REDUCTION OF FREE FATTY ACID IN WASTE COOKING OIL: STUDY BETWEEN AMBERLYST-15 AND WATER FILTER RESIN

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ABSTRACT

Biodiesel can produce from transesterification of vegetable oil or animal fat and low molecular weight alcohol. Typically, base catalysts are used in the transesterication reaction. However, waste cooking oil also can be used as a feedstock in biodiesel production. If waste cooking oil is to be used as feedstock for biodiesel production, the amount of polar compound in the waste cooking oil, especially free fatty acid (FFA) must be taken into consideration as it will greatly affect the transesterification reaction. Therefore, the aim of this study is to compare the capability of free fatty acid reduction of Amberlyst-15 and water filter resin and study the probability of synthesized biodiesel from waste cooking which is treated by cation exchange resin catalyst. The esterification were examined in the temperature range of 50–60 °C and the effect of catalyst amount (0, 2.0 and 4.0 wt%) on FFA conversion was also analyzed. In addition, the optimal result of each catalyst from esterification process is selected to synthesize biodiesel by transesterification using Potassium hydroxide as a catalyst. The acid value of oil was measured by the titration method. Amberlyst-15 and water filter resin were analyzed by using GC-MS and FTIR. The results indicated that both of Amberlyst-15 and water filter resin can be reduce free fatty acid in waste cooking oil, however, the result of the Amberlyst-15 is slightly better than water filter resin.

Keywords : Esterification, Waste cooking oil, Free fatty acid, Amberlyst-15, Water filter resin.

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Chapter 1

Introduction

1.1 Introduction

In recent years, the reduction of greenhouse gas emission has become an important problem and main cause is the pollution from transportation. Among these problem, biodiesel has attracted much attention as an alternative fuel for diesel engines since it is renewable, non-toxic, low pollutant and environmentally acceptable. Biodiesel can produce from tranesterification of vegetable oil or animal fat with low molecular weight alcohol. Generally base catalysts are used in the transesterication reaction.

Waste cooking oil also used as a feedstock in biodiesel production. It has similar performance with biodiesel produce from fresh vegetable oils and low cost [1]. However, if waste cooking oil is to be made feedstock for biodiesel production, the amount of polar compound in the waste cooking oil, especially free fatty acid (FFA) must be taken into consideration as it will greatly affect the transesterification reaction. Refined oil usually contains less than 0.5 wt% FFA whereas for waste cooking oil, free fatty acid contents range between 0.5 and 1.5 wt%.[2]

The base-catalyst method is not suitable for these waste cooking oil because soap is produced from the reaction of free fatty acid with a base catalyst. The formation of soap not only consumes the catalyst but it also can bring about the emulsification if fatty acid methyl esters and glycerol (by product of biodiesel, which would make the separation of fatty acid methyl esters and glycerol mixture difficult. But for homogeneous acid catalyst, it can simultaneously catalyst esterification and transterification and more efficient when the amount of free fatty acid in the oil exceeds 1wt% but it has a corrosion and difficult to separation from the reaction medium [3]. So the uses of homogeneous acid catalyst are replaced by heterogeneous acid catalyst. Cation exchange resin catalyst is one type of the heterogeneous acid catalyst. The advantage of using cation exchange resin catalyst are insensitive to free fatty acid content, esterification and transesterification occurs simultaneously, eliminate the washing step of biodiesel, easy separation of the catalyst from the reaction medium, resulting in lower product contamination level, easy regeneration and recycling of catalyst and reduce corrosion problem[4]. Amberlyst-15 is selected in this experiment because it has the optimal balance of surface area, acid capacity and pore

diameter to make it the catalyst for choice for etherification (MTBE, ETBE, TAME) and especially, esterification [5]. However, Amberlyst-15 has a problem of high cost. So water filter resin is a new alternative cation exchange resin catalyst which has lowered cost and easy to found. After free fatty acid is reduced, the lower free fatty acid content oil is used as a feedstock of transesterification reaction with KOH to produce biodiesel.

The aim of this study is to compare the activities of Amberlyst-15 and water filter resin for free fatty acid esterification in waste cooking oil and examine the effect of catalyst amount, reaction temperature and reaction time on the esterification process.

1.2 Objective

1) To reduce free fatty acid in waste cooking oil by esterification process using Amberlyst-15 and water filter resin and to compare their efficiency.
2) To optimize the reaction conditions of esterification process such as the catalyst amount, reaction temperature and reaction time

1.3 Scope of study

1) To study about the reduction of free fatty acid in waste cooking oil in laboratory scale and study throughout the properties of cation exchange resin ; Amberlyst-15 and water filter resin as catalysts.
2) To compare the reduction in term of the conversion of free fatty acid under the optimal reaction conditions of Amberlyst-15 and water filter resin.

1.4 Expected results

1) Water filter resin could reduce free fatty acid in waste cooking oil and it would give more or nearly percentage of free fatty acid conversion when compared with Amberlyst-15.
2) Water filter resin could be used instead of Amberlyst-15 to reduce the cost since the Amberlyst-15 has high cost.

Chapter 2

Theory and Literature Reviews

2.1 Biodiesel [6]

Biodiesel is commonly produced by the transesterification of the vegetable oil or animal fat of feedstock. There are several methods for carrying out this transesterification reaction including the common batch process, supercritical processes, ultrasonic methods, and even microwave methods.

Chemically, transesterified biodiesel comprises a mix of mono-alkyl esters of long chain fatty acids. The most common form uses methanol (converted to sodium methoxide) to produce methyl esters (commonly referred to as Fatty Acid Methyl Ester - FAME) as it is the cheapest alcohol available, though ethanol can be used to produce an ethyl ester (commonly referred to as Fatty Acid Ethyl Ester - FAEE) biodiesel and higher alcohols such as isopropanol and butanol have also been used. Using alcohols of higher molecular weights improves the cold flow properties of the resulting ester, at the cost of a less efficient transesterification reaction. A lipid transesterification production process is used to convert the base oil to the desired esters. Any Free fatty acids (FFAs) in the base oil are either converted to soap or removed from the process, or they are esterified (yielding more biodiesel) using an acidic catalyst. After this processing, unlike straight vegetable oil, biodiesel has combustion properties very similar to those of petroleum diesel, and can replace it in most current uses.

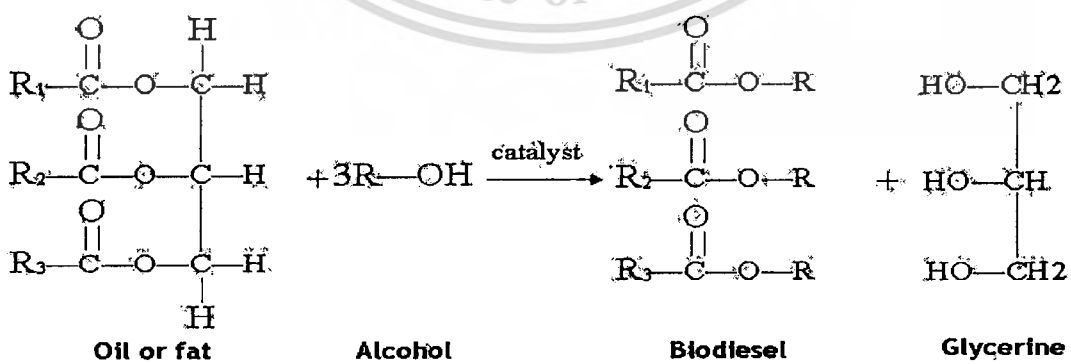


Figure 2-1. Transesterification of triglycerides with alcohols.

A by-product of the transesterification process is the production of glycerol as shown in Fig. 2-1. For every 1- acetone of biodiesel that is manufactured, 100 kg of glycerol are produced. Originally, there was a valuable market for the glycerol, which assisted the economics of the process as a whole. However, with the increase in global biodiesel production, the market price for this crude glycerol (containing 20% water and catalyst residues) has crashed. Research is being conducted globally to use this glycerol as a chemical building block. One initiative in the UK is The Glycerol Challenge.

2.1.1 Properties

Biodiesel has better lubricating properties and much higher cetane ratings than today's lower sulfur diesel fuels. Biodiesel addition reduces fuel system wear, and in low levels in high pressure systems increases the life of the fuel injection equipment that relies on the fuel for its lubrication. Depending on the engine, this might include high pressure injection pumps, pump injectors (also called *unit injectors*) and fuel injectors.

The calorific value of biodiesel is about 37.27 MJ/L. This is 9% lower than regular Number 2 petroleum diesel. Variations in biodiesel energy density are more dependent on the feedstock used than the production process. Still these variations are less than for petroleum diesel. It has been claimed biodiesel gives better lubricity and more complete combustion thus increasing the engine energy output and partially compensating for the higher energy density of petroleum diesel.

Biodiesel is a liquid which varies in color (between golden and dark brown) depending on the production feedstock. It is immiscible with water, has a high boiling point and low vapor pressure. The flash point of biodiesel (>130 °C, >266 °F) is significantly higher than that of petroleum diesel (64 °C, 147 °F) or gasoline (-45 °C, -52 °F). Biodiesel has a density of ~ 0.88 g/cm^3, less than that of water. Biodiesel has virtually no sulfur content, and it is often used as an additive to Ultra-Low Sulfur Diesel (ULSD) fuel. ASTM standards of maximum allowed quantities in diesel and biodiesel are shown in Table 2-1.

Table 2-1 ASTM standards of maximum allowed quantities in diesel and biodiesel **[7]**

Property	Diesel	Biodiesel
Standard	ASTM D975	ASTM D6751
Composition	HC[a] (C10–C21)	FAME[b] (C12–C22)
Kin. viscosity (mm^2/s) at 313 K	1.9–4.1	1.9–6.0
Specific gravity (g/mL)	0.85	0.88
Flash point (K)	333–353	373–443
Cloud point (K)	258–278	270–285
Pour point (K)	238–258	258–289
Water (vol.%)	0.05	0.05
Carbon (wt.%)	87	77
Hydrogen (wt.%)	13	12
Oxygen (wt.%)	0	11
Sulfur (wt.%)	0.05	0.05
Cetane number	40–55	48–60
HFRR[c] (μm)	685	314
BOCLE[d] scuff (g)	3600	>7000

2.1.2 Biodiesel categories [8]

1.(Straight Vegetable Oil) Vegetable oil is an alternative fuel for diesel engines and for heating oil burners. For engines designed to burn #2 diesel fuel, the viscosity of vegetable oil must be lowered to allow for proper atomization of fuel; otherwise incomplete combustion and carbon build up will ultimately damage the engine. Many enthusiasts refer to vegetable oil used as fuel as waste vegetable oil (WVO) if it is oil that was discarded from a restaurant or straight vegetable oil (SVO) or pure plant oil (PPO) to distinguish it from biodiesel.

2.Veggie / Kero Mix are the mixing of vegetable fats or oils and kerosene or diesel to reduce the viscosity. The suitable mixed ratio is 20%kerozeze: 80% Vegetable fats and oils.

3. Ester Biodiesel Blends of biodiesel and conventional hydrocarbon-based diesel are products most commonly distributed for use in the retail diesel fuel marketplace. Much of the world uses a system known as the "B" factor to state the amount of biodiesel in any fuel mix: fuel containing 20% biodiesel is labeled B20, while pure biodiesel is referred to as B100. It is common in the USA to see B99.9 because a federal tax credit is awarded to the first entity which blends petroleum diesel with pure biodiesel. Blends of 20 percent biodiesel with 80 percent petroleum diesel (B20) can generally be used in unmodified diesel engines. Biodiesel can also be used in its pure form (B100), but may require certain engine modifications to avoid maintenance and performance problems.

2.1.3 Feedstocks for biodiesel

Now we can start to deal with biodiesel. As you know, biodiesel is derived from vegetable oils. The melting point and Iodine values in vegetable oil are shown in Table 2-2. The major components of vegetable oils are *triglycerides.* The term *triacylglycerols* is being used more and more, but we will use the classical term in this discussion. *Triglycerides* are *esters of* glycerol (see- above; an alcohol with a hydroxy group on each of its three carbon atoms) with long-chain acids, commonly called *fatty acids.*

Note from the comparison of the rational names of the fatty acids with their structural formulas how the position of the double bonds is defined by numbers. The number of carbon atoms is counted by beginning with the first carbon having the functional group defining the fatty compound as acid or ester. As you can see from the former example (for example, 1-propanol and 2-propanol), this way of counting holds for other functional groups as well. The trivial names of fatty acids and their esters are far more commonly used than their rational names.

Table 2-2 The melting point and Iodine values in vegetable oil. [9]

Oils and their melting points and Iodine Values		
Oil	**Approx. melting point (°C)**	**Iodine Value**
Coconut oil	25	10
Palm kernel oil	24	37
Mutton tallow	42	40
Beef tallow	-	50
Palm oil	35	54
Olive oil	-6	81
Castor oil	-18	85
Peanut oil	3	93
Rapeseed oil	-10	98
Cotton seed oil	-1	105
Sunflower oil	-17	125
Soybean oil	-16	130
Tung oil	-2.5	168
Linseed oil	-24	178

For some kind of vegetable oil that used in biodiesel production [9];

Algae Oil

Two diverse samples of crude algal oil were obtained from Solazyme, Inc.

Babassu Oil

Babassu oil was purchased from Jedwards International, Inc. Babassu oil is extracted from the seeds of the babassu palm tree, *Attalea speciosa.* The tree is common in Brazil, Mexico, and Honduras; it grows well in areas typically cultivated for coconut or palm. The kernels contain 60-70% oil.1

Camelina Oil

Camelina oil comes from the plant, *Camelina sativa.* It is an annual flowering plant that grows well in temperate climates and is also known as gold-of-pleasure and false flax. Some varieties of camelina contain 38-40 % oil. Camelina can be grown in arid conditions and does not require significant amounts of fertilizer.4

Canola Oil

Crude degummed canola oil was obtained from a commercially available source. Canola is the seed of the species *Brassica napus* or *Brassica campestris*; the oil component contains less than two percent erucic acid and the solid component contains less than 30 micromoles per gram of glucosinolates.

Coconut Oil

Refined, bleached, deodorized (RBD) coconut oil was purchased from Jedwards International, Inc.

Corn Oil, Distiller's

Crude, dry distiller's grain (DDG) extracted corn oil was obtained from a commercially available source. The extracted corn oil comes from the DDG stream of the ethanol production process.

Palm Oil

Palm oil was obtained from a commercially available source

Soybean Oil

Refined soybean oil was obtained from a commercially available source.

