text{-}O\text{-}C\text{-}(CH_2)_7CH\text{=}CH\ \{CH_2\}_7\ CH_a \\
\quad\quad\overset{\displaystyle O}{\underset{\displaystyle \|}{}} \\
H_2C\text{-}O\text{-}C\text{-}(CH_2)_7CH\text{=}CHCH_2CH\text{=}CH(CH_2)_4CH_a
\end{array}
$$

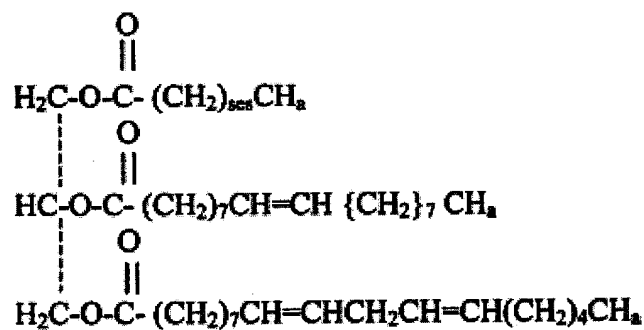Figure 2.2: Typical triglyceride molecule (Barnwal & Sharma, 2000).

Vegetable oils contain free fatty acid, FFA (generally 1 to 5 %) phospholipids, phosphatides, carotenes, tocopherols, sulphur compounds and traces of water. From the combination of number of fatty acids constitutes a vegetable oil molecule. Table 2.2 shows the structure and chemical formula for various fatty acids found in most common biodiesel production.

Table 2.2: Chemical structure of common fatty acids (Kumar *et al.*, 2002)

Fatty Acids	Systematic Name	Structure	Formula
Lauric	Dodecanoic	12:0	$C_{12}H_{24}OH$
Myristic	Tetradecanoic	14:0	$C_{14}H_{28}OH$
Palmitic	Hexadecanoic	16:0	$C_{16}H_{32}OH$
Stearic	Octadecanoic	18:0	$C_{18}H_{36}OH$
Arachidic	Eicosanoic	20:0	$C_{20}H_{40}OH$
Behenic	Docosanoic	22:0	$C_{22}H_{44}OH$
Lignoceric	Tetracosanoic	24:0	$C_{24}H_{48}OH$
Oleic	cis-9-Octadecenoic	18:0	$C_{18}H_{34}OH$
Linoleic	cis-9,cis-12- Octadecadienoic	18:0	$C_{18}H_{32}OH$
Linolenic	cis-9,cis-12,cis-15- Octadecatrienoic	18:0	$C_{18}H_{30}OH$
Erucic	cis-13-Docosenoir	22:0	$C_{22}H_{42}OH$

Besides that, fatty acid varies in terms of the carbon chain length and number of unsaturated bonds where it contains chains of a maximum number of hydrogen atoms per atom carbon. Fatty acid which has no bonds are termed "saturated" while with double bonds are often called "unsaturated". An example for saturated fatty acid is stearic acid while unsaturated fatty acid is linoleic acid. Natural vegetable oils are obtained in the crude form through solvent extraction or mechanically pressing where in this stage the crude vegetable oil consists of impurities such as free fatty acids, sterols and water. The presence of high free fatty acids and water often causes significant effect on the transesterification reaction hence leading to possible soap formation.

Natural vegetable oil and animal fats usually obtained in crude form through solvent extraction or mechanical pressing where in this stage, the crude fats contains impurities such as the free fatty acids, sterols and water. Free fatty acids and water which presence in the fats will eventually interfere the transesterification reaction. The interference will leads to the separation of FAME and glycerol and soap formation during the washing process which is also known to be the purification process.

Table 2.3: Typical fatty acid composition (%) for different common oil source (Alok, 2008)

Fatty Acid composition (%)	Soybean oil	Cottonseed oil	Palm oil	Lard oil	Tallow oil	Coconut oil
Lauric (C12:0)	0.1	0.1	0.1	0.1	0.1	46.5
Myristic (C14:0)	0.1	0.7	1.0	1.4	0.8	19.2
Palmitic (C16:0)	0.2	20.1	42.8	23.6	23.3	9.8
Stearic (C18:1)	3.7	2.6	4.5	14.2	19.4	3.0
Oleic (C18:2)	22.8	19.2	40.5	44.2	42.4	6.9
Linoleic (C18:2)	53.7	55.2	10.1	10.7	10.7	2.2
Linolenic (C18:3)	8.6	0.6	0.2	0.4	0.4	0.0

2.3.2 Waste cooking oil as feedstock for biodiesel production

Waste cooking oil which has been used for cooking can be utilized as a feedstock for biodiesel production. Waste cooking oil usually becomes thicker due to the hydrogenation where the oil may contain vegetable or animal fats from the foodstuffs which have been used for cooking.

