CHAPTER 1

Introduction

1.1 Rationale/Problem Statement

According to energy crisis and global warming expanding over the world are crucial factors which have prompted many countries to concentrate on development of substituted energy, especially, biodiesel. The main advantages of using biodiesel are renewability, better quality exhaust gas emissions, biodegradability and all the organic carbon present is photosynthetic in origin, it does not contribute to a rise in the level of carbon dioxide in the atmosphere and consequently to the greenhouse effect (Srivastava and Prasad, 2000). The biodiesel can be substituted petroleum diesel in every concentration and produced by various sources of oil and fat of plants and animals which mainly contain triglyceride. So nowadays each country uses his potential sources for industrial scale of biodiesel manufacturing such as rape seed oil in United State, etc.

In Thailand, crude palm oil (CPO) is the most potential source for biodiesel production because there are huge oil palm plantations in southern Thailand and it has the highest oil yield (5,000 kg/ha/a) (Addison, 2009 and Vanichseni et al., 2002) compared to others oil plants. The industrial scale of biodiesel production should be processed by utilizing continuous streams of alkali catalyzed transesterification to convert most of glyceride to ester or biodiesel and thus it would be obtained a good yield when the raw material is refined oil or has low free fatty acid (FFA) content. If the oil contains higher amounts of FFA (> 1 wt%), it will form soap by reacting with the base catalyst and the ester conversion is decreased due to this soap formation which can also prevent the glycerine phase separation of the biodiesel, if ethanol is used as a reactant (Hanh et al., 2009b). Therefore, raw material pretreatment becomes an important role, especially FFA reduction is described as the de-acid step. Unfortunately, commercial CPO has high phosphorus and FFA (~5 wt%) content and if it is used as the raw material for alkali catalyzed transesterification, it does need to be pretreated by degumming and de-acidification to

reduce respectively the phosphorus and FFA content. Due to phosphorus content in CPO is higher than the limitation of national biodiesel standards; therefore it must be reduced to meet the standards. In order to maximize the final yield of ester from transesterification, the FFA content of the raw material feedstock should be lowered than 0.5 wt% (Freedman et al., 1984 and Kusdiana and Saka, 2003). There are three chemical methods to reduce FFA content; the first method available is saponification or neutralization of the FFA with an alkali solution (sodium or potassium hydroxide) which also called FFA stripping, the second is glycerolysis and another one is esterification by using an acid catalyst. The main product of the first method is soap which is troublesome in further processing since it is difficult to separate the soap and this can result in a loss of biodiesel yield. The second method transforms FFA to glycerides and the latter method will yield fatty acid alkyl ester as the main product and water as a byproduct. Overall, this method will increase the ester yield and obviates the need to separate the pretreatment product before feeding it into the subsequent transesterification step. Clearly, the esterification is considered as an optimum method for reducing the FFA content of this kind of feedstock before conducting base-catalyzed transesterification particularly since acid degumming can be carried out simultaneously.

Ultrasound can also be efficiently utilized to optimize the conversion of triglyceride to biodiesel. For instance, the influence of low-frequency ultrasound (28 and 40 kHz) on biodiesel production from triglyceride, free fatty acids and fatty acid cut (C8–C10) was tested using either methanol or ethanol in the presence of different catalysts, such as sodium hydroxide (NaOH), potassium hydroxide (KOH) and sulfuric acid (H_2SO_4) and compared to a conventional transesterification process. These experiments demonstrated that the use of ultrasound significantly reduced the amount of required catalyst, whilst eliminating saponification and dramatically shortening the reaction time from 2 h to 30 minutes. Moreover, the molar ratio of methanol to fatty acids was found to be capable of reduction by as much as three times, which resulted in high biodiesel yields of 95–97 wt%, regardless of the initial material used. In addition to accelerating biodiesel production, ultrasound can be used to monitor the biodiesel production process (Rokhina et al., 2009).

Nowadays, typical processing of biodiesel uses oil and alcohol as main

reactants. Normal short chain alcohol used is methanol because it promotes the highest activity and it is low cost product. On the other hand, the disadvantages of methanol are its lower solubility with oil and toxicity as well as the fact that it is not produced locally in Thailand so has to be imported. This study focused on substituting ethanol for methanol because of its nontoxic nature, good solubility and local availability. Not only would the wider use of ethanol reduce the need to import methanol, but ethyl ester is also a completely natural and recyclable source of energy.

This research aimed to determine the optimal conditions for batch and continuous acid catalyzed esterification of CPO with ethanol assisted by high intensity ultrasonic irradiation including acid catalyzed esterification with a continuous stirred-tank reactor. These pretreatments encompassed both the degumming and acid catalysis steps in the esterification process reducing the phosphorus and FFA content, respectively.

1.2 Research Background

1.2.1 Oil Palm (*Elaeis guineensis*)

Palm oil is derived from the fleshy part or the mesocarp of the palm fruit species *Elaeis guineensis*. However in Thailand, *Tenera* (hybrid of *Dura* x *Psifera*) palm fruit is widely cultivated due to commercial and processing viability as harvesting becomes easier since the palm trees are relatively shorter, producing good fruit bunch and higher fruit oil content (Kulavanich et al., 1988). Figure 1.1 shows the cross-section of palm oil fruits indicating the mesocarp and kernel of the fruit.

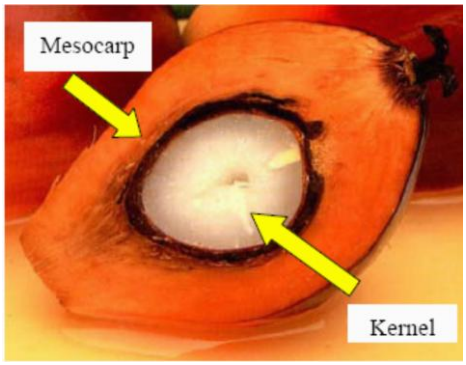


Figure 1.1 Cross-section of palm oil fruit (Noor Azian, et al., 2006)

Table 1.1 Some oil yields per area per annum

Crop	kg oil/ha	liters oil/ha	lbs oil/acre	US gal/acre
Corn (maize)	145	172	129	18
Cashew nut	148	176	132	19
Cotton	273	325	244	35
Soybean	375	446	335	48
Coffee	386	459	345	49
Linseed (flax)	402	478	359	51
Sesame	585	696	522	74
Safflower	655	779	585	83
Rice	696	828	622	88
Tung oil tree	790	940	705	100
Sunflowers	800	952	714	102
Cocoa (cacao)	863	1026	771	110
Peanuts	890	1059	795	113
Rapeseed	1000	1190	893	127
Olives	1019	1212	910	129
Castor beans	1188	1413	1061	151
Pecan nuts	1505	1791	1344	191
Jojoba	1528	1818	1365	194
Jatropha	1590	1892	1420	202
Macadamia nuts	1887	2246	1685	240
Brazil nuts	2010	2392	1795	255
Avocado	2217	2638	1980	282
Coconut	2260	2689	2018	287
Oil palm	5000	5950	4465	635

(Addison, 2009)

Remark

- 1 ha is equivalent to 6.25 Rai,
- 1 acre is equivalent to 2.53 Rai,

The compositions of crude palm oil can be classified as a mixture of 5 main chemical groups shown in Table 1.2 below.

Table 1.2 General compositions of crude palm oil.

Group	Components in the group
Oil	- Triglyceride, Diglyceride , Monoglyceride
	- Phospholipids, Glycolipid and Lipoprotein
	- Free fatty acids
Oxidized products	- Peroxides, Aldehydes, Ketones, Furfurals
Non-oil (but oil solubles)	- Carotene
	- Tocopherols
	- Squalene
	- Sterols
Impurities	- Metal particles
	- Metal ions
	- Metal complexes
Water soluble	- Water (moisture)
	- Glycerol
	- Chlorophyll pigments
	- Phenols
	- Sugars (soluble carbohydrates)

(Morad et al., 2006)

Some of these chemical groups need to be removed partially or completely through the refining process in order to produce good edible oil that has better stability and keepability. Thus, in palm oil refineries the CPO produced undergoes degumming, bleaching and deodorization obtaining refined, bleached and deodorized oil (RBDPO). Table 1.3 shows the typical composition of the main constituents of crude palm oil (Morad et al., 2006).