2.2. Fat and Oil

Fats consist of a wide group of compounds that are generally soluble in organic solvents and largely insoluble in water. Chemically, fats are generally triesters of glycerol and fatty acids. Fats may be either solid or liquid at room temperature, depending on their structure and composition. Although the words "oils", "fats", and "lipids" are all used to refer to fats, "oils" is usually used to refer to fats that are liquids at normal room temperature, while "fats" is usually used to refer to fats that are solids at normal room temperature. "Lipids" is used to refer to both liquid and solid fats, along with other related substances. The word "oil" is used for any substance that does not mix with water and has a greasy feel, such as petroleum (or crude oil) and heating oil, regardless of its chemical structure.[10]

There are many different kinds of fats, but each is a variation on the same chemical structure. All fats consist of fatty acids (chains of carbon and hydrogen atoms, with a carboxylic acid group at one end) bonded to a backbone structure, often glycerol (a "backbone" of carbon, hydrogen, and oxygen). Chemically, this is a triester of glycerol, an ester being the molecule formed from the reaction of the carboxylic acid and an organic alcohol. As a simple visual illustration, if the kinks and angles of these chains were straightened out, the molecule would have the shape of a capital letter E. The fatty acids would each be a horizontal line; the glycerol "backbone" would be the vertical line that joins the horizontal lines. Fats therefore have "ester" bonds.

2.2.1 monoglyceride and diglycerides

A diglyceride, or diacylglycerol (DAG), has two fatty acid radicals and exists in the 1,2 form as shown in Fig. 2-2 and the 1,3 form depending on how the fatty acids are attached to the glycerol molecule. A monoglyceride, or monoacylglycerol (MAG) as shown in Fig. 2-3, has only one fatty acid radical per molecule of glycerol. The fatty acid may be attached to carbon 1 or 2 of the glycerol molecule.

All esters of glycerol and fatty acids are metabolized in the same way. Monoglycerides, diglycerides, and triglycerides all have 9 Calories per gram, but some nutrition labels hide the calories of monoglycerides and diglycerides under the contention that "fat" consists only of triglycerides.

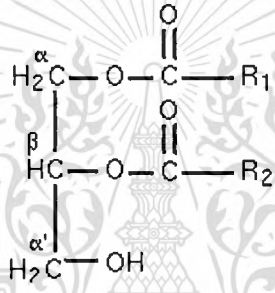


Figure 2-2. The structure of 1, 2-Diglycerides.

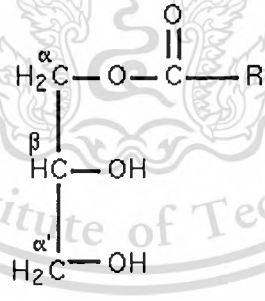


Figure 2-3. The structure of 1-Monoglycerides.

Diglycerides are surface active molecules that both attract and repel water at the same time. These hydrophilic and hydrophobic properties make them excellent emulsifying agents because they are soluble in fats and water. While substances like oil and water naturally separate, the addition of an emulsifier can help disperse the molecules evenly.

2.2.2 Triglycerides

Triglycerides are the main constituents of vegetable oils and animal fats. Triglycerides have lower densities than water (they float on water), and at normal room temperatures may be solid or liquid. When solid, they are called "fats" or "butters" and when liquid they are called "oils".

Triglycerides are formed by combining glycerol with three molecules of fatty acid. The glycerol molecule has three hydroxyl (HO-) groups. Each fatty acid has a carboxyl group (HOOC-). In triglycerides, the hydroxyl groups of the glycerol join the carboxyl groups of the fatty acid to form ester bonds.

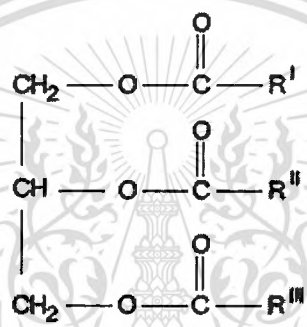


Figure 2-4 The structure of Triglycerides.

The three fatty acids (RCO_2H, $R'CO_2H$, $R''CO_2H$ in the above equation) are usually different, but many kinds of triglycerides are known. The chain lengths of the fatty acids in naturally occurring triglycerides vary in lengths, but most contain 16-, 18-, and 20-carbon atoms. Natural fatty acids found in plants and animals are typically composed only of even numbers of carbon atoms, reflecting the pathway for their biosynthesis from the two-carbon building block acetyl CoA. Bacteria, however, possess the ability to synthesis odd- and branched-chain fatty acids. As a result, ruminant animal fat contains odd-numbered fatty acids, such as 15, due to the action of bacteria in the rumen. Many fatty acids are unsaturated, some are polyunsaturated, e.g., those derived from linoleic acid.

Most natural fats contain a complex mixture of individual triglycerides. Because of this, they melt over a broad range of temperatures. Cocoa butter is unusual in that it is composed of only a few triglycerides, derived from palmitic, oleic, and stearic acids. The structure of triglycerides is shown in Fig. 2-4.

2.2.3 Fatty acid

fatty acid is a carboxylic acid with a long unbranched aliphatic tail (chain), which is either saturated or unsaturated. Most naturally occurring fatty acids have a chain of four to 28 carbons. The number of carbon atoms is usually even, because their biosynthesis involves acetyl-CoA, a coenzyme carrying a two-carbon-atom group (see fatty acid synthesis). Fatty acids are produced by the hydrolysis of the ester linkages in a fat or biological oil (both of which are triglycerides), with the removal of glycerol.

Fatty acids are aliphatic monocarboxylic acids derived from, or contained in esterified form in, an animal or vegetable fat, oil, or wax. By extension, the term is sometimes used to embrace all acyclic aliphatic carboxylic acids [11]. This would include acetic acid, which is not usually considered a fatty acid because it is so short that the triglyceride triacetin made from it is substantially miscible with water and is thus not a lipid.

It is proposed that the blend of fatty acids exuded by mammalian skin, together with lactic acid and pyruvic acid, are distinctive and enable animals with a keen sense of smell to differentiate individuals.

Up to 6 (or 4) carbon atoms, organic acids are considered "short-chain organic acids", they have substantial solubility in water. Furthermore, they do not behave physiologically like other fatty acids since they are more rapidly digested and absorbed in the intestinal tract and have unique properties in regulating sodium and water absorption through the mucosal epithelium. Biochemically, they are more closely related to carbohydrates than to fats. From 8 (or 6) to 10 (or 12) carbon atoms, fatty acids are said to have a medium chain. Physiological studies have shown that ingestion of triglycerides containing these medium-chain fatty acids may result, as for short-chain fatty acids, in increased energy expenditure via faster satiety. Thus, they facilitate weight control when included in the diet as a replacement for long-chain triglycerides (*St-Onge MP et al., J Nutr 2002, 132, 329*). Fatty acids which have 14 (or 12) and more carbon atoms are considered as long-chain fatty acids. Fatty acids with 4 to 12 carbon atoms are found mainly in milk fats (mainly butyric acid in cow and decanoic acid in sheep) but those with 10 and 12 carbon atoms are found also in certain seed oils such as coconut and other kernel fats of the palm family. A list of the most common saturated fatty acids is shown in Table 2-3.

Table 2-3. A list of the most common saturated fatty acids.

Systematic name	Trivial name	Shorthand designation	Molecular wt.	Melting point (°C)
Butanoic	butyric	4:0	88.1	-7.9
Pentanoic	valeric	5:0		
Hexanoic	caproic	6:0	116.1	-3.4
Octanoic	caprylic	8:0	144.2	16.7
Nonanoic	pelargonic	9:0	158.2	12.5
Decanoic	capric	10:0	172.3	31.6
Dodecanoic	lauric	12:0	200.3	44.2
Tetradecanoic	myristic	14:0	228.4	53.9
Hexadecanoic	palmitic	16:0	256.4	63.1
Heptadecanoic	margaric (daturic)	17:0	270.4	61.3
Octadecanoic	stearic	18:0	284.4	69.6
Eicosanoic	arachidic	20:0	312.5	75.3
Docosanoic	behenic	22:0	340.5	79.9
Tetracosanoic	lignoceric	24:0	368.6	84.2
Hexacosanoic	cerotic	26:0	396.7	88
Heptacosanoic	carboceric	27:0	410.7	
Octacosanoic	montanic	28:0	424.8	
Triacontanoic	melissic	30:0	452.9	
Dotriacontanoic	lacceroic	32:0	481	
Tritriacontanoic	ceromelissic (psyllic)	33:0	495	
Tetratriacontanoic	geddic	34:0	509.1	
Pentatriacontanoic	ceroplastic	35:0	523.1	

Butyric acid (4:0) is the lowest member of the acetic acid series found in natural fats. It occurs (2 to 4%) as a component of milk fats. It gives a rancid odor to butter when triglycerides are hydrolyzed and is present in fermentation products of carbohydrates. This fatty acid has peculiar physiological properties in causing growth arrest and apoptosis in various cell types (*Urbano A et al., Leukemia 1998, 12, 930*). It was tested in the therapy of solid tumors or leukemia (*Kasukabe T et al., Br J Cancer 1997, 75, 850*).

Valeric acid (5:0) has been identified in petroleum distillates and in oxidation products of oils and fats and fermentation of carbohydrates. It has a putrid odor.

Caproic acid (6:0) occurs in milk fats to the extent of about 2%. It was first isolated from butter in 1816 by Chevreul. It has a characteristic odor of goats, hence its name (from the Latin *caper*, goat). Caproic acid is present as glucose ester in leaf trichomes of *Datura metel.*

Caprylic acid (8:0) is widely distributed in animal and vegetable fats but rarely exceeding 8% of the total fatty acids, except in the seed oils of two Lythraceae, *Cuphea hookerina* and *C. painteri*, which contain about 70% caprylic acid (*Miller RW et al., JAOCS 1964, 41, 279*). It occurs to an extent of 1 to 4% in milk fats, and 6 to 8% in coconut and palm oils. Caprylic acid is a component of the active form of ghrelin, a 28 amino acids peptide produced by the mammalian stomach, which controls energy balance via appetite stimulation and promotion of adiposity (*Kojima M et al., Nature 1999, 402, 656*).

Pelargonic acid (9:0) is the first example of the occurrence of an odd-numbered carbon fatty acid in natural products. It occurs in secretion of sebaceous glands and in essential oil of *Pelargonium roseum* from which it derives its name. It is also a primary product of oxidative fission of oleic acid.

Capric acid (10:0) occurs as a minor component in the same fats that contain caprylic acid but also in the head oil of the sperm whale, and in wool and hair fats. It is a major constituent of elm seed oil (over 60% in *Ulmus americana* and over 70% in *Zelkova serrata*) but is absent in other Ulmaceae (*Apanthe, Morus*) (*Badami RC et al., Prog Lipid Res 1981, 19, 119*). Similarly, it was discovered that the seed oil of a Lythraceae, *Cuphea llavea*, contained about 80% of this acid (*Earle FR et al., JAOCS 1960, 37, 440*).

Lauric acid (12:0) is one of the three most widely distributed saturated fatty acids found in nature (14:0, 16:0, and 18:0). It occurs extensively in *Lauraceae* seeds (*Laurus nobilis*) where it was discovered (*Marsson T Ann 1842, 41, 329*). It is dominant in cinnamon oil (80-90%), coconut oil (40-60% as trilaurin) and is found also in *Cuphea* species (*Umbelliferae*) whose production was initiated in Germany. The recent uses of lauric acid are in the manufacture of flavourings, cocoa butter, margarine, alkyd resins, soaps, shampoos and other surface active agents, including special lubricants. Lauric acid as monoglyceride is known to the pharmaceutical industry for its good antimicrobial properties. It may play a role in combating lipid-coated RNA and DNA viruses. The major sources of lauric acid for human food are palm kernel, coconut and palm.

Myristic acid (14:0) is present in major amounts in seeds of the family *Myristicaceae* (nutmeg oil - or oil of mace - from *Myristica fragrans* contains about 60-70% of trimyristin) where it was first discovered (*Playfair L Ann 1841, 37, 152*). Nutmeg is found in Moluccas and spice islands of Indonesia. Coconut and palm kernel are also convenient sources of 14:0 (trimyristine) which may be isolated in a pure form by distillation. It is also present in milk fats (8-12%) and in the head oil of the sperm whale (15%). An excess of myristic acid in the diet induces a rise in plasma cholesterol in animals and human being (*Mensink RP et al., Arterioscler Thromb 1992, 12, 911*). Among saturated fatty acids, only myristic acid is able to make an amide link with some cellular proteins (myristoylation), modification which regulates their biological activities (*Johnson DR et al., Annu Rev Biochem 1994, 63, 869*).

Palmitic acid (16:0) is the commonest saturated fatty acids in plant and animal lipids. It was purified first by **Chevreul** in his researches on butter and tallow, but was first surely characterized by Fremy E (*Ann 1840, 36, 44*), who prepared it in pure form from palm oil, from which he named it. Despite its wide distribution, it is generally not present in fats in very large proportions. It usually forms less than 5% of the total fatty acids, sometimes as much as 10% in common vegetal oils (peanut, soybean, corn, coconut) and in marine-animal oils. Lard, tallow, cocoa butter palm oil contain 25 to 40% of this component.

Stearic acid (18:0) was described by **Chevreul** (1823) in the course of his researches on fats. It is the highest molecular weight saturated fatty acid occurring abundantly in fats and oils. It occurs in small quantities in seed and marine oils. Milk fats (5-15%), lard (10%), tallow (15-30%), cocoa and shea butters ((30-35%) are the richest sources of stearic acid. It is the principal constituent of hydrogenated fats and oils (about 90%).

The longer chains are less frequent, they can be found in uncommon seed oils (C20-24 in *Leguminoseae* and *Sapindaceae*), in palm oil (C20-C32)(*Puah CW et al., Lipids 2006, 41, 305*), in waxes (C24-30) and in some sphingolipids (C20-24). Long-chain saturated fatty acids (from C24 to C28) are produced by microalgae and it was estimated that diatoms contribute from 30 to 80% of these components in sandy sediments (*Volkman JK et al., Org Geochem 1998, 29, 1163*). These long-chain fatty acids derive from higher plant waxes and are more abundant in deep than in surface sediments (*Rieley G et al., Org Geochem 1991, 17, 901; Muri G et al., Org Geochem 2004, 35, 1083*).

Arachidic acid (20:0) occurs in appreciable quantities in groundnut (*Arachis hypogea)* oil (3%) where it was discovered in 1854 by Gössmann A (*Ann Chemie 1854, 89, 1*). Larger amounts are found in seeds of *Sapindaceae* (up to 20%). It is also found in the depot fat of some animals and in milk fats.