Waste cooking oil may contain high free fatty acid, FFA and solid particles or other contaminants that would block fuel filters or damage engine fuel system. Due to this problem proper filtration and neutralization of waste cooking may be needed. The use of waste cooking oil has its advantage of being a readily available product and cost less compared to other oils (Srivastva & Prasad, 2000). Besides that, waste oils have traditionally been used as a component of animal feeds but falling out due to the concern of contamination.

2.4 Biodiesel

Biodiesel is a term which has been widely used around the world to denote alkyl esters production through the transesterification reaction of vegetable oils with alcohol. Biodiesel is a definition which is used by the American Society for Testing Materials (ASTM) with its specification D 6751 and European Specification EN 14214 (ASTM, 2008).
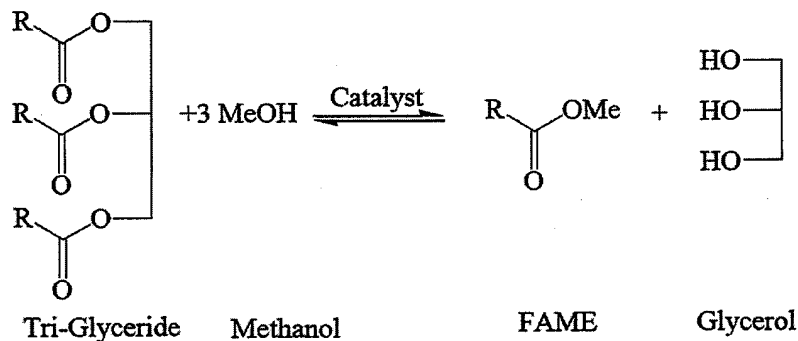
Figure 2.3: Chemical reaction of biodiesel (Freedman *et al.*, 1986).

Based on Figure 2.3, the reaction is associated with the production of biodiesel from transesterification where this reaction converts one form of ester to another. Vegetable oils are triglyceride esters (esters of 3 molecules of fatty acids with one molecule of glycerol). The oil is then reacted with monohydroxy alcohols such as methanol and ethanol hence producing corresponding esters leaving glycerol as a byproduct.
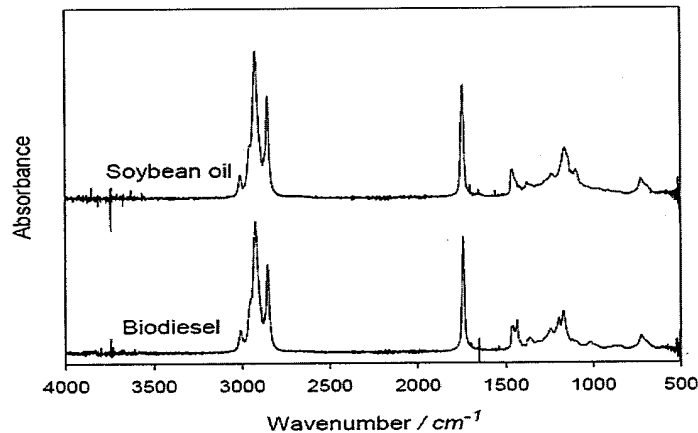
Figure 2.4: FTIR spectra of soybean oil and biodiesel (Pedroso *et al.*, 2005).

Based on Figure 2.4, the FTIR spectra of biodiesel however are expected to be very similar to oil since the compound has almost the same chemical groups. However some slight differences can be detected such as the band carbonyl band position in FTIR is sensitive to the substituent effects and to the structure of the molecule itself (Pasto *et al.*, 1992).

Biodiesel is renewable that usually derived from vegetable oil, animal fats or waste oil. The simplicity of biodiesel production can disguise the important of

maintaining high quality standards for any fuel supplied to modern diesel engines. When methanol is used as reactant, it will be a mixture of fatty acid methyl esters (FAME) whereas if ethanol is used as a reactant, the mixture will be fatty acid ethyl esters (FAEE). However in industry, methanol is selected as a reactant and widely used in biodiesel production due to its low cost and availability. Other alcohol aside from methanol and ethanol are also of interest for biodiesel production because fatty acid alkyl esters (FAAE) produce form higher alcohol may have different fuel properties in comparison to methyl or ethyl esters (Knothe *et al.*, 2005).
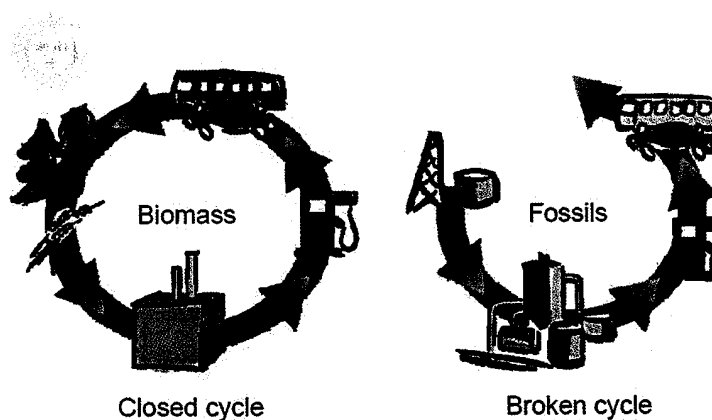
Figure 2.5: Carbon cycle for utilizing fuels from biomass - and fossils based production. (Retrieve: http://www.baff.info/English/ad_15_myths.cfm, 2013)