Table 1.3 Typical compositions of the main components of CPO

Constituent	Crude Palm Oil
Triglyceride, wt%	95
Free Fatty Acids, FFA, wt%	2 - 5
Red Colour (5 ¼ " Lovibond Cell)	Orange red
Moisture & Impurities, wt%	0.15 – 3.0
Peroxide Value, PV (meq/kg)	1 -5.0
Anisidine Value, AV	2 – 6
β-carotene content, ppm	500-700
Phosphorus, P, ppm	10-20
Iron (Fe), ppm	4-10
Tocopherols, ppm	600-1000
Diglyceride, wt%	2-6

(Morad et al., 2006)

Palm oil consists mainly of glyceride made up of a range of fatty acids. Triglyceride constitutes the major component, with small proportions of diglyceride and monoglyceride. Palm oil also contains other minor constituents, such as free fatty acids and non-glyceride components. This composition determines the oil's chemical and physical characteristics (Morad et al., 2006).

The fatty acid composition of crude palm oil is given in Table 1.4. About 50 wt% of them are saturated, 40 wt% of mono-unsaturated, and 10 wt% of polyunsaturated fatty acids. In its content of monounsaturated 18:1 acid, palm oil is similar to olive oil, which is as effective as the more polyunsaturated oils in reducing blood cholesterol and the risk of coronary heart disease. Crude palm oil contains approximately 1 wt% of minor components: carotenoid, vitamin E (tocopherol and tocotrienol), sterols, phospholipids, glycolipid, terpenic and aliphatic hydrocarbons, and other trace impurities (Table 1.5). The most important components are carotenoid and vitamin E, both of which possess important physiological properties. The iodine value is between 50 and 56 (May, 1994).

Table 1.4 Fatty acid composition of crude palm oil

	wt% of total acids	
Acid	Range	Mean
12:0	0.1-1.0	0.2
14:0	0.9-1.5	1.1
16:0	41.8-46.8	44.0
16:1	0.1-0.3	0.1
18:0	4.2-5.1	4.5
18:1	37.3-40.8	39.2
18:2	9.1-11.0	10.1
18:3	0.0-0.6	0.4

(May, 1994)

Table 1.5 Minor components of crude palm oil

Minor components	ppm
Carotenoids	500-700
Tocopherol and tocotrienols	600-1,000
Sterols	326-527
Phospholipids	5-130[a]
Triterpene alcohol	40-80[a]
Methyl sterols	40-80
Squalene	200-500
Aliphatic alcohols	100-200
Aliphatic hydrocarbon	50

a. Estimated

(May, 1994)

1.2.2 Degumming (Morad et al., 2006)

Technically, degumming is referred to an operation of purification of seed oils, which normally contain impurities in colloidal state or dissolved in them. Fats and oils contain complex organo-phosphorus compounds referred to as phospholipids (phosphatide) or more usually, as gums. Phospholipids should be removed because of their strong emulsifying action and if they are not removed, the oils will be gone through undue darkening during deodorization at high temperature. The phospholipids are removed during processing by a variety of treatments collectively referred to as degumming. The treatment usually involves hydration with water, orthophosphoric acid, and polybasic organic acids either single or in combination, followed by centrifuging the precipitated material or by adsorption on bleaching earth or filler.

In more simple words, degumming is a process of removing the unwanted gums, which the stability of the oil products will be interfered in later stages. The objective is achieved by treating the crude palm oil with the specified quantity of food grade acid normally phosphoric or citric acid of certain concentration.

1.2.2.1 Type of degumming

There are 6 types of degumming in vegetable oil industry. The difference between all these types are based on methods of processing, chemical used and degumming phosphatides content in the crude vegetable oil. The types of degumming process are following;

(a) Dry degumming

Dry degumming process involved removal of gums through precipitation by acid conditioning and via filtration during the bleaching process, not via centrifugal separation. This process is used for low-phosphatide oil such as palm oil, lauric oils, and edible tallow which suitable to be used for preparing oils before subsequently physical refining. This type of process eliminates bleaching, as separate processing step thus, it is cost-advantage and it is a well-proven process.

(b) Water degumming

Water degumming is a process of removing gums through precipitation by pure water hydration of crude oil via centrifugal separation. This method is used when

extracting gums for production of lecithin in soybean oil and crude oil in which containing 200 ppm of phosphorus content. In this process, water is the main agent used to remove the hydratable phosphatide from vegetable oils and it can be carried out in batch or continuous procedure depending on the type of the oil to be degummed and amount of oil to be processed.

(c) Acid degumming

In this acid degumming process, gums are precipitated by some form of acid conditioning process and subsequently removed by centrifugal separation. In this process method, the gums can be hydrated at temperature higher than 40°C and the process may lead to some dewaxing which usually associated with processing of sunflower and rice bran oils. In organic refining process, dilute organic (citric) acid is normally used and the residual phosphatide is removed by bleaching with silica hydrogel.

(d) Enzymatic degumming

Enzymatic degumming is a special degumming that enhanced by using some food-grade enzymes. Types of oil that uses this process method are soybean and rapeseed oil. The advantage of the enzymatic degumming is no soap stock produced during the process; therefore it is no any oil losses due to soap stock separation.

(e) EDTA- degumming

EDTA degumming is a physico-chemical degumming process. It involves a complete elimination of phospholipids by a chelating agent, Ethylene Diamine Tetraacetic Acid (EDTA), in the presence of an emulsifying additive.

(f) Membrane degumming

Membrane degumming is usually used in extraction plant. Membrane separation is primarily a size-exclusion-based pressure-driven process. It separates different components according to molecular weights or particle sizes, shapes of individual components which are dependent on their interactions with membrane surfaces and other components of the mixture. During oil processing, micelle containing 25-30 wt% of crude oil and 70-75 wt% of hexane are obtained from extraction prior to solvent removal. Phospholipids can be separated from triglyceride

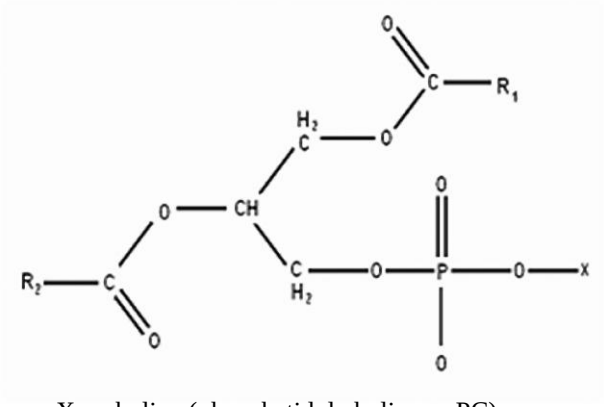
in the micelle stage using appropriate membrane. The membrane-based crude oil degumming produces permeate and retentate containing triglyceride and phospholipids, respectively. The majority of coloring materials, some of the FFA and other impurities are included in phospholipids micelles and removed as well.

1.2.2.2 Process theory of degumming

Theoretically, phospholipids, protein and carbohydrate, vegetable gum and colloidal components have negative influence towards the keepability of oil. They are considered as undesirable substances in refining process because they increase the oil loss and hamper other operations. Therefore, oils that have certain amount of these substances should be degummed in order to remove all those substances.

There are 2 kinds of phospholipids exist, hydratable and non-hydratable phosphatides. Hydratable phospholipids can be removed easily by the addition of water where the process can be conducted rapidly at elevated temperature or slowly at low temperature. However the temperature should stay below the temperature at which the phospholipids hydrate starts to become liquid crystals (usually ~ 40ºC). By taking up water, phospholipids lose their lipophilic character and become lipophobic and thus precipitate from oil.

When the non-hydratable phospholipids have to be converted to hydratable ones, the conversion of them is usually performed through acidulation followed by neutralization. Traditionally, acids used are usually sufficiently strong to hydrate phospholipids without hydrolyzing the triglyceride. At present, citric or phosphoric acid is normally being used for any type of vegetable oil. However, phosphoric acid is more preferred by the palm oil refiners because of a lower unit cost and easier handling. The main component of phospholipids is phosphatides. Figure 1.2 shows the chemical structure of phosphatides.



X = choline (phosphatidyl choline or PC)

X = ethanolamine (phosphatidylethanolamine or PE)

X = inositol (phosphatidylinositol or PI)

X = hydrogen (phosphatidyl acid or PA)

Figure 1.2 Chemical structures of phosphatides (Morad et al., 2006)

Phospholipids are present in relatively small quantities of about 5–130 ppm in palm oil as compared with other vegetables oils. The solvent extracted mesocarp oil usually contained 100-200 ppm phospholipids, however it only presents at level of 20-80 ppm in commercial crude palm oil.