Behenic acid (22:0) was first reported as a constituent of ben (behen) oil (seeds of *Moringa oleifera*) (*Voelcker A Ann 1848, 64, 342*). Except for the seed oils of the *Crucifereae* (between 0.5 and 3.4%), this fatty chain does not occur in the principal oils. Large amounts are found in hydrogenated animal and vegetal oils (8-57%).

Lignoceric acid (24:0) is present at trace levels in plant oils except in groundnut oil (about 1%) and notably in a Leguminous seed oil (*Adenanthera pavonina*) where it may amount to about 25%. It is the principal fatty acid present in carnauba wax (30% of the normal fatty acids). A major source is rice-wax bran(about40%).

2.2.3.1 Free Fatty Acids

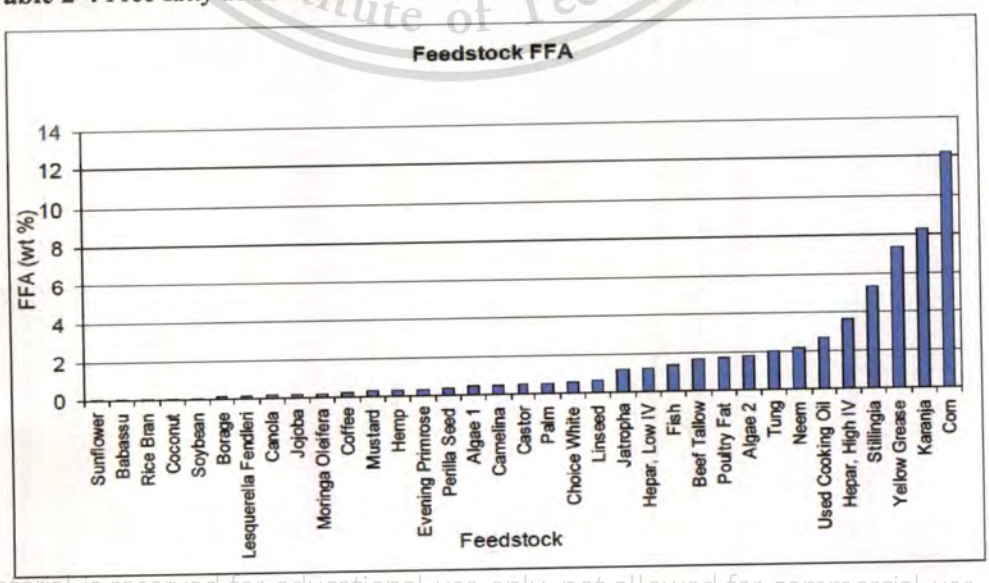
Fatty acids can be bound or attached to other molecules, such as in triglycerides or phospholipids. When they are not attached to other molecules, they are known as "free" fatty acids.

The uncombined fatty acids or free fatty acids may come from the breakdown of a triglyceride into its components (fatty acids and glycerol). However, as fats are insoluble in water, they must be bound to appropriate regions in the plasma protein albumin for transport around the body. The levels of "free fatty acid" in the blood are limited by the number of albumin binding sites available.

Free fatty acids are an important source of fuel for many tissues since they can yield relatively large quantities of ATP. Many cell types can use either glucose or fatty acids for this purpose. In particular, heart and skeletal muscle prefer fatty acids. The brain cannot use fatty acids as a source of fuel; it relies on glucose, or on ketone bodies. Ketone bodies are produced in the liver by fatty acid metabolism during periods of fasting, starvation, or otherwise low carbohydrate intake.

The FFA and water content have significant effects on the transesterification reaction negatively. They also interfere with the separation of fatty acid esters and glycerol. Especially, the viscosity of the oil increases considerably, because of the formation of dimeric and polymeric acids and glycerides in used cooking oils. Free fatty acids value for various feedstocks of biodiesel production is shown in Table 2-4.

Table 2-4 Free fatty acids value for various feedstocks of biodiesel production



2.3 Waste cooking oil [12]

Huge quantities of waste cooking oils and animal fats are available throughout the world, especially in the developed countries. Management of such oils and fats pose a significant challenge because of their disposal problems and possible contamination of the water and land resources. Even though some of this waste cooking oil is used for soap production, a major part of it is discharged into the environment. The Energy Information Administration in the United States estimated that some 100 million gallons of waste cooking oil is produced per day in USA, where the average *per capita* waste cooking oil was reported to be 9 pounds. The *per capita* waste cooking oil production in Canada may be somewhat similar to that of the United States, hence for this study, it is assumed that the *per capita* waste cooking oil production to be 9 pounds *per* year. Statistics Canada estimated the total population of Canada to be 33 million. Hence, the total waste cooking oil produced in Canada could be approximately 135,000 tons/year. In the EU countries, the total waste cooking oil production was approximately 700,000-1,000,000 tons/yr. The UK produces over 200,000 tons of waste cooking oil per year. As large amounts of waste cooking oils are illegally dumped into rivers and landfills, causing environmental pollution, the use of waste cooking oil to produce biodiesel as petrodiesel substitute offers significant advantages because of the reduction in environmental pollution.

Diesel fuel consumption significantly contributes to the formation of greenhouse gases (GHG) and other global pollutant emissions. Klass pointed out that petroleum diesel is also the major source for the emission of NOx, SOx, CO, particulate matter and volatile organic compounds (VOCs). Emission of such pollutants not only has negative impacts to the global environment but also severe impacts in human health due to their persistence in the environment.

It is reported that Canada alone utilizes approximately 23 million tons of diesel annually and 46% of this is utilized in the transportation sector. The global consumption of diesel fuel per year is approximately 934 million tons per year and the United States alone consumes 178 million tons of diesel fuel annually. If Canada plans a 5% mix in the total diesel consumption as a renewable portfolio standard (RPS) requirement, which is, approximately 1.15 million tons per year, a substantial portion of this requirement can be replaced by using biodiesel produced from waste cooking oil. The use of waste cooking oil as a biodiesel source has a potential to reduce CO2, particulate matter and other greenhouse gases as the carbon contained in biomass-derived fuel is largely biogenic and renewable.

Waste cooking oil, which is otherwise wasted, is one of the most economical choices to produce biodiesel. Since one of the major concerns on biodiesel production is the price of feedstock, utilization of waste cooking oil significantly enhances the economic viability of biodiesel production. Properties of waste cooking oil and ester batches are shown in Table 2-5. And the comparison of properties of diesel, canola oil and commercial US biodiesel are shown in Table 2-6.

Table 2-5: Properties of waste cooking oil and ester batches [13]

Batch no.	Range	Average	Specification
Acid value of oil	1.9-7.4	5.3	
Yield before washing (%)	63-87	78.3	
Yield after drying (%)	59-86	73.0	
Methyl ester properties			
Acid value[i]	0.02 - 0.73	0.28	<0.5*
Iodine no.[i]	99 - 118	105	<115*
Free glycerol (%)	0 - 0.02	0.0075	<.03*
Total glycerol (%)[ii]	0.10 - 0.57	0.24	<0.25*
Methanol content (%)	0 - 0.15	0.04	<0.3*
Water content (%)	0.07 - 0.19	0.11	<.05*
Density (g/cm^3)	0.877 - 0.888	.883	0.86-0.9*
Kin. viscosity, 40°C (cSt)	4.6 - 5.1	4.86	3.5-5.0*
CFPP (^{0}C)	0 to -14	-5.3	<0 summer*, <-15 winter*
Ash content (%)	0 - 0.019	0.007	0.01*
CCR (%), 100% dist. res[iii]	0.04 - 0.14	0.090	0.1**

i Methods recommended in EU draft specification (Commission of European Communities, 1993)

ii Handbook of analytical methods for methyl esters used as diesel substitutes, FICHTE, Vienna.

iii Determined in the laboratories of Bundesanstalt für Landtechnik, Wieselburg, Austria

* Commission of European Communities (1993)

**O Norm C 1190 (1995)

Table 2-6 Comparison of properties of diesel, canola oil and commercial US biodiesel. [14]

	Diesel	**Canola Oil**	**Biodiesel**
Density kgL^{-1} @ 15.5° C	0.84	0.92	0.88
Calorific value MJL^{-1}	38.3	36.9	33 – 40
Viscosity mm^{2}s^{-1} @ 20°C	4 - 5	70	4 – 6
Viscosity mm^{2}s^{-1} @ 40°C	4 - 5	37	4 – 6
Viscosity mm^{2}s^{-1} @ 70°C		10	
Cetane number	45	~ 40 - 50	45 – 65

2.4 Ion Exchange resin

Ion exchange materials are insoluble substances containing loosely held ions which are able to be exchanged with other ions in solutions which come in contact with them. These exchanges take place without any physical alteration to the ion exchange material. Ion exchangers are insoluble acids or bases which have salts which are also insoluble, and this enables them to exchange either positively charged ions (cation exchangers) or negatively charged ones (anion exchangers). Many natural substances such as proteins, cellulose, living cells and soil particles exhibit ion exchange properties which play an important role in the way the function in nature.

Synthetic ion exchange materials based on coal and phenolic resins were first introduced for industrial use during the 1930's. A few years later resins consisting of polystyrene with sulphonate groups to form cation exchangers or amine groups to form anion exchangers were developed (**Figure 1 and 2**). These two kinds of resin are still the most commonly used resins today.

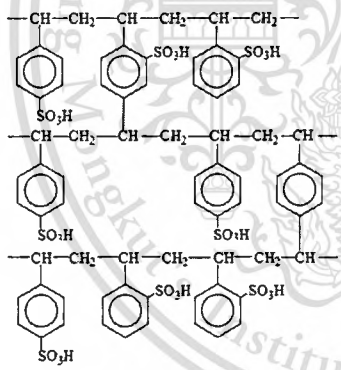


Figure 2-5. A strongly acidic sulphonate polystyrene cation exchange resin

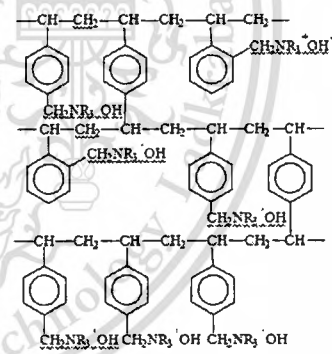


Figure 2-6. A strongly basic quaternary ammonion anion exchange resin

The order of affinity for some common cations is approximately:

$$Hg^{2+} < Li^{+} < H^{+} < Na^{+} < K^{+} \approx NH_4^{+} < Cs^{+} < Ag^{+} < Mn^{2+} < Mg^{2+} < Zn^{2+} < Cu^{2+} < Ni^{2+} < Co^{2+} < Ca^{2+} < Sr^{2+} < Pb^{2+} < Al^{3+} < Fe^{3+}$$

A corresponding list for amine based anion exchangers is:

$$OH^{-} \approx F^{-} < HCO_3^{-} < Cl^{-} < Br^{-} < NO_3^{-} < HSO_4^{-} < PO_4^{3-} < CrO_4^{2-} < SO_4^{2-}$$

A bed of resin can be used either to remove unwanted ions from a solution passed through it or to accumulate a valuable mineral from the water which can later be recovered from the resin. Examples of the removal of unwanted ions are the removal of heavy metals from metal trade wastes, the demineralistion of the whey used to manufacture specialized dairy products and the removal of salts from fruit juices.

Strong cation resins in the hydrogen form are used for the hydrolysis of starch and sucrose. Resins also find many uses in the laboratory where the chemist's ingenuity is less constrained by economic considerations. They can be used to remove interfering ions during analysis or to accumulate trace quantities of ions from dilute solutions after which they can be concentrated into a small volume by elution. A cation resin in the hydrogen form can be used to determine the total concentration of ions in a mixture of salts. The sample passing through a column is converted to the equivalent quantity of acid and the amount readily found by titration.

2.4.1 Cation-exchange resin

Ion-exchange resins are insoluble macroporous polymer that is capable to exchange specific ions within the polymer itself with other ions in a solution or reaction media. Normally, sulfonic ion-exchange resins are co-polymers of divinylbenzene (DVB), styrene and sulfonic acid groups (as the active sites-Brønsted acidity) (Özbay et al., 2008). The polymer structure of the resin is mainly characterized by the composition of the cross-linking component (normally DVB), which will then determine its surface area and pore size distribution (Pääkkönen and Krause, 2003). Besides that, their catalytic activity is also strongly dependent on their swelling properties because the swelling capacity limits reactant accessibility to the acid sites and thus affects their overall activity (Feng et al., 2010). Common types of acidic ion-exchange resin are such as Amberlyst-15, Amberlyst-35 and Nafion SAC-13. These catalysts were reported to give good performance in FFA esterification, but, weak in transesterification (Chen et al., 1999; Vicente et al., 1998). The Example of cation exchange resin is shown in Fig.2-7.

Figure 2-7.
Example of cation exchange resin.

Application of Amberlyst-15 with acidic functional groups has exhibited excellent catalytic activity in esterification reaction. Kiss et al. tested the activity of several solid acid catalysts in the esterification of dodecanoic acid with 2-ethylhexanol at 150 °C. Amberlyst-15 was found to require the least reaction time to achieve 90% conversion compared to sulfated zirconia and Nafion-NR50. Similar good results in esterification by using acidic Amberlyst-15 were also reported by Heidekum et al. (1999) and Chen et al. (1999). However, Amberlyst-15 was found to give low performance in transesterification reaction. At a relative low reaction temperature (60 °C), the conversion of sunflower oil to FAME was reported to be only 0.7%, using the following reaction conditions: atmospheric pressure for 8 h reaction time and 6:1 methanol to oil molar ratio (Vicente et al., 1998). In another study, Dos Reis et al. reported the transesterification of Babassu coconut oil using Amberlyst-15 (Dos Reis et al., 2005). It was reported that a rather good triglycerides conversion of 80% can be achieved only if the methanol to oil ratio used is increased to 100:1. The reaction temperature and time are at 60 °C and 8 h respectively. This finding was rather expected as the activity of solid acid catalysts in transesterification is normally low at low reaction temperature.

Consequently, if Amberlyst-15 is to be used, it is necessary to increase the reaction temperature to 150–200 °C to obtain sufficiently fast reaction rate. However, most ion-exchange resins such as Amberlyst-15 have low thermal stability and become unstable at temperature above 140 °C (Lotero et al., 2005). Thus, this problem certainly limits their application to reactions that require high temperatures. Study regarding the deactivation of polystyrene sulfonic acid resins in esterification of high FFAs oils at a higher reaction temperature was reported and discussed extensively by Tesser et al. (2005).