Biodiesel is miscible with petro-diesel in any proportion and possesses several technical advantages over ultra low sulphur diesel fuel (ULSD, < 15 ppm S), such as inherent low lubricity, low toxicity, derivation from renewable and domestic feedstock, superior flash point and biodegrability. Besides that, biodiesel has similar properties like diesel fuel and the advantage of the biodiesel consists of the following:

Reduction of carbon dioxide emissions: Carbon dioxide is a greenhouse gas and a major contributor of global warming. Combustion of pure biodiesel B100, when use in engines, produces less carbon dioxide emissions (Sheehan *et al.*, 1998).

1. High oxygen content: Oxygen content in biodiesel fuel facilitates its complete combustion. Biodiesel contains 10–11 % more oxygen by wt. as compared to diesel.

2. Reduction of carbon monoxide emissions: Carbon monoxide is also an important greenhouse gas and causes serious health hazards by blocking oxygen intake in humans and animals. B100 reduces carbon monoxide emissions by 35 % (Sheehan *et al.*, 1998).

3. Reduction of particulate matter emissions: Particulate matter is a mixture of complex organic and inorganic compounds, such as carbon residues, unburnt fuel, lubricating oil components, metal ash, etc., some of which are carcinogenic in nature. B100 reduces particulate matter emission by 32 % (Sheehan *et al.*, 1998).

4. Reduction of sulfur oxides emissions: sulphur dioxide causes respiratory tract irritation. Biodiesel fuel is sulphur–free, as long as sulphuric acid is not used in the biodiesel production process. B100 reduces net sulphur oxide emissions by 8 % (Sheehan *et al.*, 1998).

5. Higher flash point: Flash point is the temperature at which a fuel becomes flammable. Biodiesel has higher flash point ($\geq$ 120 °C) than diesel fuel ($\geq$ 55 °C), which makes it less hazardous during fuel transport and storage.

6. Toxicity test shows that biodiesel is considerably less toxic than diesel fuel (Hawa, 1997).

7. Biodiesel provides greater lubricity than petroleum diesel thus reducing engine wear. Biodiesel used as a lubricity enhancer for low sulphur petroleum diesel formulations.

Table 2.4: Chemical structures of common FAME (Alok, 2008)

No	Components	Chemical Formula	Molecular Weight (kg/mol)
1	Methyl Myristate	$C_{14}H_{30}O_2$	242.1
2	Methyl Pentadecanoate	$C_{16}H_{32}O_2$	256.42
3	Methyl Palmitate	$C_{17}H_{34}O_2$	270.457
4	Methyl Stearate	$C_{19}H_{38}O_2$	298.511
5	Methyl Oleate	$C_{19}H_{36}O_2$	296.495
6	Methyl Linoleate	$C_{19}H_{34}O_2$	294.479
7	Methyl Linolenate	$C_{19}H_{24}O_2$	292.463

Table 2.5: Detailed requirement of biodiesel according to ASTM D6751 (ASTM, 2008)

Property	Unit	Grade S15 Limits	Grade S500 Limits	Test method
Kinematic viscocity at 40°C	mm^{2}s^{-1}	1.9-6.0	1.9-6.0	ASTM D445
Flash point(closed up)	°C	130.0 min	130.0 min	ASTM D93
Sulphur content	% mass	0.0015 max	0.05 max	ASTM D5453
Carbon residu	% mass	0.050 max	0.050 max	ASTM D4530
Acid number	mg KOH g^{-1}	0.8 max	0.8 max	ASTM D664
Cloud point	°C	Report*	Report*	ASTM D2500
Cetane number	-	47 min	47 min	ASTM D613
Sulphated ash content	% mass	0.020 max	0.020 max	ASTM D874
Water and sediment	% volume	0.050 max	0.050 max	ASTM D1796
Copper strip corrosion	rating	No. 3 max	No.3 max	ASTM D130
Free glycerol	% mass	0.020	0.020	ASTM D6584
Total glycerol	% mass	0.240	0.240	ASTM D6584
Phosphorus	% mass	0.001 max	0.001 max	ASTM D4951
Distillation temperature	°C	360 max	360 max	ASTM D1160

Table 2.6: Detailed requirement of biodiesel according to European Standard
EN14214 (European Standard, 2003)