Phospholipids have been reported to show antioxidant affects. Their antioxidant-synergistic effects can be attributed to the sequestering of soluble pro-oxidant metal ions to form inactive species. There is also a synergism between phospholipids and naturally occurring antioxidants such as α-tocopherol and quercetin. Hydratable insoluble metal ions could also dispersed by phospholipids through miscellar action. Since phospholipids and glycolipids cause reverse micelle, vesicle or emulsion droplet formation, phospholipids can remove metal ions and their hydrophilic salts from the lipid phase to reduce oxidation.

1.2.2.3 Degumming agents

There are two types of degumming agents that are usually being used in palm oil refining industry, are phosphoric and citric acid.

Phosphoric acid (H_3PO_4), is a colorless and odorless liquid. A food grade phosphoric acid with concentration of 85 wt% is normally used in palm oil refining process.

Citric acid or 2-hydroxy-1,2,3-propanetricarboxylic acid, an organic carboxylic acid containing three carboxyl groups; it is a solid at room temperature, melted at 153ºC and decomposed at a higher temperature.

1.2.3 Esterification (Clark, 2004)

Esterification is the general name for a chemical reaction in which two reactants (typically an alcohol and an acid) form an ester as the reaction product. Esters are common in organic chemistry and biological materials, and often have a characteristic pleasant, fruity odor. This leads to their extensive use in the fragrance and flavor industry. Esterification is a reversible reaction. Hydrolysis- literally "water splitting" involves adding water and a catalyst (commonly NaOH) to an ester to get the sodium salt of the carboxylic acid and alcohol. As a result of this reversibility, many esterification reactions are equilibrium reactions.

1.2.3.1 The mechanism for the esterification reaction

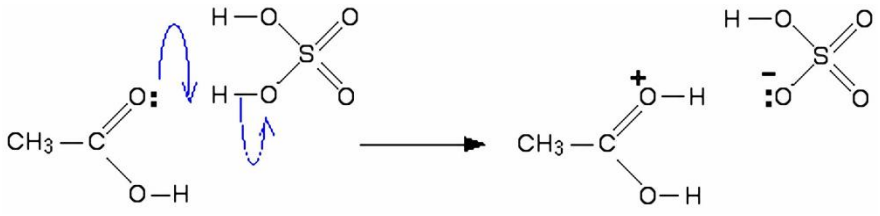
This example looks in detail at the mechanism for the formation of esters from carboxylic acids and alcohols in the presence of concentrated sulfuric acid acting as the catalyst. It uses the formation of ethyl ethanoate from ethanoic acid and ethanol as a typical example (Eq 1.1). The reaction is slow and reversible. To reduce the chances of the reverse reaction happening, the ester is distilled off as soon as it is formed.

$$CH_3COOH + CH_3CH_2OH \xleftrightarrow{\text{Conc. } H_2SO_4} CH_3COOCH_2CH_3 + H_2O \quad \text{(Eq 1.1)}$$

All the steps in the mechanism below are shown as one-way reactions because it makes the mechanism look less confusing. The reverse reaction is actually done sufficiently and differently that it affects the way the mechanism is written.

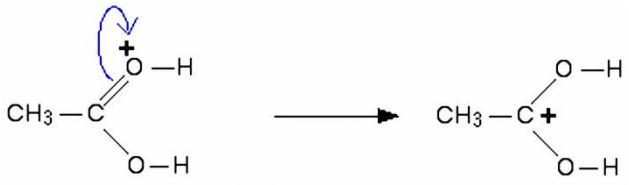
Step 1

In the first step, the ethanoic acid takes a proton (a hydrogen ion) from the concentrated sulfuric acid. The proton becomes attached to one of the lone pairs on the oxygen atom which is double-bonded to the carbon atom.



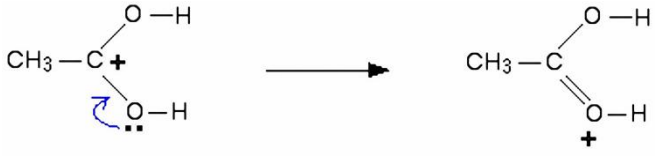
(Eq 1.2)

The proton transferring to the oxygen gives it a positive charge, but it is actually misleading to draw the structure in this way. The positive charge is delocalised over the whole of the right-hand end of the ion, with a fair amount of positiveness on the carbon atom. In other words, an electron pair shifting gives this structure:



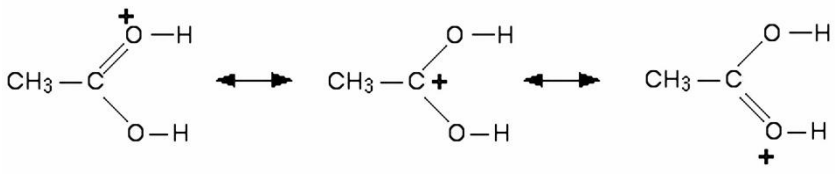
(Eq 1.3)

It can also imagine another electron pair shift producing a third structure:



(Eq 1.4)

But none of these is the correct structure of the ion formed. The truth lies somewhere in between all of them. One way of writing the delocalized structure of the ion is like this:



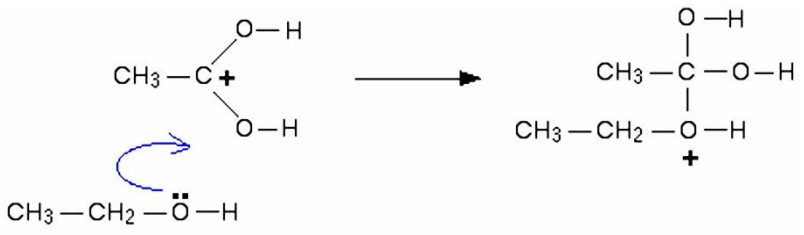
(Eq 1.5)

The double headed arrows are shown that each of the individual structures makes a contribution to the real structure of the ion. They don't mean that the bonds are flipping back and forth between one structure and another. The various structures are known as **resonance structures** or **canonical forms**. There will be some degree of positive charge on both of the oxygen atoms, and also on the carbon atom. Each of the bonds between the carbon and the two oxygen atoms will be the same - somewhere between a single bond and a double bond.

For the purposes of the rest of this discussion, it should use the structure where the positive charge is on the carbon atom.

Step 2

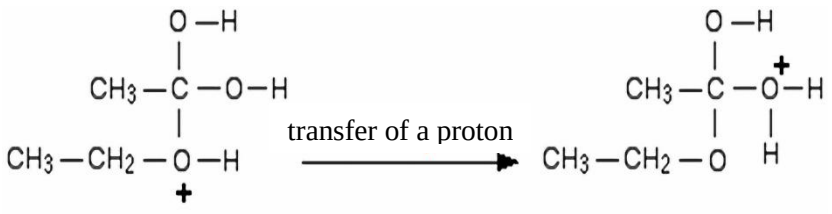
The positive charge on the carbon atom is attacked by one of the lone pairs on the oxygen atom of the ethanol molecule.



(Eq 1.6)

Step 3

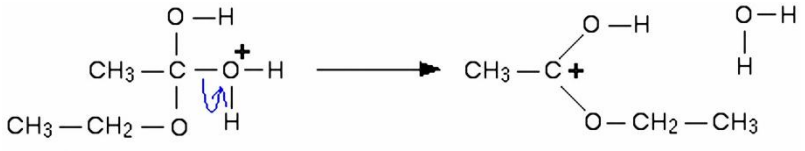
What happens next is that a proton (a hydrogen ion) gets transferred from the bottom oxygen atom to one of the others. It gets picked off by one of the other substances in the mixture (for example, by attaching to a lone pair on an unreacted ethanol molecule), and then dumped back onto one of the oxygen atom more or less at random. The net effect is:



(Eq 1.7)

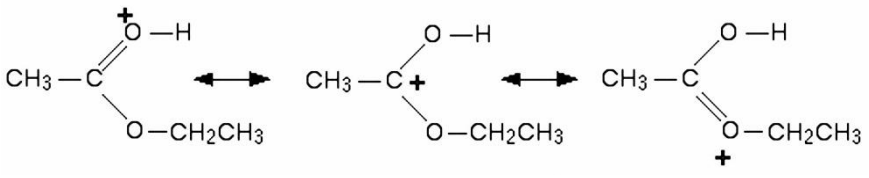
Step 4

Now a molecule of water is lost from the ion.