2.4.2 Amberlyst15 [5]

Amberlyst-15wet is a macroreticular resin based on crosslinked styrene divinylbenzene copolymers, strongly acidic, sulfonic acid, and polymeric catalyst. Its continuous open pore structure makes it an excellent heterogeneous acid catalyst for a wide variety of organic reaction. Amberlyst-15wet catalysts' polymeric structure is extremely resistant to breakdown by osmotic, mechanical and thermal shock. It also chloride, oxygen and chromates than most other polymeric catalysts. Amberlyst-15wet can be used directly in aqueous systems or in organic media after conditioning with a water miscible solvent. It has the optimal balance of surface area, acid capacity and pore diameter to make it the catalyst of choice for etherification (MTBE, ETBE,

TAME), esterification and hydration reactions. And it can also be used for chemical processing applications to remove impurities (metal ions) and basic organic compounds (amines, etc.) from aqueous and non-aqueous environment (appropriate pretreatment required). The Typical Properties of Amberlyst-15wet are shown in Table 2-7. And Suggested operating condition are shown in Table 2-8 and Table 2-9.

Table 2-7 Typical Properties of Amberlyst-15wet

Physical form	Opaque beads
Ionic form as shipped	Hydrogen
Concentration of active sites [1]	≥ 1.7 eq/L ≤ 4.7 eq/kg
Moisture holding capacity [1]	52 to 57% (H^+ form)
Shipping weight	770 g/L (48 lbs/ft^3)
Particle size	
Uniformity coefficient	≤ 1.70
Harmonic mean size	0.600 to 0.850 mm
Fines content [1]	< 0.355 mm : 1.0% max
Coarse beads	> 1.180 mm : 5.0% max
Nitrogen BET	
Surface area	53 m^2/g
Average pore diameter	300 Å
Total pore volume	0.40 ml/g
Shrinkage	Water to methanol: 5%
	Water to MTBE: 9%
	Water to hexane: 22%
	Water to dry: 37%

[1] *Contractual value*
Test methods are available on request.

Table 2-8 Suggested operating condition

Suggested Operating Conditions	
Maximum operating temperature	120°C (250°F)
Minimum bed depth	1000 mm (39 inches)
Operating flow rate	1 to 5 BV*/h (LHSV)
Pressure drop limitation	1 bar (15 psig) across the bed

** 1 BV = 1 m^3 solution per m^3 of resin*

Amberlyst-15wet can be used for processes where ionic or organic impurities have to be removed or recovered from process liquor. Both cationic and anionic compounds can be removed through either ionic or adsorptive interaction of the polymers and its acidic group with the impurity. Its excellent resistance against oxidation makes it a superior resin in many applications.

Table 2-9 Suggested operating condition

pH range		0 to 14	
Maximum operating temperature		120 °C (250 °F)	
Minimum bed depth		1000 mm (39 inches)	
Service flow rate		1 to 40 BV/h (0.125 to 5 gpm/ft^3)	
Regenerants		**HCl**	**H_2SO_4**
Flow rate	(BV/h)	4 to 8	4 to 8
Flow rate	(gpm/ft^3)	0.5 to 1.0	0.5 to 1.0
Concentration	(%)	4 to 10	1 to 5
Level	(g/L)	40 to 100	40 to 200
Level	(lbs/ft^3)	2.5 to 6	2.5 to 12
Minimum contact time		30 minutes	
Slow rinse		2 BV (15 gal/ft^3) at regeneration flow rate	
Fast rinse		2 to 4 BV (15 to 30 gal/ft^3) at service flow rate	

2.4.3 Water Filter Resin

Resin filters consist of a module that contains resins that can remove contaminants such as lead and other heavy metals, as well as minerals that cause deposits in kettles and coffee makers. These contaminants have an electrical charge and are removed by attaching to an opposite charge found on the resin. Resin filters can be combined with activated carbon filters to remove a wide range of particles and dissolved substances.

2.4.4 Regenerating an Ion-exchange resin

As stated earlier, an ion-exchange resin in industrial use is usually regenerated every 12 to 48 hours. Depending on the use of the resin, this can be done in several different ways, each with their own advantages and disadvantages depending on both chemical and economic factors.

Regeneration is important because reducing the regenerant level lowers water quality by allowing a small proportion of the ions which are being taken up by the resin to slip through without exchange. For example, with twin bed deionisers, incomplete regeneration of the cation resin to the hydrogen form allows leakage of some sodium (the least held of the cations commonly found in natural supplies) into water passing to the anion exchange vessel. Consequently the water leaving the anion unit still contains this sodium in the form of sodium hydroxide solutions usually of pH 8 to 9. However, the excessive amounts of regenerant required for complete regeneration means that this is rarely practical. In practice a

compromise is usually reached, and commonly resins are regenerated to about two thirds of the total capacity. In addition, for many uses total purification is not necessary. For example, the water with a pH of 8 to 9 mentioned earlier is highly suitable for use in boilers, as they require slightly alkaline water.

Some impurities such as silica can only be removed by a strongly basic resin. For example, dissolved silica is a major component of most water supplies. Normally it exists as a neutral polymer, and it becomes negatively charged only at high pH levels. This means that it can only be removed from water in the highly alkaline environment of a strong base resin in the hydroxyl form.

The exchange process is often made more efficient by introducing the regenerant at the bottom of the resin column and passing it upwards through the bed (counter current regeneration). This ensures that the resin at the bottom becomes more highly regenerated than that above it. Treated water leaving the column flowing downwards then comes in contact with this resin last and undergoes the highest possible degree of exchange.

2.4.5 Advantages and Disadvantages in the use of ion-exchange resins

The advantages of ion exchange processes are the very low running costs. Very little energy is required, the regenerant chemicals are cheap and if well maintained resin beds can last for many years before replacement is needed. There are, however, a number of limitations which must be taken into account very carefully during the design stages. When these limitations itemized appear to represent a formidable list and the impression can be given that ion exchange methods might have too many short comings to useful in practice. However, this is not the case as the advantages mentioned above are very great and compensation can readily be made for most restrictions.

2.5 Factors effect on transesterifacation process [18]

The main factors affecting transesterification are the molar ratio of glycerides to alcohol, catalyst, reaction temperature and pressure, reaction time and the contents of FFAs and water in oils.

2.5.1 Effect of molar ratio and alcohol type

The molar ratio of alcohol to oil is one of the most important variables influencing the conversion into esters. Although the stoichiometric molar ratio of methanol to triglyceride for transesterification is 3:1, higher molar ratios are used to enhance the solubility and to increase the contact between the triglyceride and alcohol molecules. A higher molar ratio is required to drive the reaction to complete at a faster rate. The molar ratio of 6:1 or higher generally gives the maximum yield (higher than 98 wt. %). Lower molar ratios require a longer time to complete the reaction. With higher molar ratios production is increased but recovery is decreased due to poor separation of glycerol. At optimum molar ratio only the process gives higher yield and easier separation of the glycerol. The optimum molar ratios depend on the type and quality of the vegetable oil used.

Acid-catalyzed reactions require the use of high alcohol-to-oil molar ratios in order to obtain good product yields in practical reaction times. However, ester yields do not proportionally increase with molar ratio. For instance, for soybean methanolysis using sulfuric acid, ester formation sharply improved from 77% using a methanol-to-oil ratio of 3.3:1–87.8% with a ratio of 6:1. Higher molar ratios showed only moderate improvement until reaching a maximum value at a 30:1 ratio (98.4%).

Another important variable affecting the yield of ester is the type of alcohol to triglyceride. In general, short chain alcohols such as methanol, ethanol, propanol, and butanol can be used in the transesterification reaction to obtain high methyl ester yields. Canakci and Van Gerpen investigated the effect of different alcohol types on acid-catalyzed transesterification of pure soybean oil.

2.5.2 Effect of water and FFA contents

The water and FFA content are key parameters for determining the viability of the vegetable oil transesterification process. In the base-catalyzed transesterification process, the acid value of the vegetable oil should be less than 1 and all materials should be substantially anhydrous. If acid value is greater than 1, more alkali is injected to neutralize the FFAs. The

presence water has a greater negative effect than that of the FFAs. Water can cause soap formation and frothing. The resulting soaps can induce an increase in viscosity, formation of gels and foams, and made the separation of glycerol difficult.

Table 2-10 Comparison of the yields in alkaline-catalyzed, acid-catalyzed and supercritical methanol **[19]**

Raw material	FFA[a] content (wt.%)	Water content (wt.%)	Yields of methyl esters (wt.%)		
			Alkaline-catalyzed	Acid-catalyzed	SCM[b]
Rapeseed oil	2.0	0.02	97.0	98.4	98.5
Palm oil	5.3	2.1	94.4	97.8	98.9
Frying oil	5.6	0.2	94.1	97.8	96.9
Waste palm oil	>20.0	>61.0	-	-	95.8

[a] FFA - free fatty acid.
[b] SCM - supercritical methanol.

In the conventional transesterification of fats and vegetable oils for biodiesel production, free fatty acids and water always produce negative effects since the presence of free fatty acids and water causes soap formation consumes catalyst and reduces catalyst effectiveness. In catalyzed methods, the presence of water has negative effects on the yields of methyl esters. However, the presence of water affected positively the formation of methyl esters in supercritical methanol method. Recently, Kusdiana and Saka studied the effect of water on the yield of methyl esters by the supercritical methanol treatment (623 K, 43 MPa, 4 min of treatment with a methanol to oil molar ratio of 42:1) compared with those from alkaline- and acid-catalyzed method. In the supercritical methanol method the amount of water added into the reaction system did not have a significant effect on the conversion. Effects of water and FFA contents on the alkaline- and acid-catalyzed and supercritical transesterification of triglycerides are shown in Figures.2-8 and 2-9.

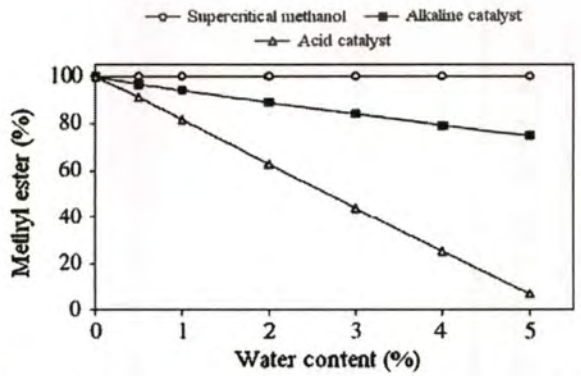


Figure 2-8 Yields of methyl esters as a function of water content in transesterification of triglycerides

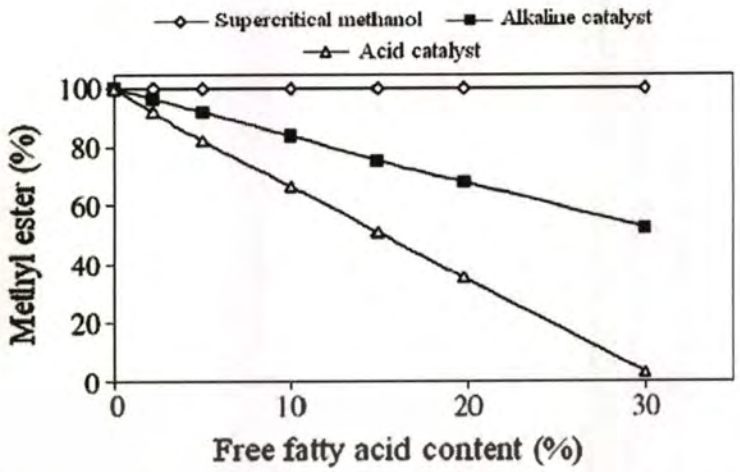


Figure 2-9 Yields of methyl esters as a function of free fatty acid content in transesterification of triglycerides

2.5.3 Effect of reaction temperature and time.

The reaction temperature influences the reaction rate and yield of ester. Therefore, generally the reaction is conducted close to the boiling point of methanol, 318–338 K at atmospheric pressure. Further increase in temperature is reported to have a negative effect on the conversion. Iso et al. examined the effect of reaction temperature on production of propyl oleate at the temperature range from 313 K to 343 K with free P. fluorescens lipase. In this study, the conversion ratio to propyl oleate was observed highest at 333 K, whereas the activity highly decreased at 343 K. Foon et al. studied the effect of temperature on the transesterification of palm oil using a molar ratio of oil to methanol of 1:10, catalyzed by NaOMe and NaOH, and at 323 K, 333 K and 343 K, respectively. For reactions using NaOH, the effect of temperature was more significant. For the NaOH catalyzed reactions, it is best to carry them out at 333 K. Darnokol et al. [studied transesterification of palm oil with methanol (6:1) and 1% KOH at different reaction temperatures. According to study results, the best yield was obtained at 338 K (82%). Effect of temperature on the ethyl esters production from soybean oil in propane medium with lipase from Yarrowia lipolytica was investigated by Hildebrand et al. The experiments were performed in the temperature range of 308–338 K at 50 bar, enzyme concentration of 5 wt.%, oil to ethanol molar ratio of 1:6, and solvent to substrates mass ratio of 2:1. Fig. 12 presents the results of these experiments.

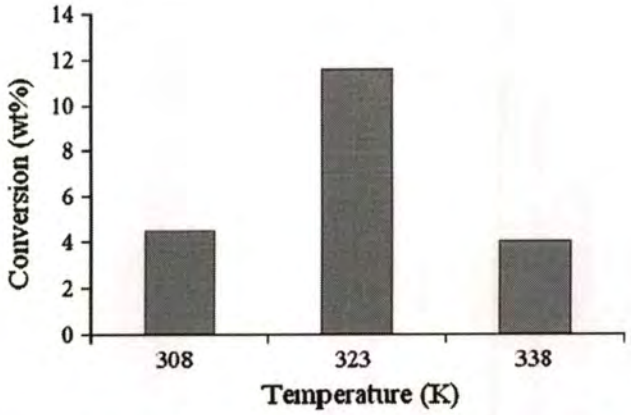


Figure 2-10. Effect of temperature on the ethyl esters production from soybean oil in propane medium with lipase from Yarrowia lipolytica

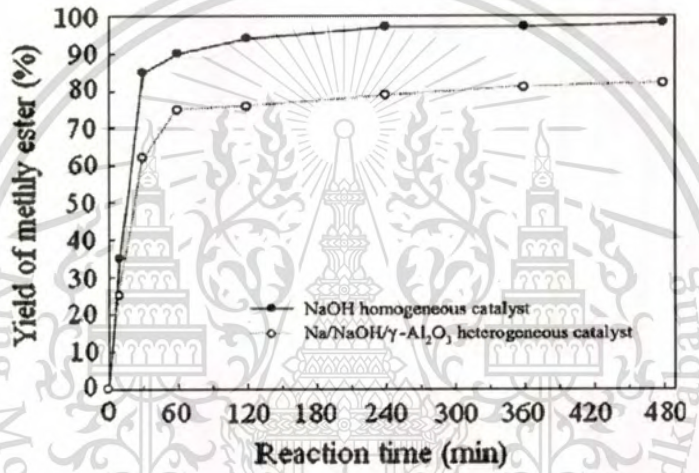


Figure 2-11. Effect of reaction time on the biodiesel production yield. Methanol/VO molar ratio 6:1, reaction temperature 333 K, stirring speed 300 rpm, without co-solvent.