Property	Unit	Limits		Test methods
		Minimum	Maximum	
Ester Content	% (mm^{-1})	96.5		EN 14103
Density at 15°C	kg m^{-1}	860	900	EN ISO 3675
Viscosity at 40°C	mm^{2}s^{-1}	3.5	5	EN ISO 3104
Flash point	°C	120	-	ISO 3679
Acid value	mg KOH g^{-1}		0.5	EN 14104
Cetane index		510	-	EN ISO 5165
Sulphur content	mg kg^{-1}	-	10	-
Sulphated ash content	%(mm^{-1})	-	0.02	ISO 3987
Water content	mg kg^{-1}	-	500	EN ISO 12937
Total contamination	mg kg^{-1}	-	24	EN 12662
Copper strip corrosion (3 hr at 50°C)	rating	1	-	EN ISO 2160
Oxidation stability 110°C	hr	6.0	-	EN 14112
Iodine value	-	-	120	EN 14111
Linolenic acid methyl ester	% (mm^{-1})	-	12	EN 14103
Methanol content	% (mm^{-1})	-	0.2	EN 14110
Monoglyceride content	% (mm^{-1})	-	0.8	EN 14105
Diglyceride content	% (mm^{-1})	-	0.2	EN 14105
Triglyceride content	% (mm^{-1})	-	0.2	EN 14105
Free glycerol	% (mm^{-1})	-	0.02	EN 14105
Total glycerol	% (mm^{-1})	-	0.025	EN 14105
Alkaline content (Na+K)	mg kg^{-1}	-	5	EN 14108
Phosporous content	mg kg-1	-	10	EN 14107

2.5   Ultrasound assisted process in biodiesel production

The application of ultrasonic waves is known to produce unique chemical and physical effects on immiscible mixtures such as oil and alcohol. Ultrasonic waves are energy which vibrates more than 20,000 per second. The term ultrasonic can be defined as sound waves beyond human hearing limit. This is because human is unable to hear sound waves with more high pitch sound waves of an average of 10-

12 kHz. Ultrasonic or ultrasound signals are in the order of 20 kHz to 100 kHz which is above the human hearing.

Ultrasound is generated by a transducer made from a piezoelectric material (Ushakov, 2005). Thus the piezoelectric material produces characteristic mechanical vibration of ultrasonic frequency in response to an alternating current. Beyond the audible range, that is at frequency higher than 20 kHz, the ultrasonic waves produces pressure differences in the solution medium that enhances chemical and physical process (Mason and Lorimer, 2003).
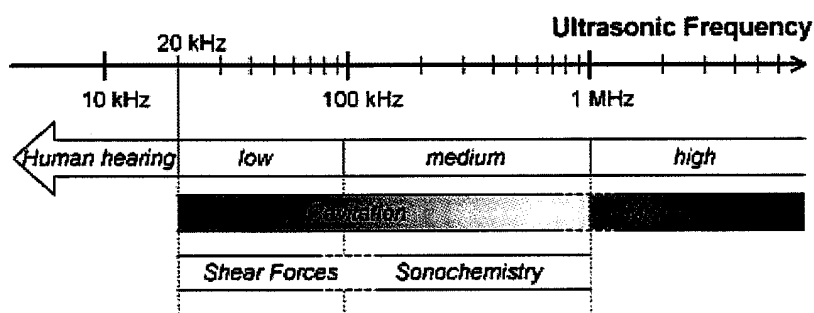
Figure 2.6: The frequency range of ultrasonic in cavitation principles (Retrieve: http://www.ultrawaves.co.uk/technology.htm, 2011).

Sound frequencies are recorded in units of Hertz where 1 Hertz is equals to 1 cycle per second. The hearing threshold is not the same for other animal species thus dogs respond to ultrasonic whistles and bats navigate by using frequencies above 50 kHz. The use of ultrasonic in chemical field is called sonochemistry and it is normally use with frequency between 20 and 40 kHz because this range employed in common laboratory equipments. Acoustic cavitation in liquids can be well generated above 20 kHz of frequency but high frequency ultrasound from around 5 MHz and above will not produce cavitation as in this frequency range it is use in medical imaging. Ultrasound produces sonochemical and mechanoacoustic effects which affects the chemical and physical structure of the liquid ((Bussemaker and Zhang, 2013).

From the studies, ultrasonic produces three effects where the first effect will cause the rapid movement of fluids which is cause by variation of sonic pressure hence causes the solvent compression and refraction cycles (Mason, 1999). The second important effect is cavitation of liquids. Cavitation happens when large

negative pressure gradient is applied to the liquid where eventually the liquid breaks down and formation of cavitation takes place causing cavitation bubbles to be produce from the effect. With the high intensity of ultrasonic frequency, small cavities grow rapidly through inertial effects and finally the bubbles grow and collapse violently. Cavitation is considered as a major factor which influences the reaction speed. The final effect of ultrasonic is acoustic streaming mixing.