(Eq 1.8)

The product ion has been drawn in a shape to closely reflect the final product. The structure for the latest ion is just like the one discussed in step 1. The positive charge is actually delocalized all over that end of the ion, and there will also be contributions from structures where the charge is on the either of the oxygen atoms.

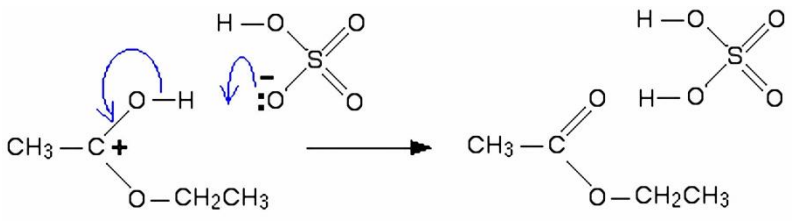


(Eq 1.9)

It is easier to follow what is happening if we keep going with the structure with the charge on the carbon atom.

Step 5

The hydrogen is removed from the oxygen atom by reaction with the hydrogen sulfate ion which was formed way back in the first step.

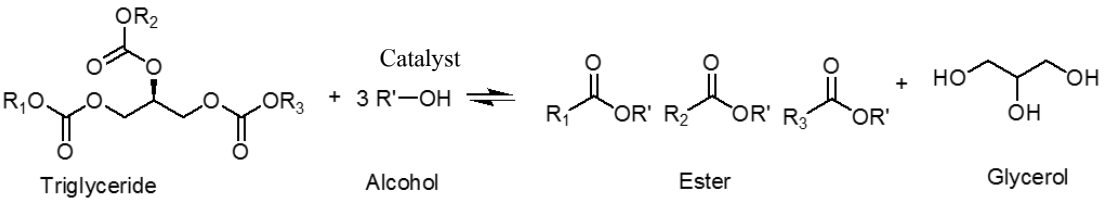


(Eq 1.10)

The ester has been formed and the sulfuric acid catalyst has been regenerated.

1.2.4 Transesterification

Transesterification also called alcoholysis is the displacement of alcohol from an ester by another alcohol in a process similar to hydrolysis, except than an alcohol is used instead of water. This process has been widely used to reduce the viscosity of triglyceride. The transesterification reaction is represented by the general equation:



(Eq 1.11)

1.2.5 Biodiesel (University of Strathelyde, 2008)

Biodiesel is an alternative fuel similar to conventional or ‘fossil’ diesel. Biodiesel can be produced from straight vegetable oil, animal oil/fats, tallow and waste cooking oil. The process used to convert these oils to biodiesel is called transesterification. The largest possible source of suitable oil comes from oil crops

such as rapeseed, palm or soybean. Waste vegetable oil can often be sourced for a small price. (The waste oil must be treated before conversion to biodiesel by removing impurities). The result is biodiesel produced from waste vegetable oil can compete with fossil diesel.

Biodiesel has many environmentally beneficial properties. The main benefit of biodiesel is that it can be described as ‘carbon neutral’. This means that the fuel produces no net output of carbon in the form of carbon dioxide (CO_2). This effect occurs because when the oil crop grows it absorbs the same amount of CO_2 as is released when the fuel is combusted. In fact this is not completely accurate as CO_2 is released during the production of the fertilizer required to fertilize the fields in which the oil crops are grown. Fertilizer production is not the only source of pollution associated with the production of biodiesel, other sources include the esterification process, the solvent extraction of the oil, refining, drying and transporting. All these processes require an energy input either in the form of electricity or from fuel, both of which will generally result in the release of green house gases. To properly assess the impact of all these sources requires use of a technique called life cycle analysis. Biodiesel is rapidly biodegradable and completely non-toxic, meaning spillages represent far less of a risk than fossil diesel spillages. Biodiesel has a higher flash point than fossil diesel and so is safer in the event of a crash.

1.2.5.1 Biodiesel productions

There are three basic routes to biodiesel production from oils and fats:

- Base catalyzed transesterification of the oil.
- Direct acid catalyzed transesterification of the oil.
- Conversion of the oil to its fatty acids and then to biodiesel.

Almost all biodiesel is produced using base catalyzed transesterification as it is the most economical process requiring only low temperatures and pressures and producing a 98 wt% conversion yield. The transesterification process is the reaction of a triglyceride with an alcohol to form esters and glycerol. A triglyceride has a glycerine molecule as its base with three long chain fatty acids attached. The characteristics of the fat are determined by the nature of the fatty acids attached to the

glycerine. The nature of the fatty acids can in turn affect the characteristics of the biodiesel. During the transesterification process, the triglyceride is reacted with alcohol in the presence of a catalyst, usually a strong alkaline like sodium hydroxide. The alcohol reacts with the fatty acids to form the mono-alkyl ester, or biodiesel and crude glycerol. In most production methanol or ethanol is the alcohol used (methanol produces methyl esters, ethanol produces ethyl esters) and is base catalyzed by either potassium or sodium hydroxide. Potassium hydroxide has been found to be more suitable for the ethyl ester production; either base can be used for the methyl ester. A common product of the transesterification process is Rape Methyl Ester (RME) produced from raw rapeseed oil reacted with methanol. The reaction between the fat or oil and the alcohol is a reversible reaction and so the alcohol must be added in excess to drive the reaction towards the product side and ensure complete conversion.

A successful transesterification reaction is signified by the separation of the ester and glycerol phases after the reaction time. The heavier, co-product, glycerol settles out and may be sold as it is or it may be purified for use in other industries, e.g. the pharmaceutical, cosmetics etc.

1.2.6 Sonochemistry (Thompson and Doraiswamy, 1999 and Suslick, 1989)

Sonochemistry is the use of ultrasound to enhance or alter chemical reactions. Sonochemistry in the true sense of the term occurs when ultrasound induces “true” chemical effects on the reaction system, such as forming free radicals which accelerate the reaction. However, ultrasound may have other mechanical effects on the reaction, such as increasing the surface area between the reactants, accelerating dissolution, and/or renewing the surface of a solid reactant or catalyst.

Ultrasound has proven to be a very useful tool in enhancing the reaction rates in a variety of reacting systems. It has successfully increased the conversion, improved the yield, changed the reaction pathway, and/or initiated the reaction in biological, chemical, and electrochemical systems. This nonclassical method of rate enhancement, a field termed *sonochemistry*, is becoming a widely used laboratory technique. However, its use in industry is limited because the process of producing ultrasound is very inefficient and burdened with high operating costs. It is starting to attract attention because the operating costs may be off-set by reducing or eliminating

other process costs. The use of ultrasound may enable operation at milder operating conditions (e.g. lower temperatures and pressures), eliminate the need for extra costly solvents, and reduce the number of synthesis steps while simultaneously increasing end yields, permit the use of lower purity reagents and solvents, and/or increase the activity of existing catalysts. For these reasons, use of ultrasound appears to be a promising alternative for high-value chemicals and pharmaceuticals. In addition, research is continually underway to make it a feasible option in the ongoing effort to intensify large-scale processes.

Much of the pioneering work in the field has been done by chemists and physicists who have found that **the chemical, and some mechanical, effects of ultrasound are a result of the implosive collapse of cavitation bubbles.**

Ultrasound occurs at a frequency above 16 kHz, higher than the audible frequency of the human ear, and is typically associated with the frequency range of 20 kHz to 500 MHz. The frequency level is inversely proportional to the power output. Low-intensity, high frequency ultrasound (in the megahertz range) does not alter the state of the medium through which it travels and is commonly used for nondestructive evaluation and medical diagnosis. However, high-intensity, low-frequency ultrasound does alter the state of the medium and is the type of ultrasound typically used for sonochemical applications. Many of these applications are briefly explained in the Kirk-Othmer Encyclopedia of Chemical Technology (1983).