The methyl ester conversion rate increases with the reaction time. Different researchers have reported different reaction times for the transesterification process. Kim et al. studied the transesterification reaction, with methanol (6:1), of vegetable oils using NaOH and Na/NaOH/c-Al2O3 as catalysts at 333 K. They reached the maximum biodiesel yield within 1 h. both for the case of homogeneous and heterogeneous catalyst system. For the homogeneous catalyst system, the maximum biodiesel production yield was higher by 20% than that of the heterogeneous catalyst system. Results of this study are shown in Fig. 2-11. Demirbas investigated the changes in yield percentage of methyl esters as treated with subcritical and supercritical methanol at different temperatures as a function of reaction time

2.5.4 Effect of catalyst content and type.

Catalysts used for the transesterification of triglycerides are classified as alkali, acid, enzyme. Alkali-catalyzed transesterification is much faster than acid-catalyzed transesterification and is most often used commercially. Stavarache et al. investigated the effect of different catalyst concentrations on base-catalyzed transesterification during biodiesel production from vegetable oil by means of ultrasonic energy. The best yields were obtained when the catalyst was used in small concentration, i.e. 0.5% wt/wt of oil. The effect of different catalysts types on methanolysis of RBD palm oil with a low FFA content of <0.1% was examined by May. In that study, it was concluded that Na, NaOH and KOH are effective catalysts. Meneghetti et al.investigated the effect of different catalyst types at different temperatures during the production of free and bound ethyl ester from castor oil. Results of this study showed that HCl is much more effective than NaOH at higher reaction temperatures.

2.6 Instrument of catalyst and oil characterization

2.6.1 X-ray Diffraction (XRD)

What is X-ray Powder Diffraction (XRD)

X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. The analyzed material is finely ground, homogenized, and average bulk composition is determined. Diffraction diagram of X-ray diffraction (XRD) was shown in figure 2-12.

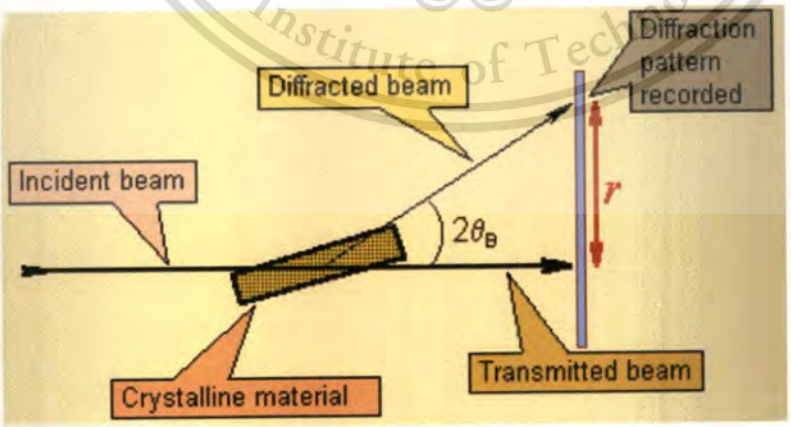


Figure 2-12. Diffraction diagram of X-ray diffraction (XRD)

2.6.1.1 Fundamental Principles of X-ray Powder Diffraction (XRD)

Max von Laue, in 1912, discovered that crystalline substances act as three-dimensional diffraction gratings for X-ray wavelengths similar to the spacing of planes in a crystal lattice. X-ray diffraction is now a common technique for the study of crystal structures and atomic spacing. X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy

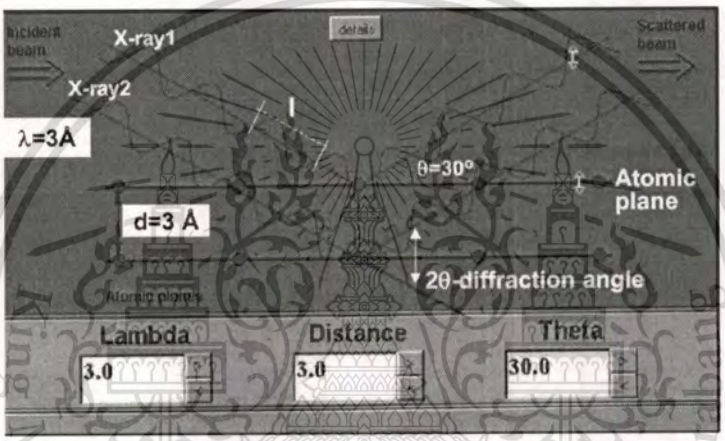


Figure 2-13. Bragg's Law ($n\lambda=2d \sin\theta$).

This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then detected, processed and counted. By scanning the sample through a range of 2θ angles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. Conversion of the diffraction peaks to d-spacings allows identification of the mineral because each mineral has a set of unique d-spacings. Typically, this is achieved by comparison of d-spacing with standard reference patterns.

All diffraction methods are based on generation of X-rays in an X-ray tube. These X-rays are directed at the sample, and the diffracted rays are collected. A key component of all diffraction is the angle between the incident and diffracted rays. Powder and single crystal diffraction vary in instrumentation beyond this.

2.6.1.2 X-ray Powder Diffraction (XRD) Instrumentation

X-ray diffractometers consist of three basic elements: an X-ray tube, a sample holder, and an X-ray detector. X-rays are generated in a cathode ray tube by heating a filament to produce electrons, accelerating the electrons toward a target by applying a voltage, and bombarding the target material with electrons. When electrons have sufficient energy to dislodge inner shell electrons of the target material, characteristic X-ray spectra are produced. These spectra consist of several components, the most common being K_α and K_β. K_α consists, in part, of K_{α_1} and K_{α_2}. K_{α_1} has a slightly shorter wavelength and twice the intensity as K_{α_2}. The specific wavelengths are characteristic of the target material (Cu, Fe, Mo, Cr). Filtering, by foils or crystal monochrometers, is required to produce monochromatic X-rays needed for diffraction. $K_{\alpha_1}$and K_{α_2} are sufficiently close in wavelength such that a weighted average of the two is used. Copper is the most common target material for single-crystal diffraction, with CuK_α radiation = 1.5418Å. These X-rays are collimated and directed onto the sample. As the sample and detector are rotated, the intensity of the reflected X-rays is recorded. When the geometry of the incident X-rays impinging the sample satisfies the Bragg Equation, constructive interference occurs and a peak in intensity occurs. A detector records and processes this X-ray signal and converts the signal to a count rate which is then output to a device such as a printer or computer monitor was shown in figure 2-14.

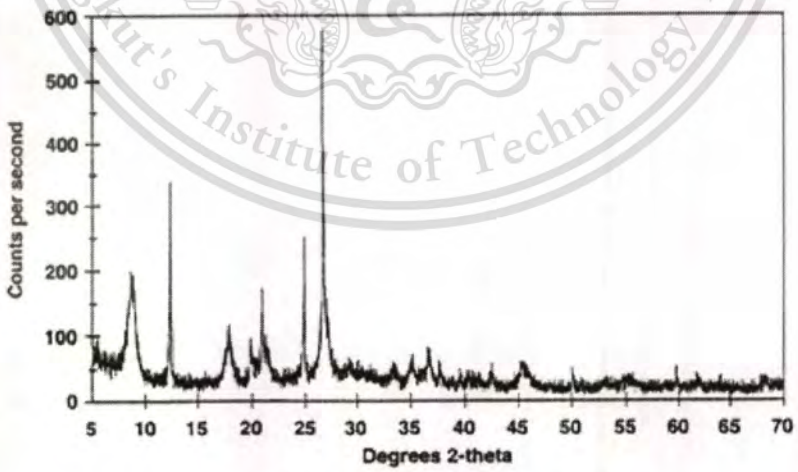


Figure 2-14. X-ray diffraction signal

The geometry of an X-ray diffractometer is such that the sample rotates in the path of the collimated X-ray beam at an angle θ while the X-ray detector is mounted on an arm to collect the diffracted X-rays and rotates at an angle of 2θ. The instrument used to maintain the angle and rotate the sample is termed a *goniometer*. For typical powder patterns, data is collected at 2θ from ~5° to 70°, angles that are preset in the X-ray scan.

2.6.1.3 Applications

X-ray powder diffraction is most widely used for the identification of unknown crystalline materials (e.g. minerals, inorganic compounds). Determination of unknown solids is critical to studies in geology, environmental science, material science, engineering and biology. Other applications include:

- characterization of crystalline materials
- identification of fine-grained minerals such as clays and mixed layer clays that are difficult to determine optically
- determination of unit cell dimensions
- measurement of sample purity

With specialized techniques, XRD can be used to:

- determine crystal structures using Rietveld refinement
- determine of modal amounts of minerals (quantitative analysis)
- characterize thin films samples
- make textural measurements, such as the orientation of grains, in a polycrystalline sample

Strengths

- Powerful and rapid (< 20 min) technique for identification of an unknown mineral
- In most cases, it provides an unambiguous mineral determination
- Minimal sample preparation is required
- XRD units are widely available
- Data interpretation is relatively straight forward

Limitations

- Homogeneous and single phase material is best for identification of an unknown
- Must have access to a standard reference file of inorganic compounds (d-spacings, *hkl*s)
- Requires tenths of a gram of material which must be ground into a powder
- For mixed materials, detection limit is ~ 2% of sample
- For unit cell determinations, indexing of patterns for non-isometric crystal systems is complicated
- Peak overlay may occur and worsens for high angle 'reflections'

2.6.2 Fourier Transform Infrared (FTIR)

FT-IR stands for Fourier Transform Infrared, the preferred method of infrared spectroscopy. In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through(transmitted)(Figure 2-15). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Like a fingerprint no two unique molecular structures produce the same infrared spectrum. This makes infrared spectroscopy useful for several types of analysis.

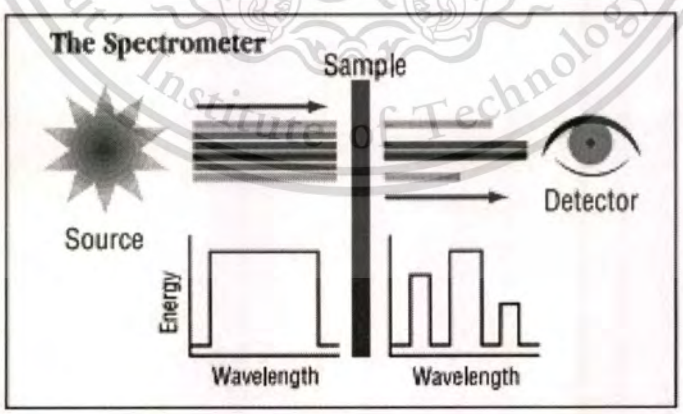


Figure 2-15. Absorption of infrared radiation by the sample

So, what information can FT-IR provide?

• It can identify unknown materials

• It can determine the quality or consistency of a sample

• It can determine the amount of components in a mixture

This booklet is an introduction to the concepts behind FT-IR spectroscopy. It covers both the basic theory of FT-IR and how it works as well as discussing some the practical aspects of FT-IR use. We hope that it gives you a good understanding of the importance and usefulness of this powerful technique.

Infrared spectroscopy has been a workhorse technique for materials analysis in the laboratory for over seventy years. An infrared spectrum represents a fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material. Because each different material is a unique combination of atoms, no two compounds produce the exact same infrared spectrum. Therefore, infrared spectroscopy can result in a positive identification (qualitative analysis) of every different kind of material. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present. With modern software algorithms, infrared is an excellent tool for quantitative analysis.

Fourier Transform Infrared (FT-IR) spectrometry was developed in order to overcome the limitations encountered with dispersive instruments. The main difficulty was the slow scanning process. A method for measuring all of the infrared frequencies simultaneously, rather than individually, was needed. A solution was developed which employed a very simple optical device called an interferometer.

The interferometer produces a unique type of signal which has all of the infrared frequencies "encoded" into it. The signal can be measured very quickly, usually on the order of one second or so. Thus, the time element per sample is reduced to a matter of a few seconds rather than several minutes.

Most interferometers employ a beam splitter which takes the incoming infrared beam and divides it into two optical beams. One beam reflects off of a flat mirror which is fixed in place. The other beam reflects off of a flat mirror which is on a mechanism which allows this mirror to move a very short distance (typically a few millimeters) away from the beam splitter. The two beams reflect off of their respective mirrors and are recombined when they meet back at the beam splitter. Because the path that one beam travels is a fixed length and the other is constantly changing as its mirror moves, the signal which exits the interferometer is the result of these two beams "interfering" with each other. The resulting signal is called an interferogram which has the unique property that every data point (a function of the moving mirror position) which makes up the signal has information about every infrared frequency which comes from the source.

This means that as the interferogram is measured, all frequencies are being measured simultaneously. Thus, the use of the interferometer results in extremely fast measurements.

Because the analyst requires a frequency spectrum (a plot of the intensity at each individual frequency) in order to make an identification, the measured interferogram signal can not be interpreted directly. A means of "decoding" the individual frequencies is required. This can be accomplished via a well-known mathematical technique called the Fourier transformation. This transformation is performed by the computer which then presents the user with the desired spectral information for analysis was shown in figure 2-16.

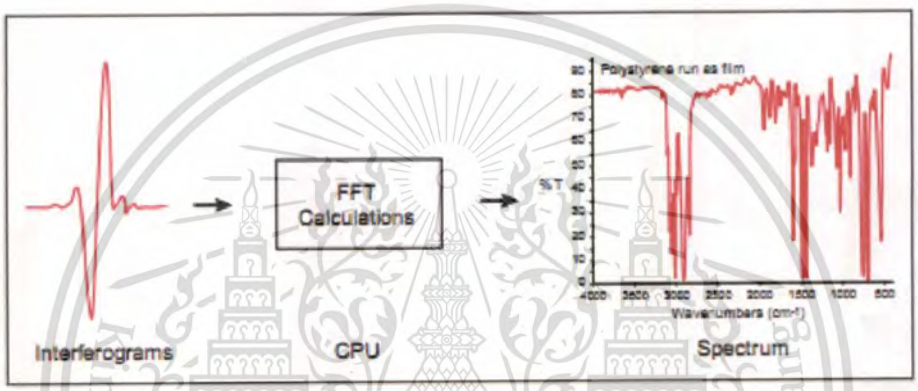


Figure 2-16 The transformation of interferograms to spectrum.