In an emerging technology, ultrasonic has the potential as an alternative method in biodiesel production as the use of ultrasound technology reduces the chemical reaction time and its loading and most of all it is considered as a green technique (Bussemaker and Zhang, 2013).
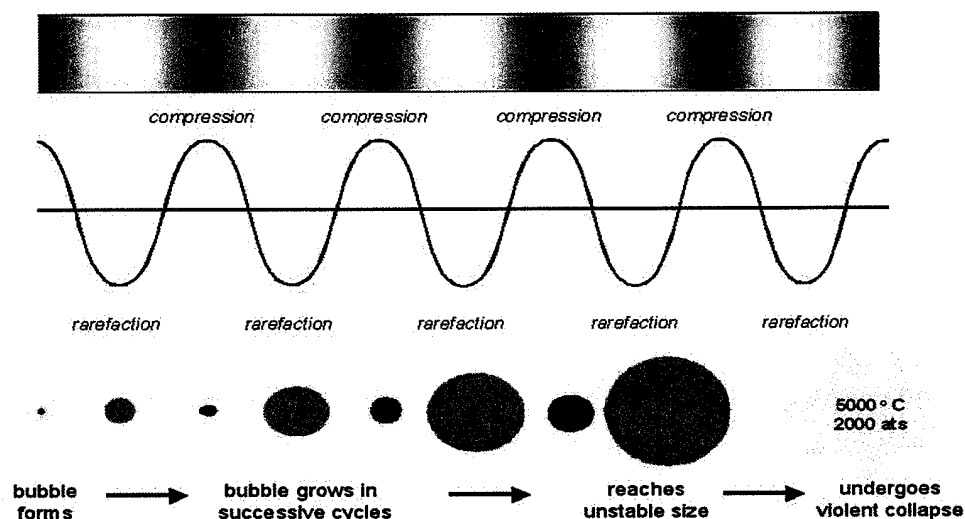

Figure 2.7: Generation of an acoustic bubble due to cavitation effect (Retrieve: http://www.sonochemistry.info/introduction.htm, 2007).

Ultrasonic assisted process in transesterification is important as it helps to increase the yield of biodiesel production. Oil and methanol are not miscible completely in biodiesel processing and with the assistance of ultrasonic, the effectiveness method helps to achieve a better mixing and enhancing liquid- liquid mass transfer (Ji et al., 2006). Besides that, ultrasonic assisted transesterification does not only shorten the reaction time but also minimized the molar ratio of alcohol and oil hence reduces energy consumption compared to conventional mechanical stirring method. According to (Wu et al., 2007) on its study which regards to the disperse of droplet size of ultrasonically formed biodiesel mixtures, the author

measures the size of the droplet by using light scattering techniques for both rotary and ultrasonically mix biodiesel reactants. From the research, the result shows that the ultrasonic produces smaller droplets than of standard mixing.
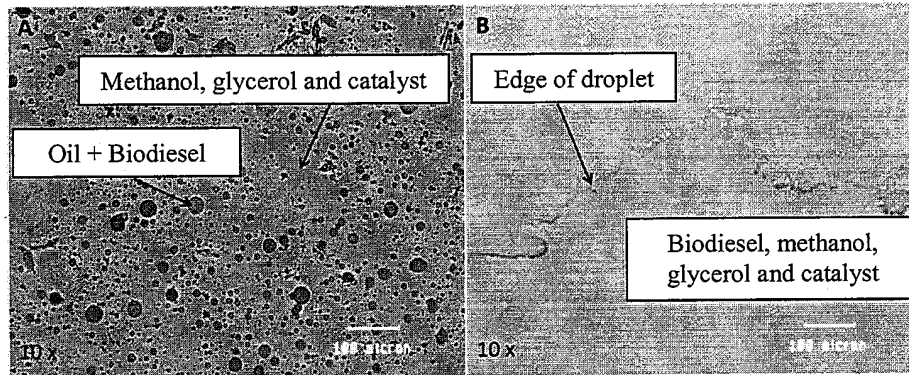

Figure 2.8: (A) View of reaction mixture under microscope after sonication for 15 sec. (B) View of reaction mixture after transesterification by the commercial method (Priyanka *et al.,* 2010).