1.2.6.1 Theory

The chemical and mechanical effects of ultrasound are caused by cavitation bubbles which are generated during the rarefaction, or negative pressure, period of sound waves. During the negative-pressure cycle, the liquid is pulled apart at sites containing some gaseous impurity (nucleation sites), forming a void. Nucleation sites are also known as “weak spots” in the fluid. Nucleation in the absence of ultrasound can be seen every day when drinking a carbonated beverage. The bubbles of carbon dioxide form at scratches in the glass where gaseous impurities, such as air, are harbored and act as nucleation sites. When using ultrasound, the cavitational activity is directly proportional to the number density of particles present in the medium. Chemical effects due to ultrasound are not observed

when there are no dissolved gases in the system, when the sound intensity is not greater than the cavitation threshold of the system or when the reactant is not volatile enough to enter the cavitation bubble during its formation. As ultrasound passes through a liquid, the expansion cycles exert negative pressure on the liquid, pulling the molecules away from one another. If the ultrasound is sufficiently intense, the expansion cycle can create cavities in the liquid. This will occur when the negative pressure exceeds the local tensile strength of the liquid, which varies according to the type and purity of liquid. (Tensile strength is the maximum stress that a material can withstand from a stretching load without tearing.) Normally, cavitation is a nucleated process; that is, it occurs at pre-existing weak points in the liquid, such as gas-filled crevices in suspended particulate matter or transient microbubbles from prior cavitation events. Most liquids are sufficiently contaminated by small particles that cavitation can be readily initiated at moderate negative pressures.

Once formed, small gas bubbles irradiated with ultrasound will absorb energy from the sound waves and grow. Cavity growth depends on the intensity of the sound. At high intensities, a small cavity may grow rapidly through inertial effects. If cavity expansion is sufficiently rapid during the expansion half of a single cycle, it will not have time to recompress during the compression half of the acoustic cycle.

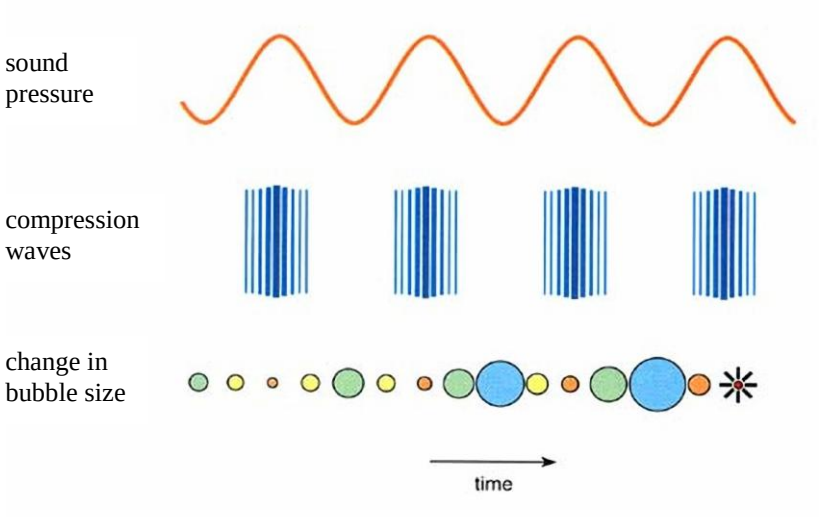


Figure 1.3 Cavitation by ultrasound irradiation (Suslick, 1989)

The physical and chemical effects of ultrasound are a result of both stable and transient cavitational events, which are described in the following sections. Two competing theories exist to explain the chemical effects due to cavitation: the *hot-spot theory* and *the electrical theory*. The hot-spot theory postulates that when the bubbles cavitate, localized hot spots are formed which reach temperatures and pressures in excess of 5000 K and 500 atm. The electrical theory postulates that an electrical charge is created on the surface of a cavitation bubble, forming enormous electrical field gradients across the bubble which is capable of bond breakage upon collapse. The hot-spot theory is generally more accepted, although Margulis (1992, 1994) reports many phenomena which contradict this theory but are supported by the electrical theory. A Letter to the Editor published in 1996 completely discounted the electrical theory as a valid mechanism behind sonoluminescence and sonochemistry.

1.2.6.2 Bubble dynamics.

The chemical effects of ultrasound have been attributed to the collapse of both stable and transient cavitational events. Stable cavities oscillate for several acoustic cycles before collapsing, or never collapse at all. Transient cavities, conversely, exist for only a few acoustic cycles. The following sections provide a brief explanation of bubble dynamics and its modeling.

(a) Stable cavities.

Stable cavities are bubbles which form and oscillate around a mean radius in a sound field and exist for many acoustic cycles. For this occurrence their growth rate during the rarefaction must be equivalent to their rate of contraction during the compression phase. This specifies that rectified diffusion, or the unequal transfer of mass into the bubble during the acoustic wave cycle, is not occurring. Because many ultrasonic transducers are designed with a set frequency, operating under resonance conditions is achieved by changing the system parameters in order to alter the bubble resonant frequency to match that of the transducer. This can be done by varying the hydrostatic pressure and the system temperature. Other factors which affect the resonating frequency of the bubble include the characteristics of the liquid, such as its density and surface tension. Conversely, varying the ultrasonic frequency

in order to drive the bubble dynamics toward transient cavitation was also investigated.

(b) Rectified diffusion.

At lower acoustic intensities cavity growth can also occur by a slower process called rectified diffusion. Rectified diffusion is the event where cavitation bubbles grow more during expansion than they shrink during contraction due to the unequal diffusion of gases and vapor from the bulk liquid phase into the bubble. Cavity growth during each expansion is, therefore, slightly larger than shrinkage during the compression. Thus, over many acoustic cycles, the cavity will grow. The growing cavity can eventually reach a critical size where it can efficiently absorb energy from the ultrasonic irradiation. Called the resonant size, this critical size depends on the liquid and the frequency of sound; at 20 kHz, for example, it is roughly 170 micrometers. At this point the cavity can grow rapidly during a single cycle of sound.

(c) Transient cavitation.

A transient cavity is one which exists for only a few acoustic cycles. During its existence it grows several times larger than its initial size and, upon implosion, creates extreme temperatures and pressures within its cavity.

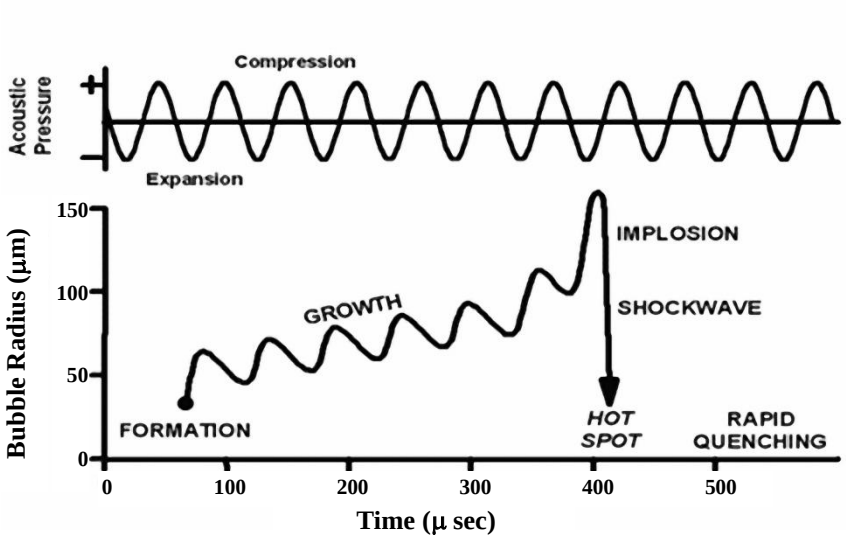


Figure 1.4 Transient cavitation process (Suslick, 1989)

1.2.6.3 Factors affecting cavitation

The ambient conditions of the reaction system can greatly influence the intensity of cavitation, which directly affects the reaction rate and/or yield. These conditions include the reaction temperature, hydrostatic pressure, irradiation frequency, acoustic power, and ultrasonic intensity. Other factors which significantly affect the cavitational intensity are the presence and nature of dissolved gases, choice of solvent, sample preparation, and choice of buffer. Each of these factors is described in detail below.