2.6.2.1 The Sample Analysis Process

The normal instrumental process is as follows:

1. The Source: Infrared energy is emitted from a glowing black-body source. This beam passes through an aperture which controls the amount of energy presented to the sample (and, ultimately, to the detector).

2. The Interferometer: The beam enters the interferometer where the "spectral encoding" takes place. The resulting interferogram signal then exits the interferometer.

3. The Sample: The beam enters the sample compartment where it is transmitted through or reflected

off of the surface of the sample, depending on the type of analysis being accomplished. This is where specific frequencies of energy, which are uniquely characteristic of the sample, are absorbed.

4. The Detector: The beam normally passes to the detector for final measurement. The detectors used are specially designed to measure the special interferogram signal.

4. The Detector: The beam normally passes to the detector for final measurement. The detectors used are specially designed to measure the special interferogram signal.

5. The Computer: The measured signal is digitized and sent to the computer where the Fourier transformation takes place. The final infrared spectrum is then presented to the user for interpretation and any further manipulation.

Because there needs to be a relative scale for the absorption intensity, a background spectrum must also be measured. This is normally a measurement with no sample in the beam. This can be compared to the measurement with the sample in the beam to determine the "percent transmittance." This technique results in a spectrum which has all of the instrumental characteristics removed. Thus, all spectral features which are present are strictly due to the sample. A single background measurement can be used for many sample measurements because this spectrum is characteristic of the instrument itself.

2.6.2.2 Advantages of FT-IR

Some of the major advantages of FT-IR over the dispersive technique include:

• Speed: Because all of the frequencies are measured simultaneously, most measurements by FT-IR are made in a matter of seconds rather than several minutes. This is sometimes referred to as the Felgett Advantage.

• Sensitivity: Sensitivity is dramatically improved with FT-IR for many reasons. The detectors employed are much more sensitive, the optical throughput is much higher (referred to as the Jacquinot Advantage) which results in much lower noise levels, and the fast scans enable the coaddition of several scans in order to reduce the random measurement noise to any desired level (referred to as signal averaging).

• Mechanical Simplicity: The moving mirror in the interferometer is the only continuously moving part in the instrument. Thus, there is very little possibility of mechanical breakdown.

• Internally Calibrated: These instruments employ a HeNe laser as an internal wavelength calibration standard (referred to as the Connes Advantage). These instruments are self-calibrating and never need to be calibrated by the user.

These advantages, along with several others, make measurements made by FT-IR extremely accurate and reproducible. Thus, it a very reliable technique for positive identification of virtually any sample. The sensitivity benefits enable identification of even the smallest of contaminants. This makes FT-IR an invaluable tool for quality control or quality assurance

wide variety of software algorithms, have dramatically increased the practical use of infrared for quantitative analysis. Quantitative methods can be easily developed and calibrated and can be incorporated into simple procedures for routine analysis.

Thus, the Fourier Transform Infrared (FT-IR) technique has brought significant practical advantages to infrared spectroscopy. It has made possible the development of many new sampling techniques which were designed to tackle challenging problems which were impossible by older technology. It has made the use of infrared analysis virtually limitless.

2.6.3 Gas chromatography–mass spectrometry (GC-MS)

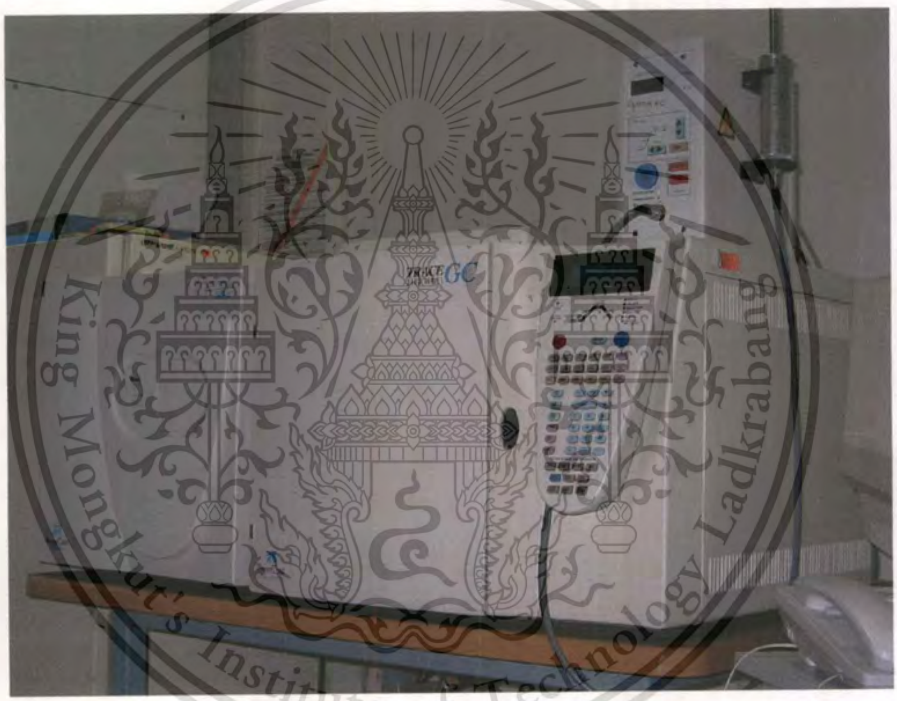


Figure 2-17. Gas chromatography–mass spectrometry (GC-MS)

Gas chromatography–mass spectrometry (GC-MS) (figure 2-17) is a method that combines the features of gas-liquid chromatography and mass spectrometry to identify different substances within a test sample. Applications of GC-MS include drug detection, fire investigation, environmental analysis, explosives investigation, and identification of unknown samples. GC-MS can also be used in airport security to detect substances in luggage or on human beings. Additionally, it can identify trace elements in materials that were previously thought to have disintegrated beyond identification.

beings. Additionally, it can identify trace elements in materials that were previously thought to have disintegrated beyond identification.

GC-MS has been widely heralded as a "gold standard" for forensic substance identification because it is used to perform a *specific test.* A specific test positively identifies the actual presence of a particular substance in a given sample. A *non-specific test* merely indicates that a substance falls into a category of substances. Although a non-specific test could statistically suggest the identity of the substance, this could lead to false positive identification.

2.6.3.1 Instrumentation

The GC-MS is composed of two major building blocks: the gas chromatograph and the mass spectrometer. The gas chromatograph utilizes a capillary column which depends on the column's dimensions (length, diameter, film thickness) as well as the phase properties (e.g. 5% phenyl polysiloxane). The difference in the chemical properties between different molecules in a mixture will separate the molecules as the sample travels the length of the column. The molecules take different amounts of time (called the retention time) to come out of (elute from) the gas chromatograph, and this allows the mass spectrometer downstream to capture, ionize, accelerate, deflect, and detect the ionized molecules separately. The mass spectrometer does this by breaking each molecule into ionized fragments and detecting these fragments using their mass to charge ratio.

These two components, used together, allow a much finer degree of substance identification than either unit used separately. It is not possible to make an accurate identification of a particular molecule by gas chromatography or mass spectrometry alone. The mass spectrometry process normally requires a very pure sample while gas chromatography using a traditional detector (e.g. Flame Ionization Detector) detects multiple molecules that happen to take the same amount of time to travel through the column (*i.e.* have the same retention time) which results in two or more molecules to co-elute. Sometimes two different molecules can also have a similar pattern of ionized fragments in a mass spectrometer (mass spectrum). Combining the two processes reduces the possibility of error, as it is extremely unlikely that two different molecules will behave in the same way in both a gas chromatograph and a mass spectrometer. Therefore, when an identifying mass spectrum appears at a characteristic retention time in a GC-MS analysis, it typically lends to increased certainty that the analyte of interest is in the sample.

Purge and Trap GC-MS

For the analysis of volatile compounds a Purge and Trap (P&T) concentrator system may be used to introduce samples. The target analytes are extracted and mixed with water and introduced into an airtight chamber. An inert gas such as Nitrogen (N_2) is bubbled through the water; this is known as purging. The volatile compounds move into the headspace above the water and are drawn along a pressure gradient (caused by the introduction of the purge gas) out of the chamber. The volatile compounds are drawn along a heated line onto a 'trap'. The trap is a column of adsorbent material at ambient temperature that holds the compounds by returning them to the liquid phase. The trap is then heated and the sample compounds are introduced to the GC-MS column via a volatiles interface, which is a split inlet system. P&T GC-MS is particularly suited to volatile organic compounds (VOCs) and BTEX compounds (aromatic compounds associated with petroleum)

2.6.3.2 Types of Mass Spectrometer Detectors

The most common type of mass spectrometer (MS) associated with a gas chromatograph (GC) is the quadrupole mass spectrometer, sometimes referred to by the Hewlett-Packard (now Agilent) trade name "Mass Selective Detector" (MSD). Another relatively common detector is the ion trap mass spectrometer. Additionally one may find a magnetic sector mass spectrometer, however these particular instruments are expensive and bulky and not typically found in high-throughput service laboratories. Other detectors may be encountered such as time of flight (TOF), tandem quadrupoles (MS-MS) (see below), or in the case of an ion trap MS^n where n indicates the number mass spectrometry stages.

2.6.3.3 Analysis

A mass spectrometer is typically utilized in one of two ways: Full Scan or Selective Ion Monitoring (SIM). The typical GC-MS instrument is capable of performing both functions either individually or concomitantly, depending on the setup of the particular instrument.

2.6.3.4 Full scan MS

When collecting data in the full scan mode, a target range of mass fragments is determined and put into the instrument's method. An example of a typical broad range of mass fragments to monitor would be *m/z* 50 to *m/z* 400. The determination of what range to use is largely dictated by what one anticipates being in the sample while being cognizant of the solvent and other possible interferences. A MS should not be set to look for mass fragments too low or

else one may detect air (found as *m/z* 28 due to nitrogen), carbon dioxide (*m/z* 44) or other possible interferences. Additionally if one is to use a large scan range then sensitivity of the instrument is decreased due to performing fewer scans per second since each scan will have to detect a wide range of mass fragments.

Full scan is useful in determining unknown compounds in a sample. It provides more information than SIM when it comes to confirming or resolving compounds in a sample. During instrument method development it may be common to first analyze test solutions in full scan mode to determine the retention time and the mass fragment fingerprint before moving to a SIM instrument method.

Related Literature

NalanOzbay and group [20]

Although WCO plays a crucial role for the economical production of biodiesel, free fatty acid (FFA) level in the nature of WCO cause saponification problems during transesterification. Acidic ion-exchange resins can be used to decrease WCO free fatty acid level. In this study, activities of resins (Amberlyst-15 (A-15), Amberlyst-35 (A-35), Amberlyst-16 (A-16) and Dowex HCR-W2) in direct FFA esterification were examined in the temperature range of 50–60 _C and the effect of catalyst amount (1–2 wt%) on FFA conversion was also analyzed. FFA conversion increased with increasing reaction temperature and catalyst amount. Order of catalytic activities was found as A-15 > A-35 > A-16 > Dowex HCR-W2. This was related to the size of average pore diameters and magnitude of BET surface area.

Ji-Yeon Park and group [21]

To produce biodiesel from high free fatty acid (FFA) oils, the esterification characteristics of two kinds of heterogeneous acid catalysts, Amberlyst-15 and Amberlyst-BD20, were compared. When the FFA contents of oils were 50.0 and 99.8 wt%, the activity of Amberlyst-15 gradually decreased with recycling, whereas the activity of Amberlyst-BD20 was maintained during recycling. The activity of Amberlyst-15 was inhibited by the water produced during the esterification process, but the activity of Amberlyst-BD20 was not similarly affected by water. In images obtained with a scanning electron microscope (SEM), many pores were seen within the Amberlyst-15 catalyst, whereas Amberlyst-BD20 showed few pores. Despite the fact that the pores of the catalyst play a role in increasing the number of active sites, Amberlyst-BD20, which had fewer pores, was deemed to have more desirable performance in reducing the inhibition by water of the esterification of high FFA oils.

Umer Rashid and group [22]

Present work reports an optimized protocol for the production of biodiesel through alkaline-catalyzed transesterification of rapeseed oil. The reaction variables used were methanol/oil molar ratio (3:1–21:1), catalyst concentration (0.25–1.50%), temperature (35–65 C), mixing intensity (180–600 rpm) and catalyst type. The evaluation of the transesterification process was followed by gas chromatographic analysis of the rapeseed oil fatty acid methyl esters (biodiesel) at different reaction times. The biodiesel with best yield and quality was produced at methanol/oil molar ratio, 6:1; potassium hydroxide catalyst concentration, 1.0%; mixing intensity, 600 rpm and reaction temperature 65 C. The yield of the biodiesel produced under optimal condition was 95–96%. It was noted that greater or lower the concentration of KOH or methanol than the optimal values, the reaction either did not fully occur or lead to soap formation.

The quality of the biodiesel produced was evaluated by the determinations of important properties such as density, specific gravity, kinematic viscosity, higher heating value, acid value, flash point, pour point, cloud point, combustion point, cold filter plugging point, cetane index, ash content, sulphur content, water content, copper strip corrosion value, distillation temperature and fatty acid composition. The produced biodiesel was found to exhibit fuel properties within the limits prescribed by the latest American Standards for Testing Material (ASTM) and European EN standards.

Chapter 3

Research Progression

3.1 Instrument and apparatus

1) 3 necked, round bottom flask
2) Magnetic bar
3) Hot plate stirrer
4) Condenser
5) Thermometer
6) 250 ml Erlenmeyer flask
7) Burette
8) Glass vial
9) Separation funnel
10) Graduated cylinder
11) Pipette
12) Beaker
13) Stirring rod
14) Electronic balance
15) Oil bath
16) Funnel
17) Gas chromatography –mass spectrometry (GC-MS)
18) Fourier Transform –Infrared Spectrometer; FT-IR Perkin Elmer model SPECTRUM GX (FTIR)
19) X-ray diffraction (XRD)

3.2 Chemicals

1) Waste cooking oil
2) Amberlyst-15 (Rohm and Haas Company) catalyst
3) Water filter resin
4) Methanol (AR grade, Lab-scan company)
5) Potassium hydroxide (AR grade, CARLO ERBA company)
6) Phenolphthalein (AR grade, CARLO ERBA company)
7) Sodium hydroxide (AR grade, Fisher Scientific company)
8) Ethanol (AR grade, CARLO ERBA company)
9) Paraffin liquid (for oil bath, Fisher Scientific company)
10) Distillation water

3.3 Procedure

3.3.1 Catalyst preparation

1) Place approximately 5 grams of resin in the funnel of the apparatus.