Based on Figure 2.8, the use of ultrasonic enhance the emulsification of oil and alcohol as compared to commercial stirring method which undergone transesterification process. This can be observed through the formation of bubbles generated during the ultrasonication for 15 seconds as compared to the commercial method. As studied by (Singh *et al.,* 2007) utilized ultrasonic for base catalyzed transesterification uses soybean oil, methanol and potassium hydroxide, KOH as catalyst in a power adjusted ultrasonic reactor. The author claimed that the use of ultrasonic has improved the yields of the biodiesel as compared to conventional method. The ultrasonic frequency selected by the author is 28 kHz with power varies from 79 to 131 kW. From the studies, the total reaction time for 98% yielding of methyl esters was reported to be at 5 minutes (Singh, *et al.,* 2007). Ultrasonic technology in biodiesel process has indeed proven to be an efficient mixing tool where it provides sufficient energy to initiate the reaction hence shortening the reaction time during the transesterification process and the reduction of molar ratio to alcohol to oil (Singh *et al.,* 2007; Vyas *et al.,* 2010). Ultrasonic irradiation of liquids causes two immiscible liquids to emulsify where it is caused by the generated shockwaves which disrupts and interferes the phase boundary.
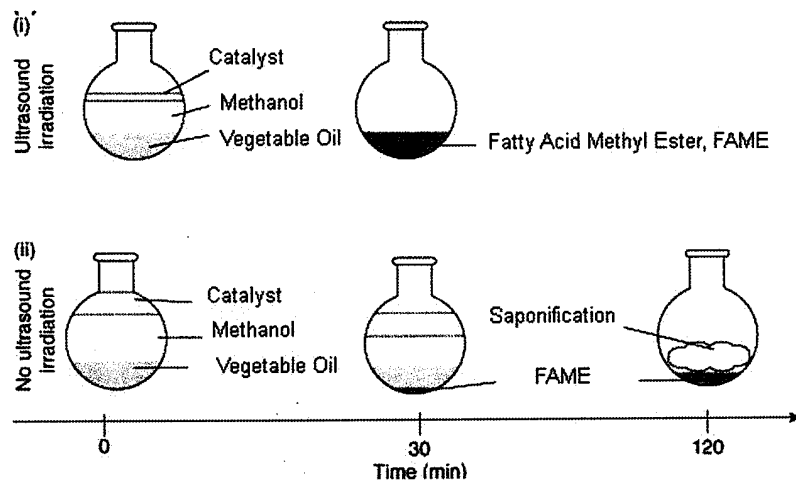
Figure 2.9: Biofuel production and process monitoring (Ekaterina *et al.*, 2009).

Based on Figure 2.9, it is observed that ultrasound irradiation enhances the emulsification process where less time is taken during the transesterification reaction as compared to no ultrasound irradiation which takes longer time to emulsify both immiscible liquids hence saponification happens during the process could be due to unreacted transesterification process. Biodiesel production through ultrasonic method involves in few steps where the steps includes mixing of vegetable oil with alcohol (methanol or ethanol) and catalyst (sodium hydroxide or potassium hydroxide), heating of the mixture, sonication of the mixture and the separation process of fatty acid methyl ester, FAME and glycerol. Besides that, few factors has been identified in the production of biodiesel with the assistance of ultrasonic where the effect of alcohol, types of catalyst used, ultrasonic power in biodiesel processing and ultrasonic frequency affect the production of biodiesel.

Lower ultrasonic frequencies such as 20-40 kHz increase the mass transfer (Khanal *et al.,* 2007). An increase in ultrasonic power will leads to the ultrasonic effects on liquefaction (Sasmal *et al.,* 2012) thus dissolution and hydrolysis yields (Yunus *et al,* 2010). According to (Achmad, 2011) the use of ultrasonic helps reduce the methanol usage hence making ultrasonic a technique valuable in industrial scale production.

2.5.1 Ultrasonic cavitations

Generally, ultrasound frequency in liquid medium produces two primary effects which are the cavitations and heating (Yachmenev *et al.,* 2009). Cavitation is the formation and the immediate implosion of cavities in liquid where this phenomenon generates large numbers of micro bubbles in a liquid when negative pressure is applied. The propagation of sound waves through the liquid medium will generate compression and rarefaction in the liquid (Mason, 1999). Figure 2.10 shows the formation of cavitation bubbles as an effect from the use of ultrasound method. Cavitation occurs at low frequency (16 to 100 kHz) in which most of the ultrasound energy is dissipated into the medium whereas heating occurs at high frequency (>100 kHz) and in this case, small amounts of energy is dissipated. High pressure, compression and low pressure rarefaction are produced by the pressure waves in the liquid medium. The cavitation bubbles contract and expand with the compression and rarefaction in order to bring more molecules into the bubble process (Peregrine, 1994).

The collapse of the cavitation bubble produces localized temperatures of ~5500 °C and pressure of 500 atm which gets dissipated into the medium and is restricted to a particular place near the surface of substrate in the medium. Higher acceleration results in higher fraction of the energy transformed to cavitation. Shearing forces are created in the liquid surrounding the cavitation bubble resulting in a strong mechanical effect. These effect significantly increase the mass and heat transfer to the surface of the substrate while activating the catalyst transport to the substrate (Yachmenev *et al.,* 2009)
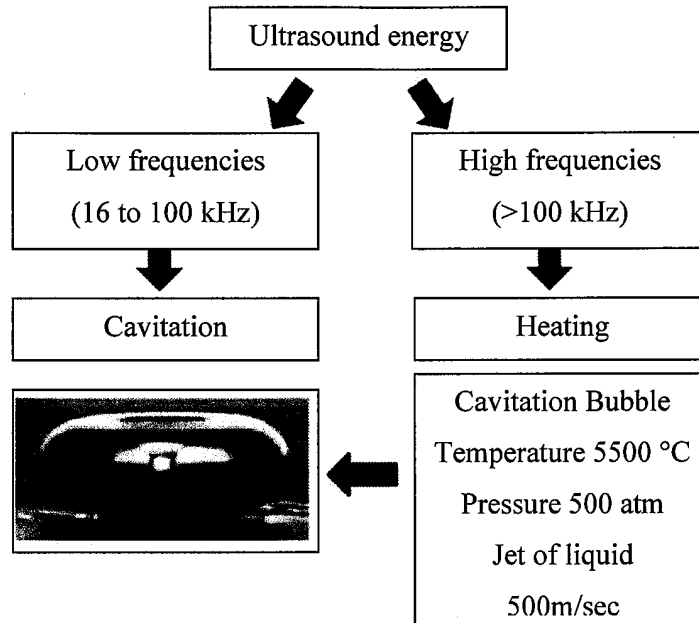
Figure 2.10: Cavitation bubbles formed as an effect of ultrasound (Yachmenev *et al.*, 2009)