(a) Presence and nature of dissolved gases

Dissolved gases act as nucleation sites for cavitation. As gases are removed from the reaction mixture because of the implosion of the cavitation bubbles, initiation of new cavitational events becomes increasingly difficult. Bubbling gases through the mixture facilitates the production of cavitation bubbles, but the type of gas used is important. As a general rule, a gas with a high specific heat ratio gives a greater cavitational effect than one with a low specific heat ratio. Because the collapse of the bubble occurs in such a small amount of time (~ 3.5 μs), it can be assumed to occur diabatically. Monatomic gases, such as argon and helium, convert more energy upon cavitation than diatomic gases, such as nitrogen and oxygen, because of the larger ratio of specific heats. Gases which are extremely soluble in the reaction mixture may reduce the cavitational effect because the bubbles formed may redissolve before collapse occurs. The bubbles which do not dissolve often become so large (because of facile penetration of gas into the bubble) that they float to the surface and explode. The thermal conductivity of the gas is also important because, although the collapse is modeled as adiabatic, there is a small amount of heat which is transferred to the bulk liquid mixture during collapse. As the thermal conductivity of the gas increases, the amount of heat loss due to thermal dissipation also increases.

(b) Ambient temperature

Contrary to chemical reactions in general, an increase in the ambient reaction temperature results in an overall decrease in the sonochemical effect. The

decrease is a result of a sequence of events. First, as the reaction temperature is raised, the equilibrium vapor pressure of the system is also increased. This leads to easier bubble formation (due to the decrease of the cavitation threshold); however, the cavitation bubbles which are formed contain more vapor. As discussed above, vapor reduces the ultrasonic energy produced upon cavitation because it cushions the implosion in addition to using enthalpy generated in the implosion for the purposes of condensation. In general, the largest sonochemical effects are observed at lower temperatures when a majority of the bubble contents is gas.

In certain reaction systems, an optimum reaction temperature may lead to more favorable results. In such systems, an increase in temperature will increase the kinetic reaction to a point at which the cushioning effect of the vapor in the bubble begins to dominate the system. When this occurs, the rate of the reaction decreases upon further increase in ambient reaction temperature. The rate may even reach a plateau with temperature and then decrease as the temperature increases. The observed temperature effect was dominated by the reaction kinetics in and around the cavitating bubble. However, increasing the temperature was also simultaneously decreasing the intensity of cavitation, thus reducing the amount of free radicals produced within the bubble. It was speculated that these free radicals were required for the degradation reaction to occur and that they diffuse from the vapor cavity to the gas-liquid film where reaction ensues. As the rates of the counter diffusing reactants became comparable, a further increase in temperature had little or no effect on the reaction (i.e. the percent change in thymine concentration reached a plateau as a function of temperature). However, as the temperature continued to be increased, the declining production of free radicals began to have a negative effect on the rate of degradation.

(c) Ambient pressure

An increase in the ambient reaction pressure generally results in an overall increase in the sonochemical effect because of the decrease in the vapor pressure of the mixture. Decreasing the vapor pressure increases the intensity of the implosion, thus increasing the ultrasonic energy produced upon cavitation.

However, there is a limitation to this, as found by Moulton et al. (1983, 1987) when investigating the ultrasonic hydrogenation of soybean oil. When they operated at an ambient pressure of 200 psig and greater, they found ultrasound to have little effect on the catalyst activity. When the pressure was decreased to 115 psig, the effects of ultrasound were significantly increased. It appeared that operating at pressures of 200 psig and above increased the cavitation threshold in the system to a level at which the cavitation bubbles could no longer be produced or were produced in such small quantities that they did not significantly effect the overall reaction. For any given system an optimum operating pressure will most likely exist.

Cum et al. (1988) found that operating the system under resonance conditions increased the rate and yield of the reaction.

(d) Choice of solvent

Cavities are more readily formed when using a solvent with a high vapor pressure, low viscosity, and low surface tension. However, the intensity of cavitation is benefited by using solvents with opposing characteristics (i.e. low vapor pressure, high viscosity, and high surface tension). Other researchers found that cavitation was inhibited when using the extremely volatile solvent diethyl ether, which has a vapor pressure of ~ 0.73 atm at 25°C. When choosing a solvent for a particular reaction system, the appropriate "family" of solvents to use is frequently dictated by the type of chemistry involved (i.e. due to temperature, solubility and/or other issues). Once a family of solvents is identified, then the effects of the various solvents within that family on cavitation can be investigated.

(e) Ultrasonic frequency

The frequency of the ultrasound has a significant effect on the cavitation process because it alters the critical size of the cavitation bubble. At very high frequencies, the cavitational effect is reduced because either (1) the rarefaction cycle of the sound wave produces a negative pressure which is insufficient in its duration and/or intensity to initiate cavitation or (2) the compression cycle occurs faster than the time required for the microbubble to collapse.

In summary, lower frequency ultrasound produces more violent cavitation, leading to higher localized temperatures and pressures at the cavitation site. However, higher frequencies may actually increase the number of free radicals in the system because, although cavitation is less violent, there are more cavitational events and thus more opportunities for free radicals to be produced. In addition, the shortened bubble lifetime may increase the amount of free radicals which are able to escape from the cavitation site to the bulk mixture, where they facilitate the bulk reaction. It is contended that the optimum frequency is system specific and depends on whether intense temperatures and pressures are required (thus enhanced by lower frequencies) or if the rate of single electron transfer is more important (enhanced by higher frequencies).

(f) Acoustic power

Many authors have found that as the power delivered to the reaction mixture increases, the rate of the reaction increases to a maximum and then decreases with a continued increase in power. A possible explanation for the observed decrease at high powers is the formation of a dense cloud of cavitation bubbles near the probe tip which acts to block the energy transmitted from the probe to the fluid.

1.2.6.4 Methods of producing cavitation

Cavitation can be generated within fluid using transducers (devices which convert one form of energy to another). Gas-driven transducers, such as dog whistles, use high-velocity gas flow to generate ultrasound. Liquid-driven transducers, such as submarine propellers, force liquid across a vibrating plate or through an orifice, creating a cavitation zone. Electromechanical transducers, the most commonly used transducers in sonochemical research, convert electrical energy to sound energy.

When using gas- or liquid-driven transducers, cavitation is generated in situ; i.e., cavities are formed within the fluid by forcing the fluid through a physical object which generates shearing forces great enough to tear the fluid apart. Direct sonication occurs when a device which generates sound waves, such as a probe or horn, is place directly in a fluid system. Indirect sonication occurs when the sound waves propagate through some other medium before they come into contact with the vessel containing the reaction mixture, which is often the case when using an ultrasonic cleaning bath. As is evident by the nature of sonication, probe systems

produce higher intensities in reaction mixtures as compared to ultrasonic cleaning baths. Cavitation generated in situ can reach intensities comparable to direct sonication where hydrodynamically induced cavitation with a throttling valve to increase the hydrolysis of fatty oils. The yields and reaction conditions obtained using a hydrodynamic system, were similar to those of a probe system. Cavitation can also be induced in situ using a focused electromagnetic acoustic transducer (EMAT) which produces a high-intensity lithotripter shock wave in the fluid concerned. Once the shock wave is induced, cavitational bubbles are formed in the negative pressure region of the wave, causing rupturing of the fluid. Secondary cavitational transients, created by the collapse of the primary bubbles, may also occur.

(a) Piezoelectric vs Magnetostrictive transducers.

The two main types of electrochemical transducers used in industrial applications are piezoelectric and magnetostrictive. Piezoelectric transducers are constructed using a piezoelectric material, such as quartz, which expands and contracts in an alternating *electric* field, thus producing sound waves from the electric signal. Magnetostrictive transducers are constructed from materials, such as nickel alloys, which expand and contract in an alternating *magnetic* field. Each transducer has its own advantages and disadvantages, as outlined in Table 1.6.

Table 1. 6 Comparison of piezoelectric and magnetostrictive transducers

Piezoelectric transducers	Magnetostrictive transducers
- relatively inexpensive - relatively small and light - damaged at temperatures > ~150 °C - will age considerably, i.e., have a reduced power output, with continuous operation at high temperatures and/or over long periods of time - may be damaged by large impact - structure will be damaged if operated “dry”	- more expensive than piezoelectric for similar power ratings - heavier and bulkier than piezoelectric - with special precautions, can be operated at temperatures >250 °C - will not degrade or fail over time by their very nature; some have been used successfully for over 20 years of commercial operation - extremely resistant to mechanical damage, such as large impacts - no damage when operated “dry”

(Thomson and Doraiswamy, 1999)

As is evident from the table, piezoelectric transducers are normally used with small-volume processes. When large volumes and/or long, continuous reaction times are required, the more robust magnetostrictive transducer may be the preferred option.