2) Convert this sample to the hydrogen form with 1 liter of 1M nitric acid.

3) Rinse the resin with distillation water until pH value is equal to pH value of distillation water.

4) Use the remaining sample to determine the solids content, drying at 110°C overnight.

3.3.2 Determination of exchange capacity

1) Weigh an approximately 1.0-gram (nearest mg.) of catalyst into a dry 250 mL. Erlenmeyer flask.

2) Use the remaining sample to determine the solids content, drying at 50°C about 2 h.

3) To the sample in the Erlenmeyer flask add exactly 200 mL. of standardized 0.1N sodium hydroxide solution hat has been prepared in 5% sodium chloride.

4) Allow the stoppered sample to stand overnight.

5) Back-titrate 50-mL. aliquots of the supernatant liquid to the phenolphthalein end point with standard 0.1N sodium hydroxide.

3.3.3 Source of waste cooking oil

- Used oil from frying sausage at fast-food restaurant King Mongkut' s Institute of Technology Ladkrabang.

3.3.4 Pre-treatment of waste cooking oil

Since waste cooking oil is used as raw material in the biodiesel production, it is necessary to treat the waste cooking oil by using vacuum filter with filter paper no.4. After that the waste cooking oil was heated at 120°C for 2 hour for water elimination.

3.3.5 Determination of free fatty acid existing in the waste cooking oil

1) Weight 5 g of the waste cooking oil into 250 mL Erlenmeyer flask.
2) Add 50 mL of Ethanol and shake to mix them.
3) Add 2-3 drops of Phenolphthalein and titrate with 0.05 M of Sodium hydroxide.
4) Record the volumes of NaOH used and repeat 2 times and average the results.

3.3.6 Esterification of waste cooking oil by using Amberlyst-15 and water filter resin

1) Stir 20 vol. % (34.2 mL) of methanol and various amount of catalyst (Table 3-1and Table 3-2) for 5 minutes.
2) Esterification reaction was performed in a 500 ml of 3 necks, round bottom flask equipped with condenser to avoid alcohol vaporization.
3) 3 necks, round bottom flask were immersed in oil bath. The hot plate stirrer was used to heat and control the stirring rate of reaction mixture.
4) Add methanol and catalyst from (1) and 200 g or 171 mL of waste cooking oil.
5) Samplings were done manually at reaction times every 30 minutes.

Table 3-1 : Various amount of catalyst, Reaction time and Temperature used to study the effect of Esterification reaction for reduce free fatty acid in waste cooking oil by Amberlyst-15

Catalyst	% catalyst (%wt oil)	Temperature (°C)	Reaction Time (min)
Amberlyst-15	0	50	30, 60, 90, 120, 150
		60	30, 60, 90, 120, 150
	2	50	30, 60, 90, 120, 150
		60	30, 60, 90, 120, 150
	4	50	30, 60, 90, 120, 150
		60	30, 60, 90, 120, 150

Table 3-2: Various amount of catalyst, Reaction time and Temperature used in study the effect of Esterification reaction for reduce free fatty acid in waste cooking oil by water filter resin

Catalyst	% catalyst (%wt oil)	Temperature (°C)	Reaction Time (min)
Water filter resin	0	50	30, 60, 90, 120, 150
		60	30, 60, 90, 120, 150
	2	50	30, 60, 90, 120, 150
		60	30, 60, 90, 120, 150
	4	50	30, 60, 90, 120, 150
		60	30, 60, 90, 120, 150

Chapter 4

Result and discussion

This research aim to study about the reduction of free fatty acid in waste cooking oil by esterification in laboratory scale and study throughout activity of cation exchange resin: Amberlyst15 and water filter resin in term of conversion. Then examine the effect of catalyst amount, reaction temperature, and reaction time on the esterification. Finally we study and determine the optimum condition of the esterification reaction.

4.1 Properties of catalyst: Amberlyst-15 and water filter resin.

Table 4-1. Result from the catalyst characterization.

Property	Amberlyst-15	Water filter resin
Exchange capacity (meq/g)	7.23	6.06
Structure	Sulfonated styrene divinyl benzene	Sulfonated styrene divinyl benzene
Orientation	Random (Amorphous)	Random (Amorphous)

4.1.1 The determination of exchange capacity of catalyst.

Table 4-2 Exchange capacity of Amberlyst-15 and water filter resin.

Catalyst	V_{NaOH} (mL)	Exchange capacity (meq/g)
Amberlyst-15	7.4	7.23
Water filter resin	3.0	6.06

The exchange capacity of catalyst were determine from the number of groups capable of exchanging cation is conveniently determined by converting the resin groups to the hydrogen with an excess of acid, rinsing to remove this excess acid and equilibrating the resin with a known excess of standard sodium hydroxide 0.1M.

From Table 4-2 The exchange capacity of Amberlyst-15 is equal 7.23 meq/g whereas the exchange capacity of water filter resin is equal to 6.06 meq/g.

Hence, the exchange capacity of Amberlyst-15 is higher than water filter resin.

4.1.2 The determination of structure of catalyst by using (FTIR)

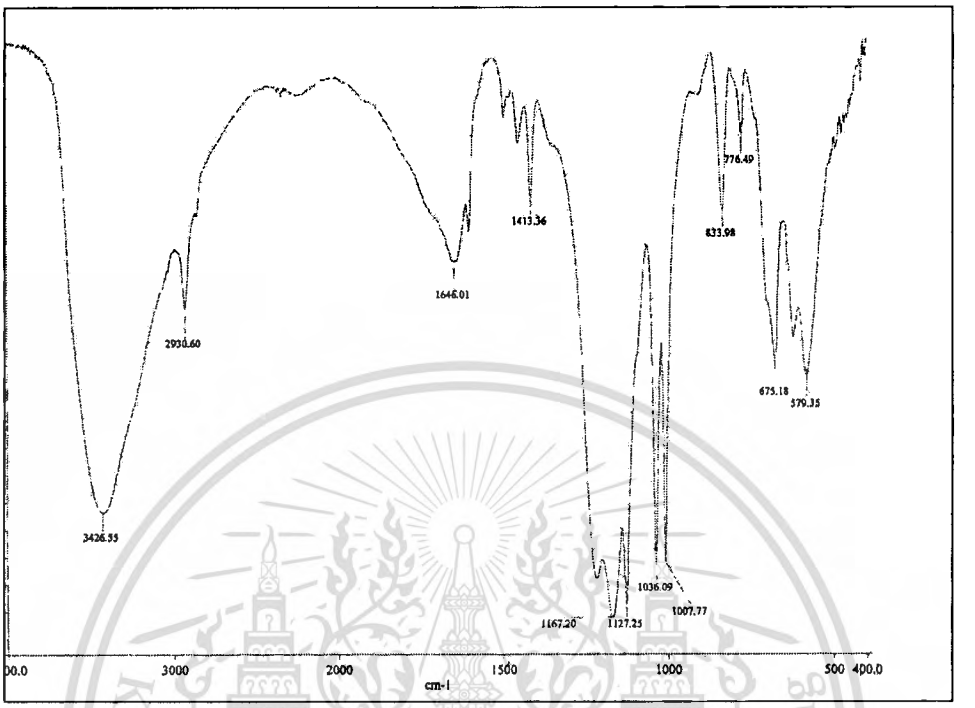


Figure 4-1. FT-IR spectrum of water filter resin

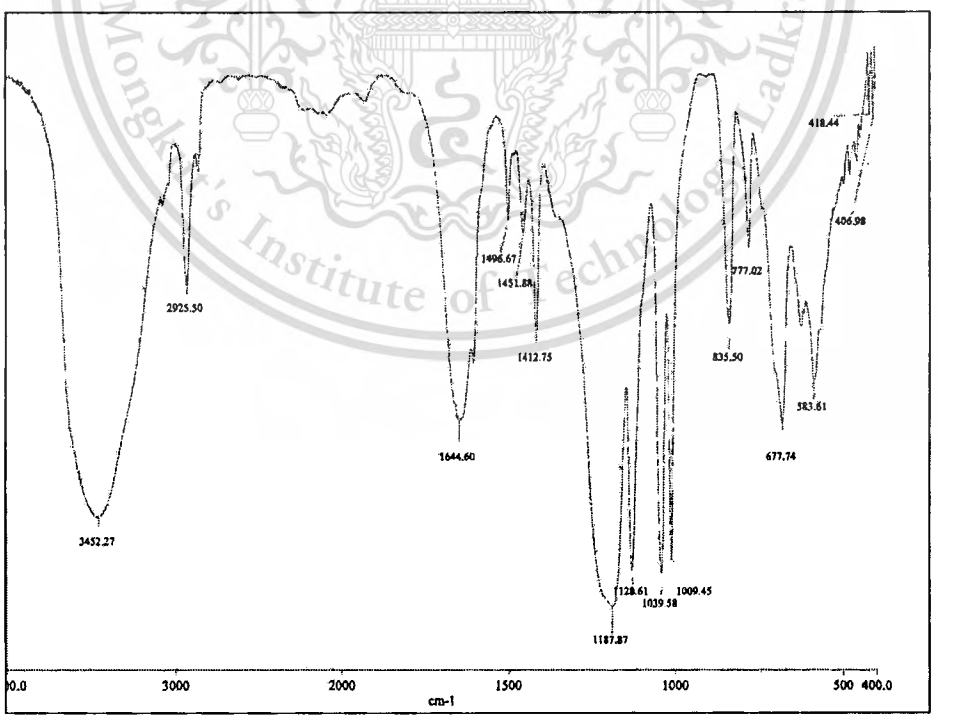


Figure 4-2. FT-IR spectrum of Amberlyst-15

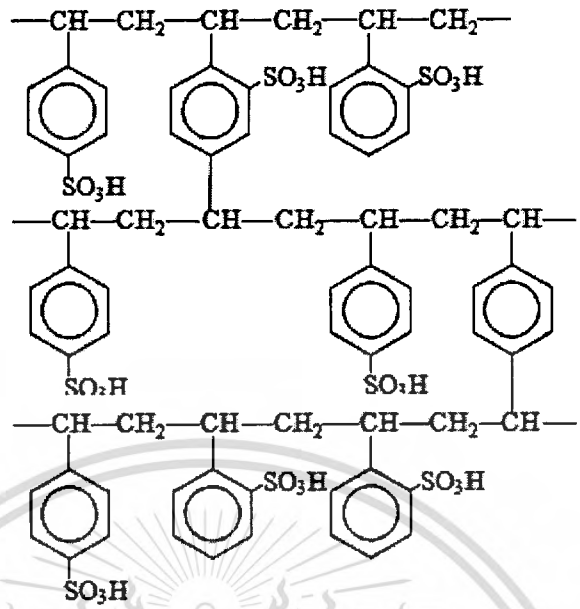


Figure 4-3. The strongly acidic sulfonated polystyrene cation exchange resin.

From the result of Fourier Transform Infrared Spectrometer (FT-IR), Figure 4-1 and Figure 4-2 showed the spectrum of Amberlyst-15 and water filter resin, respectively. It can be observed that they have similar peak which are reported in the appearance of two broad and strong peaks: one at 1300-1050 cm^{-1} assign to $-SO_3H$ groups; the second at 3500-3300 cm^{-1} assign to –OH stretching. In addition, there are four more important peaks: aliphatic C-H stretching at 3000-2800 cm^{-1}, C=C stretching at 1650 cm^{-1}, S-O stretching at 700-600 cm^{-1} and overtone or combination bands at 2000-1667 cm^{-1} to confirm the aromatic are in the structure.

Hence, it can be conclude that Amberlyst-15 and water filter resin have similar structure with sulfonated styrene divinyl benzene cation exchange resin which shown in figure. 4-3.

4.1.3 The characterization of catalyst by using X-ray diffraction (XRD)

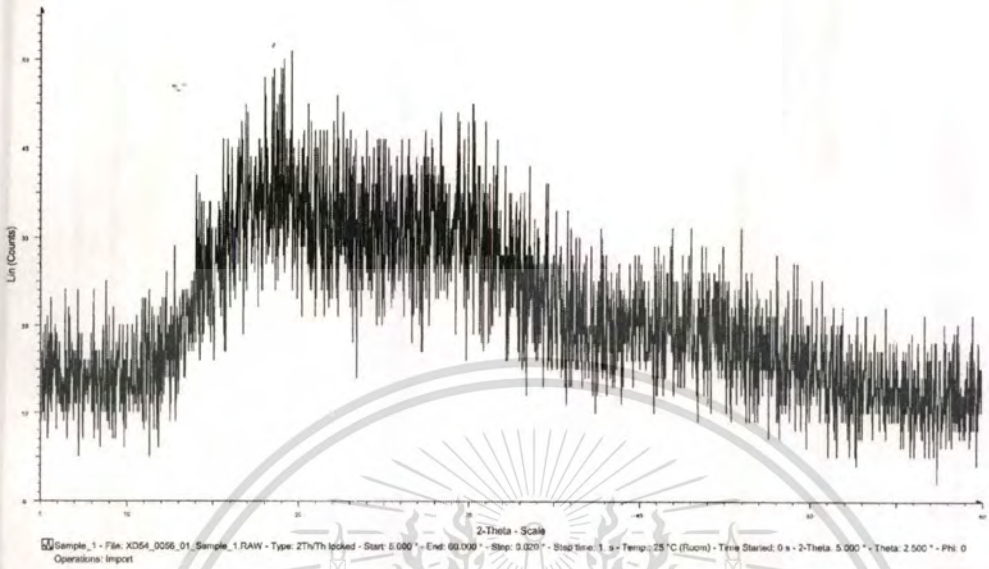


Figure 4-4. The XRD pattern of water filter resin.