In the lower frequency range (20 kHz to 100 kHz) big cavitation bubbles are generated which excite extremely high shear forces and strong effects. In the middle frequency range (100 kHz to 1 MHz) the bubbles are smaller but the cavitation is more effective, generating radical sono-chemical reactions in the water. Sonicating such a liquid with a frequency of over 1 MHz, the liquid begins to flow on molecular level.

The cavitation bubble has a variety of effects within the liquid medium depending upon the type of system in which it is generated. These systems can be broadly divided into homogeneous liquid, heterogeneous solid/liquid and heterogeneous liquid/liquid. Within chemical systems these three groupings represent most processing situations.

The effect of cavitation results in higher heterogeneity systems (solid- liquid) compared to the initial homogeneous system. The characteristic frequency of transducers limits many research applications using ultrasonics (Bussemaker and Zhang, 2013). Besides that, according to (Gierer, 1990), the quantity, lifetime and implosion pressure of cavitation bubbles produced are influenced mainly by the power of ultrasound. The power generator varies the characteristic of the transducer

where power is directly proportional to the amplitude of the ultrasonic wave thus influencing the occurrence of cavitation Gogate *et al.,* 2011).

When sound waves propagate through a liquid medium, they generate compression and rarefaction regions in the liquid. The intermolecular distances between the liquid molecules also expand and contract along these waves. At very low pressure in the rarefaction region, the intermolecular spaces exceed the critical molecular distance and the liquid tears apart to form void spaces or micro bubbles. These micro bubbles oscillate with the wave motion and grow in size by taking in vapor from the surrounding liquid medium and by aggregating with other micro bubbles (Mason, 1999). The growth and subsequent collapse of cavitation bubbles is shown in Figure 2.11.The bubble collapse produces high shear forces which mix the liquid vigorously and fracture nearby particles.

Propagation of sound waves in alternate compression and rarefaction pattern

Cavitation bubble forms in negative cycle

Growth of bubble in negative cycle

Unstable size and high negative pressure inside the bubble cause violent collapse and result in localized high temperature and shear forces
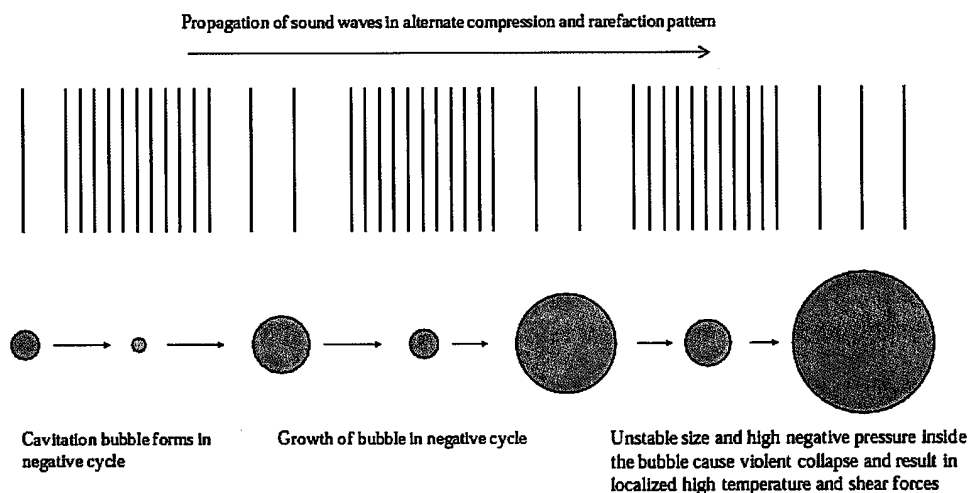
Figure 2.11: Growth and collapse of cavitation bubble in a liquid medium when ultrasonic waves are applied (Kropf, 2008).