1.2.6.5 Ultrasonic system types

(a) Ultrasonic bath

Ultrasonic baths were originally manufactured for cleaning purposes. Typical baths have the transducers attached to the bottom, although the transducers can be submersed in a conventional tank to obtain similar effects. Bath systems are widely used in sonochemical research because they are readily available and relatively inexpensive. The reaction vessel is typically immersed in the coupling fluid contained in the bath (indirect sonication). However, the bath itself can be used as the reaction vessel but would require additional mechanical agitation. In addition, the bath walls would be exposed to the reaction mixture and/or irradiation, making them susceptible to corrosion or erosion.

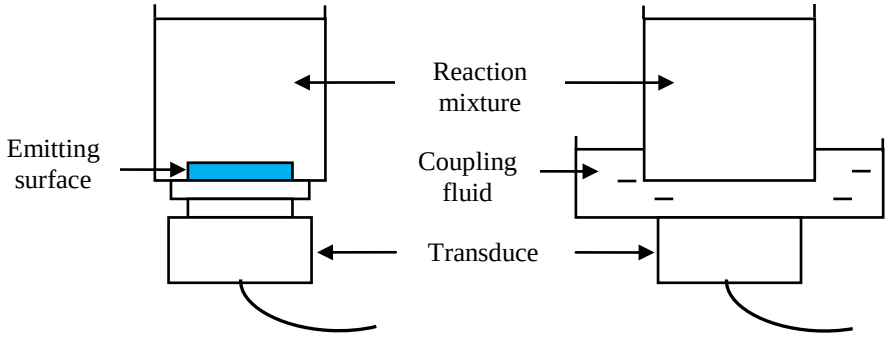
When indirect sonication is used, the ultrasonic power which reaches the reaction vessel is relatively low as compared to other ultrasonic systems, such as a probe. In addition, obtaining reproducible results may be difficult because the amount of power reaching the reaction mixture is highly dependent upon the placement of the sample in the bath. The results can also vary with time as the bath warms during operation. Because every bath has different characteristics, it is important to determine the optimum conditions for each bath and to place the reaction vessel in the same location for each experiment. In addition, it is important to use the same type of reaction vessel for each reaction because the shape of the bottom of the reaction vessel significantly influences the wave pattern, even when placed in the same position in the bath. Another disadvantage to using a bath system is that the coupling fluid surrounding the reaction vessel(s) will eventually increase in temperature, making the maintenance of isothermal conditions difficult. Cooling coils can be placed within the bath, but they will have an effect on the sound field and may reduce the amount of power reaching the vessel.

(b) Probe (horn) systems

Probe systems, also called horn systems, are being more frequently used for sonochemical research in the laboratory. This may be because manufacturers are aware that this type of research is increasing and are providing equipment to meet the demand. In addition, probe systems are capable of delivering large amounts of power directly to the reaction mixture which can be regulated by varying the amplitude delivered to the transducer. Disadvantages in using a probe system include erosion and pitting of the probe tip, which may contaminate the reaction solution. Fortunately several probes are available with removable tips, making replacement relatively inexpensive. The localized areas of ultrasonic intensity in a fluid are highly dependent on the power delivered to the transducer. However, as the power delivered increases, the ultrasonic intensity increases at the center of the reactor and dissipates in the radial direction. At an input power of 200 W, the active region in the radial direction is equal to that of the horn (the remaining radial direction had negligible activity).

(c) Planar Transducers.

This type of setup is typically made in the laboratory and consists of a planar transducer (Figure 1.5) connected to a vessel which contains either the reaction mixture (a. Direct sonication) or a coupling fluid (b. Indirect sonication) into which the reaction vessel is immersed. “Cup-horn” designs are very similar to planar transducer designs, with the exception that the horn is designed to allow for cooling capabilities, facilitating the maintenance of isothermal conditions. Both planar transducer and cup-horn systems are capable of delivering higher powers than ultrasonic bath systems. However, they are both difficult to scale-up.



a. Direct sonication b. Indirect sonication

Figure 1.5 Planar transducer systems (Thomson and Doraiswamy, 1999)

1.2.6.6 Conclusions

The advances in the field of ultrasound in the last 20 years have been plentiful, but there is still a lot of new frontier to be covered. Researchers have found that ultrasound chemically enhances reactions which depend on a SET (single electron transfer) process as a key step. Reaction systems which follow an ionic mechanism are enhanced by the mechanical effects of ultrasound. These enhancements are a result of increases in the intrinsic mass-transfer coefficient, increases in surface area resulting from particle degradation, and, in some cases, increases in the driving force for dissolution. In some reaction systems, ultrasound changes the reaction pathway from ionic to one which involves a SET step.

Several other aspects of sonochemical behavior are unclear. The manner by which free radicals are produced within the cavitation bubble remains elusive, although several researchers have concluded that they are formed during the adiabatic implosion of the cavitation bubble. Ultrasound has been found to enhance the effective diffusivity in a solid-liquid system, increase the intrinsic mass-transfer coefficient, induce supersaturation, and increase the activation energy and frequency factor of various reaction systems. However, the actual mechanisms behind these enhancements have not been discerned. In addition, the amount of available engineering data in the areas of ultrasonic reactor design and scale-up are lacking. It will take the combined work of scientists from all fields to resolve the role of ultrasound in reacting systems and to make it a viable rate enhancement technique for commercial industrial processes.

1.3 Literature Review

Wright et al. (1944) noted that the starting materials used for alkali-catalyzed transesterification of glyceride must meet certain specifications. The glyceride should have an acid value less than 1 mgKOH/g and all materials should be substantially anhydrous. If the acid value was greater than 1 mgKOH/g, more NaOH was required to neutralize the free fatty acids. Water also caused soap formation, which consumed the catalyst and reduce catalyst efficiency. The resulting soaps caused an increase in viscosity, formation of gels and made the separation of glycerol difficult.

Bradshaw and Meuly (1944) and Feuge and Grose (1949) also stressed the importance of oils being dry and containing less than 0.5 wt% of free fatty acid.

Freedman et al. (1984) stated that ester yields were significantly reduced if the reactants were not dry and containing free fatty acids less than 0.5 wt%.

Ma et al. (1998) investigated the effects of free fatty acids and water on transesterification of beef tallow with methanol. Their results showed that the water and free fatty acid content of beef tallow should be kept below 0.06 and 0.5 wt%, respectively in order to get the best conversion. Water content was a more critical variable in the transesterification process than was free fatty acid.

Crabble et al. (2001) stated that the presence of free fatty acid in vegetable oils makes the oil more acidic. In the alkali-catalyzed method, the amount of catalyst used depends very much on the acidity of the vegetable oil. More catalyst is necessary to eliminate fatty acids in crude and used frying/waste vegetable oil since they usually contain more fatty acids than do the refined ones. The presence of fatty acid in high content in vegetable oil deactivates alkali catalysts, and the addition of an excessive amount of alkali as compensation give rise to the formation of emulsions, which increase viscosity, thus leading to the formation of gel and the problems associated with glycerol separation and the loss in yield of methyl ester.

Kusdiana and Saka (2004) studied the effect of free fatty acid on the yield of methyl ester in the supercritical methanol method. They chose oleic acid as a model of free fatty acid because oleic acid is most abundant in rapeseed oil. They showed that both acid- and alkali- catalyzed transesterification resulted in a lower conversion when free fatty acid content increased in the reaction system. In the acid-

catalyzed method, a reaction system with 20 wt% of free fatty acid reduced the conversion to about a half, while in the alkali-catalyzed method only 35 wt% methyl esters were obtained.

Stavarache et al. (2005) studied the transesterification of vegetable oil with short-chain alcohols, in the presence of base-catalyst, by means of low frequency ultrasound (Honda Electronics Ultrasonic Cleaners WS1200-28 and WS1200-40 of 28 and 40 kHz, respectively) with a total power of 1200 W, working power being set at 60%) in order to obtain biodiesel fuel. By using ultrasounds the reaction time is much shorter (10–40 minutes) than for mechanical stirring. The quantity of required catalyst is 2 or 3 times lower. The molar ratio of alcohol: oil used is only 6:1. Normal chain alcohols react fast, while secondary and tertiary alcohols show some or no conversion after 60 min of reaction. Surprisingly, 40 kHz ultrasounds are much more effective in the reduction of the reaction time (10–20 minutes). Twenty eight kilohertz give slightly better yields (98–99 wt%), but longer reaction time, while higher frequencies are not useful at all for the transesterification of fatty acids.