In the bulk liquid, immediately surrounding the bubble where the rapid collapse of the bubble generates shear forces which can produce mechanical effects and in the bubble itself where any species introduced during its formation will be subjected to extreme conditions of temperature and pressure on collapse leading to chemical effects. Unlike cavitation of the bubble, the bubble collapse in the bulk liquid, collapse of a cavitation bubble on or near to a surface is unsymmetrical because the surface provides resistance to liquid flow from that side. The result is an

inrush of liquid predominantly from the side of the bubble's remote from the surface resulting in a powerful liquid jet being formed, targeted at the surface. The effect is equivalent to high pressure jetting and is the reason that ultrasound is used for cleaning. This effect can also activate solid catalysts and increase mass and heat transfer to the surface by disruption of the interfacial boundary layers.

The disruptions in the liquid layer must be present for cavitations to occur through acoustic stress. The influence such as the undissolved gases, suspended gas bubbles, organic double layers and particulate matter substantially reduce the tensile strength of the liquid to a point where acoustic stress can cause bubble formation (Crum, 1979; Yount, 1982).

High and low pressure gradients result from acoustic stress in solution. When an undissolved gas pocket or a microbubble experiences a low pressure gradient, it results to the expansion of the bubbles. Figure 2.12 and Figure 2.13 shows that the weak spots in a liquid layer that generate nucleation of bubbles from rifts in the liquid that produce voids from undissolved gases or microbubbles. The micro bubble formation is a result of pressure wave oscillations on a dust mote in solution. There is a net mass transfer of volatile material from the region of high pressure (bulk solution) into the region of low pressure (bubble). During the compression stage of the acoustic cycle there is a net mass transfer of volatile materials from inside the bubble to the bulk solution. The cavity is larger during the expansion phase than the compression phase. The larger cavity has a greater surface area and can therefore facilitate a larger rate of mass transfer of the gases. The net result is more vapours and gas enters the cavity or microbubble than leaves it. This results in bubble growth (Sweet, 1998).
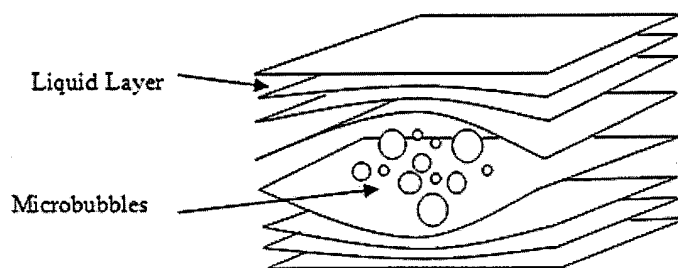

Figure 2.12: Weak spots in a liquid layer that generate nucleation of bubbles from rifts in the liquid that produce voids from undissolved gases or microbubbles (Sweet, 1998).
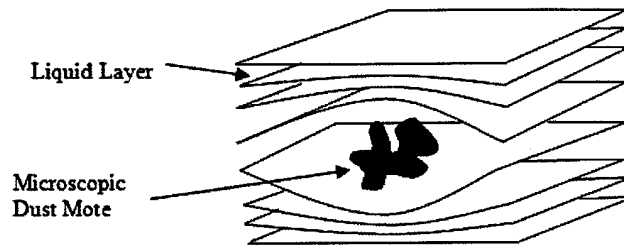
Figure 2.13: Weak spots in a liquid layer that generate nucleation sites due to the presence of dust motes (Sweet, 1998).
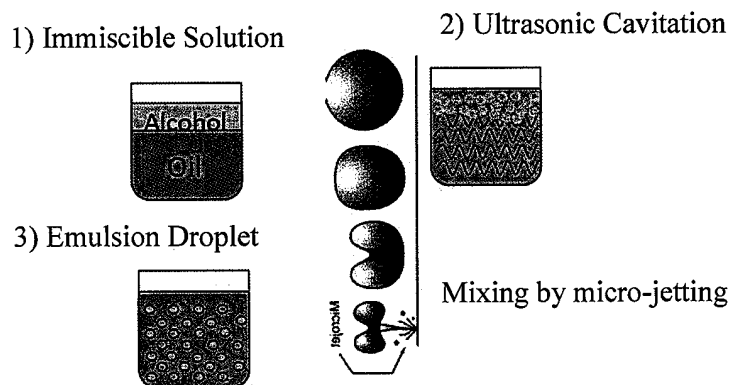

Figure 2.14: Mixing achievement in ultrasonic emulsification in biodiesel production (Kropf, 2011).

Based on Figure 2.14, the alcohol and oil are immiscible liquids and the use of ultrasonic causes cavitation of the liquids where large numbers of micro bubbles generated in a liquid due to the presence of the negative pressure being applied. From the observation of (Achmad, 2011), under the influence of ultrasonic, the reaction is fast enough which does not leads to the accumulation of glycerol as compared to the conventional transesterification based on stirring and heating in which this technique were known to react slowly.

2.6 Factors affecting biodiesel production

Although biodiesel is a renewable fuel for diesel engines, proper consideration has to be taken into account on factors which will affect the quality of biodiesel produced during the transesterification reaction of vegetable oils or other waste oils. The transesterification is affected by the molar ratio of oil to alcohol, presence of water,

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