Stavarache, et al. (2007) studied the batch transesterification of vegetable oil with methanol, in the presence of potassium hydroxide as catalyst, by means of low frequency ultrasound (40 kHz) with the aim of gaining more knowledge on intimate reaction mechanism. The ester preparation involved a batch transesterification reaction, followed by washing and drying. The one step reaction utilized a 100 wt% excess methanol, or a total molar ratio of methanol to oil of 6:1. The quantity of catalyst was 0.5 wt% of the oil, determined as optimum in a previous study. All experiments were performed in an Erlenmeyer type flask, having 100 ml total volume, immersed into the cleaning bath in the optimum position towards the transducer in order to ensure maximum ultrasound entering the reaction mixture. The ultrasonic reactions were performed using Honda Electronics Ultrasonic Cleaner WS 1200–40, with a total power of 1200 W, working power being set at 70%. The reaction temperature was 36 ± 2°C for all experiments and was maintained constant by circulating water through the bath. They can suppose that in the first two steps of the ultrasonically driven transesterification (TG→DG and DG →MG) the fatty acids in positions 1 and 3 are esterified. The saturated fatty acids have a natural preference for these positions and therefore they should be esterified at the very beginning of the

reaction, fact plentifully demonstrated by the behavior of palm oil. After 20 min of ultrasonic irradiation the reaction is almost complete or in the last stage of completion for all types of fatty acids. The presence of MG in high amount, even after 60 minutes of ultrasonic irradiation, proves that the fatty acids in position 2 are not easily esterified. The major part of the ultrasonically driven transesterification of vegetable oils under base catalysis took place in the first 3–10 minutes of reaction if not faster, making from this technique a unique one for FAME synthesis. Diglyceride were found in small amounts during the ultrasonically driven transesterification process, while monoglycerides were detected in high amount, indicating that the last step of transesterification – MG + ROH $\rightarrow$ Gly + ME – is slower. The conversion of FAME at the end of 60 minutes of sonication was almost same regardless the type of oil, meaning that the reaction mixture was in steady state (i.e. equilibrium concentration was reached). They can conclude that the ultrasonically driven transesterification is a tool applicable to almost all types of vegetable oils. The saturated fatty acids were transesterified mostly at the beginning of the reaction, while the amount of unsaturated fatty acids esters increased as the reaction progressed.

Marchetti and Errazu (2008) studied direct esterification of triglyceride to biodiesel and effects of the main variables involved in the process, reaction temperature, amount of catalyst, initial amount of free fatty acid and molar ratio alcohol to oil. They used concentrated sulfuric acid (98 wt%) as the catalyst and used anhydrous ethanol as the reactant. A mixture of refined sunflower oil with pure oleic acid was used to make an acid oil model. The lab scale reactor of 500 ml with mechanic agitation was used and also accompanied with a warmer jacket. Ethanol was used in the experiments instead of methanol since it is less toxic and safer to handle. They also studied modifications in initial amount of free fatty acids. The result showed that the amount of FFA was reduced from 10.684 to 0.54 wt%.

Kelkar et al. (2008) illustrated the use of cavitation for intensification of biodiesel synthesis (esterification) reaction, which is mass transfer limited reaction considering the immiscible nature of the reactants, i.e., fatty acids and alcohol. Esterification of fatty acid cut (C8–C10) with methanol in the presence of concentrated H_2SO_4 as a catalyst has been studied in hydrodynamic cavitation reactor as well as in the sonochemical reactor. It has been observed that ambient operating

conditions of temperature and pressure and reaction times of <3 hours, for all the different combinations of acid and methanol studied in the present work, was sufficient for giving > 90 mol% conversion. This clearly establishes the efficacy of cavitation as an excellent way to achieve process intensification of the biodiesel synthesis process. Optimization in terms of the operating molar ratio of the fatty acid to alcohol (1:10 ratio is the optimum in the present case) and catalyst loading (2 wt% of conc. H_2SO_4 catalyst) results in > 95 mol% conversion in about 90 minutes of processing time.

Hanh et al. (2009a) described that if oil contains higher amounts of FFA (>1 wt%), FFA form soap with the base catalysts. Consequently, it is considered that the ester conversion is decreased by the formation of soap that can prevent separation of the biodiesel from the glycerin. At present, there were little data about the esterification of free fatty acid with alcohol under ultrasonic irradiation condition as well as the effects of molar ratio (ethanol to free fatty acid), acid catalyst concentration (H_2SO_4 and CH_3COOH), and temperature. They investigated production of fatty acid ethyl ester (FAEE) from oleic acid with short-chain alcohols (ethanol, propanol, and butanol) under ultrasonic irradiation. The ultrasonic experiments were carried out using a Honda Electronics Ultrasonic Cleaner (WS 1200-40, 40 kHz with a maximum power of 1200 W). Batch esterification of oleic acid was carried out to study the effect of test temperatures of 10–60°C, molar ratios of alcohol to oleic acid of 1:1–10:1, quantity of catalysts of 0.5–10 wt% of oleic acid and irradiation times of 10 hours. The optimum condition for the esterification process was molar ratio of alcohol to oleic acid at 3:1 with 5 wt% of H_2SO_4 at 60°C with an irradiation time of 2 h.

Hanh et al. (2009b) investigated the biodiesel production through transesterification of triolein with various alcohols such as methanol, ethanol, propanol, butanol, hexanol, octanol and decanol was at molar ratio 6:1 (alcohol: triolein) and 25°C in the presence of base catalysts (NaOH and KOH) under ultrasonic irradiation (Honda Electronics Ultrasonic Cleaner WS 1200-40; 40 kHz) and mechanical stirring (1800 rpm) conditions. It was found that the rate of the alkyl ester formation under the ultrasonic irradiation condition was higher than that under the stirring condition. The relationships between ester conversion (wt%) and

irradiation time for various alcohols at molar ratio 6:1 (alcohol: triolein) and 1 wt% KOH under the ultrasonic irradiation condition was shown that ester conversions for all alcohols increase rapidly just after the irradiation and then reach maximum around 15 minutes. The highest ester conversion is obtained at the transesterification of triolein with methanol and ethanol. In addition, it was confirmed that the rate depended upon the kind of alcohols; as the number of carbon in alcohol increased, the rate of the ester formation tended to decrease. On the other hand, the secondary alcohols such as 2-propanol, 2-butanol, 2-hexanol, and 2-octanol showed little ester conversion, suggesting that steric hindrance strongly affected the transesterification of triolein.

1.4 Research Objectives

1.4.1 To design and construct equipment used for the batch acid degumming and acid catalyzed esterification of CPO.

1.4.2 To perform batch acid degumming and acid catalyzed esterification of CPO with ethanol assisted by ultrasonic irradiation.

1.4.3 To design and construct equipment used for the continuous acid degumming and acid catalyzed esterification of CPO.

1.4.4 To perform continuous acid degumming and acid catalyzed esterification of CPO with ethanol assisted by ultrasonic irradiation.

1.4.5 To design and construct CSTR used for the continuous acid degumming and acid catalyzed esterification of CPO.

1.4.6 To perform continuous acid degumming and acid catalyzed esterification of CPO with ethanol by CSTR.

1.4.7 To investigate the optimum conditions for the batch and continuous acid degumming and acid catalyzed esterification of CPO with ethanol assisted by ultrasonic irradiation and for conducting by CSTR.

1.5 Scopes of Research Work

1.5.1 To reduce phosphorus content of CPO less than 10 ppm using continuous acid degumming process.

1.5.2 To reduce FFA content of CPO lower than 0.5 wt% using continuous acid catalyzed esterification of CPO with ethanol assisted by ultrasonic irradiation.

1.5.3 To fabricate the lab scale equipment (capacity of 1 L) for continuous acid degumming and acid catalyzed esterification of CPO with ethanol assisted by ultrasonic irradiation.

1.5.4 To fabricate the lab scale equipment (capacity of 50 L) for acid degumming and continuous acid catalyzed esterification of CPO with ethanol using CSTR.

1.6 Expected Benefits

1.6.1 Phosphorus content of CPO is reduced to meet the EN 14214: 2008, biodiesel standard (ME standard).

1.6.2 The CPO as the raw material for biodiesel production is treated by lowering FFA content to the optimized level of 0.5 wt% before conducting the alkali catalyzed transesterification.

1.6.3 The optimal conditions for the batch and continuous acid catalyzed esterification of CPO with ethanol assisted by ultrasonic irradiation and conducting by CSTR are investigated.