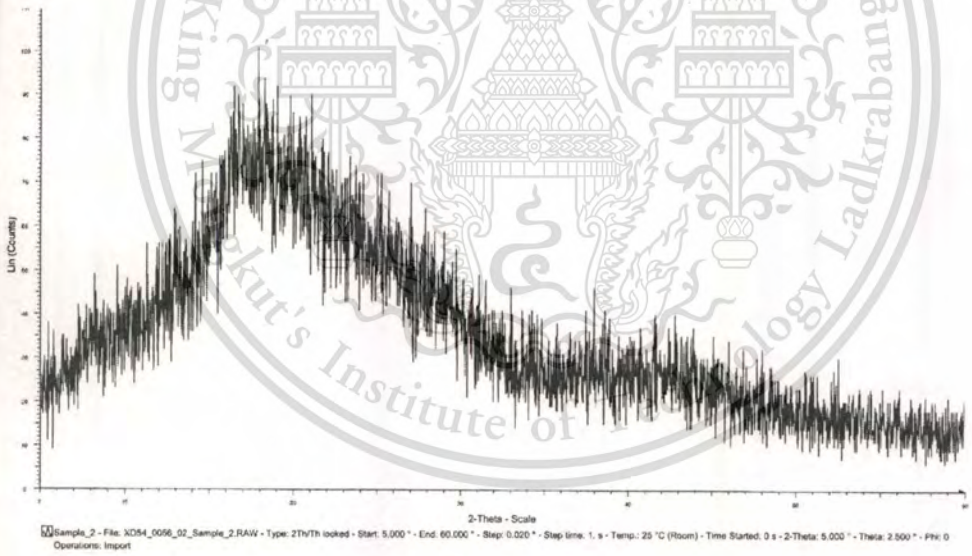


Figure 4-5. The XRD pattern of Amberlyst-15.

The Amberlyst-15 and water filter resin were determine the orientation of structure by using X-ray Diffraction (XRD), CuK_{α} radiation of wavelength 1.54 A and direction data were recorded from 5-60° 2-theta angles. From figure 4-4 and figure 4-5, both of Amberlyst-15 and water filter resin have the hump about 22, 2-Theta-scale. So it can be indicated that both of Amberlyst-15 and water filter resin were arranged in random orientation and amorphous structure.

4.2 The determination of component of free fatty acid in waste cooking oil by using Gas-Chromatography (GC-MS)

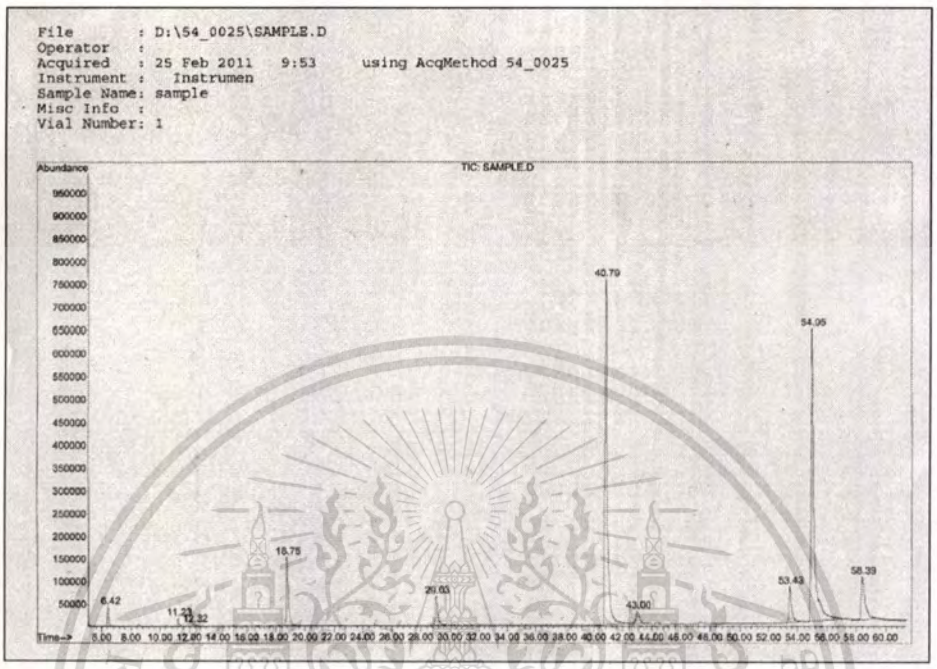


Figure 4-6. The components of free fatty acid in waste cooking oil before reduce free fatty acid in the peak form.

Table 4-3. The components of free fatty acid in waste cooking oil before reduce free fatty acid in the percentage.

Fatty acid	% of total
Octanoic acid	0.73
Decanoic acid	0.45
Glycerin	0.18
Lauric acid	6.01
Tetradecanoic acid	3.27
Palmitic acid	36.53
9-hexadecenoic acid	1.80
Steric acid	4.17
Oleic acid	39.35
Linoleic acid	7.45

Note: In-house Method : T-BC-01 based on AOAC 991.39(2005)

From Figure 4-6 and Table 4-3, the percentage of free fatty acid in form of oleic acid was 39.35% which is highest percentages. So the oleic acid is the main component of free fatty acid in waste cooking oil in this experiment.

4.3 The reduction of free fatty acid in waste cooking by esterification process using Amberlyst-15 and Water filter resin.

In this part free fatty acid in waste cooking oil was reported in form of oleic acid because oleic acid is the main component of in waste cooking oil, determine by titration with exactly concentration of 0.0505 M NaOH and compare the result of each catalyst in term of conversion of free fatty acid under the effect of temperature, time and amount of catalyst.

4.3.1 The determination of initial free fatty acid in waste cooking oil

Table 4-4 The initial free fatty acid value in waste cooking oil by titration.

Weight of oil (g)	NaOH used (mL)	%Free fatty acid (Oleic acid)
5.3420	32.60	8.70
5.3398	32.05	8.56
5.3406	32.30	8.60
Average		8.62

From the Table 4-4 the percentage of free fatty acid in from of oleic acid was 8.62%, which is the factor affecting the transesterifacation process due to the formation of soap. So before transesterification process, free fatty acid should be reduced to suitable amount by esterifacation process.

The reduction of free fatty acid in waste cooking oil was reduce through the esterification process (Figure 4-7), free fatty acid react with methanol by use acid as a catalyst and transform to ester product.

Figure 4-7. Esterification process

4.3.2 Effect of temperature

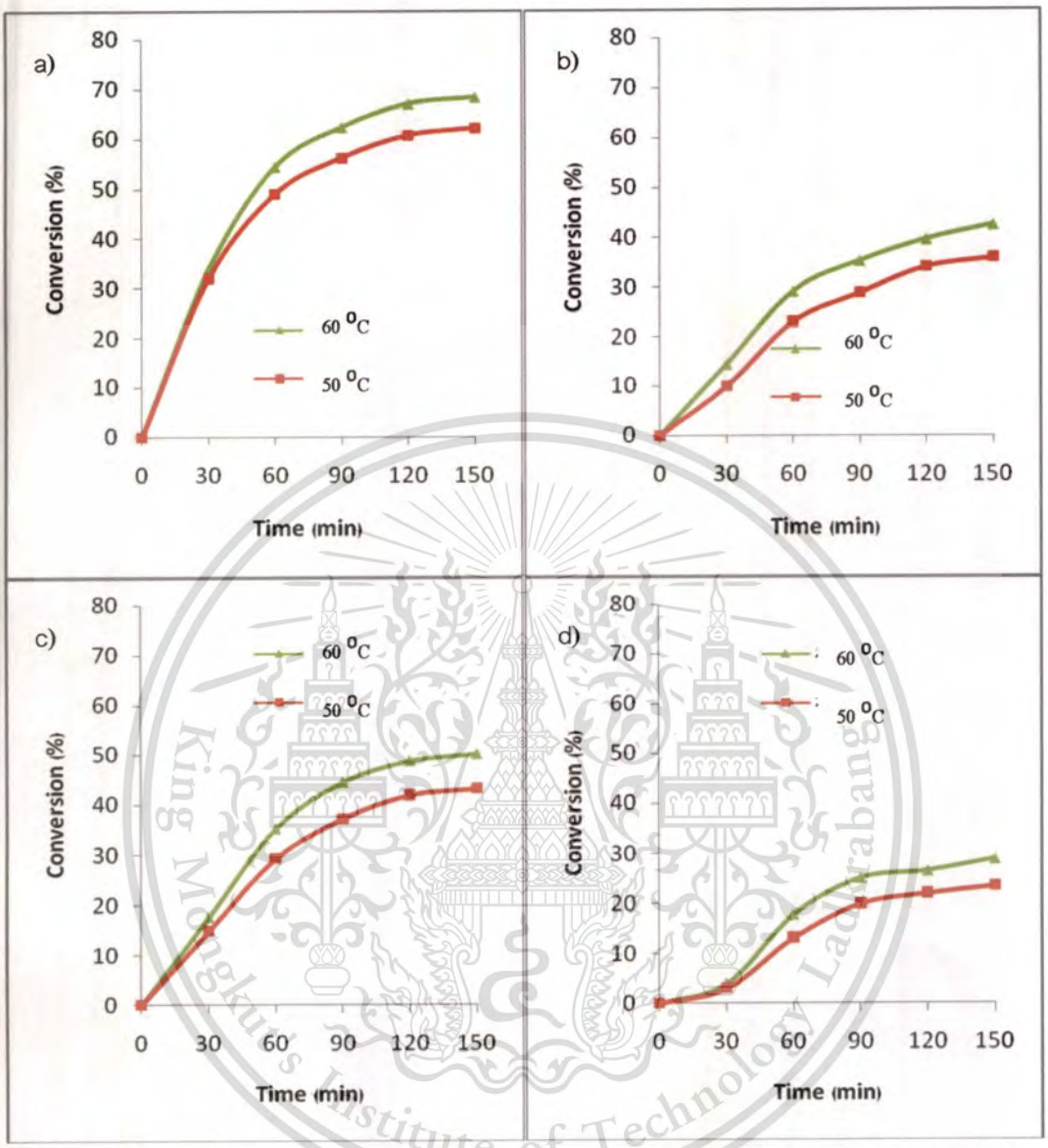


Figure 4-8. Effect of reaction temperature on conversion of FFA(4 wt% of Amberlyst-15 (a), 2 wt% of Amberlyst-15 (b), 4 wt% of water filter resin (c), 2 wt% of water filter resin (d).

When esterification reactions were carried out at temperature less than boiling point of methanol and at atmospheric pressure.

The effect of temperature on the free fatty acid conversion at different catalyst amount (2 and 4 wt. %) is present in Figure. 4-8. Because of the increase in reaction rate and equilibrium constant for endothermic reaction, It was seen that free fatty acid content decreased with increasing reaction temperature. The free fatty acid conversions were 68.44% maximum (4% Amberlyst-15, 60°c). This behavior was independent of the type and the amount of catalyst.

4.3.3 Effect of amount of catalyst

At constant reaction temperature, acidity (depend on free fatty acid content) decreased with increasing catalyst amount. This may be cause by the increase in acid site of the catalysts. In case of non-catalyzed reaction, almost no esterification was observed.

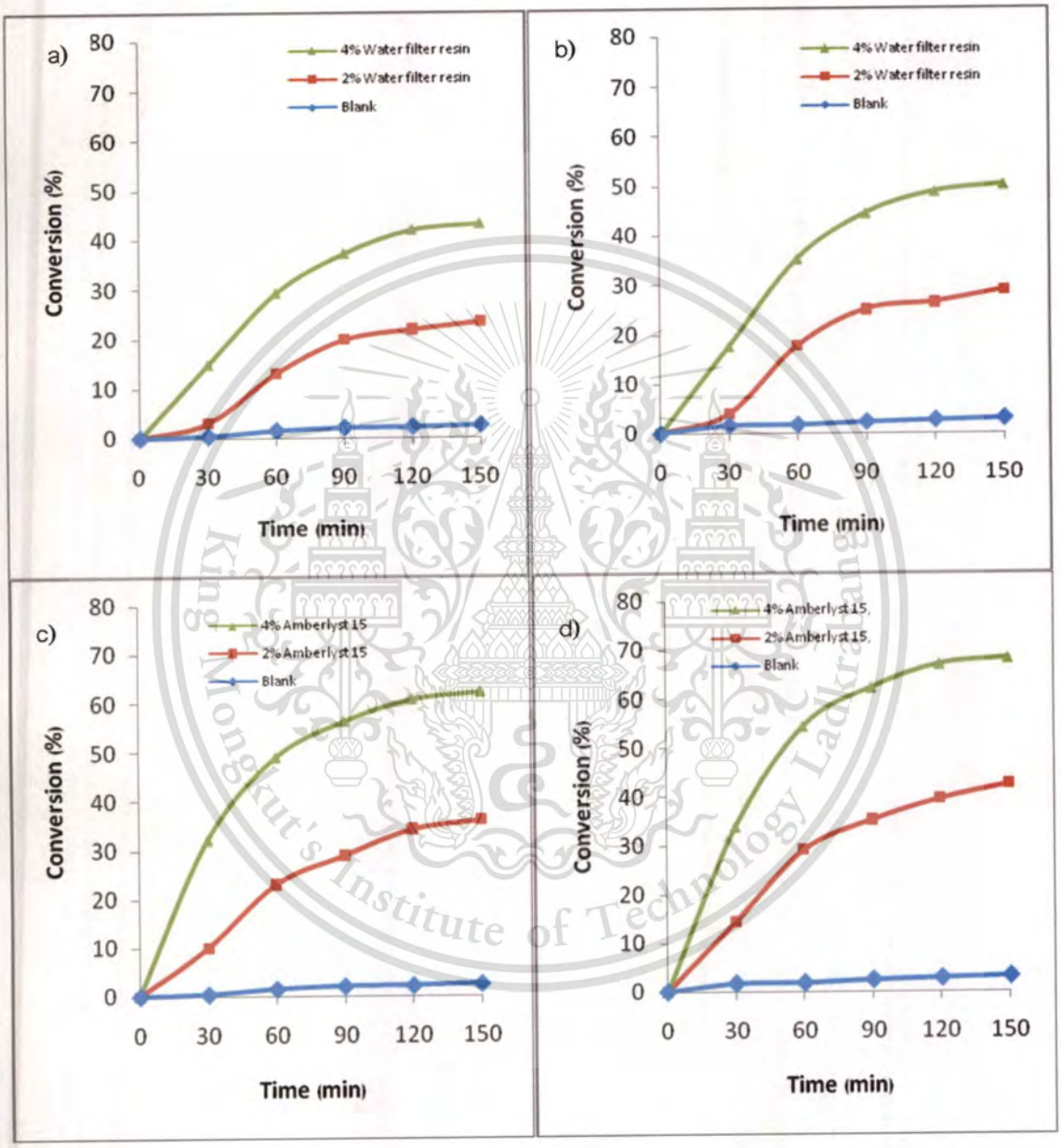


Figure 4-9. Effect of amount of catalyst at 50°C (water filter resin (a), Amberlyst-15 (c)). Effect amount of catalyst at 60°C (water filter resin (b), Amberlyst-15 (d)).

4.3.4 Effect of time

From figure 4-8 and 4-9 the conversion of acidity increase (acidity decrease) with increasing time. In case of non-catalyst reaction almost was independent of time, temperature.

4.3.5 Effect of type of catalyst

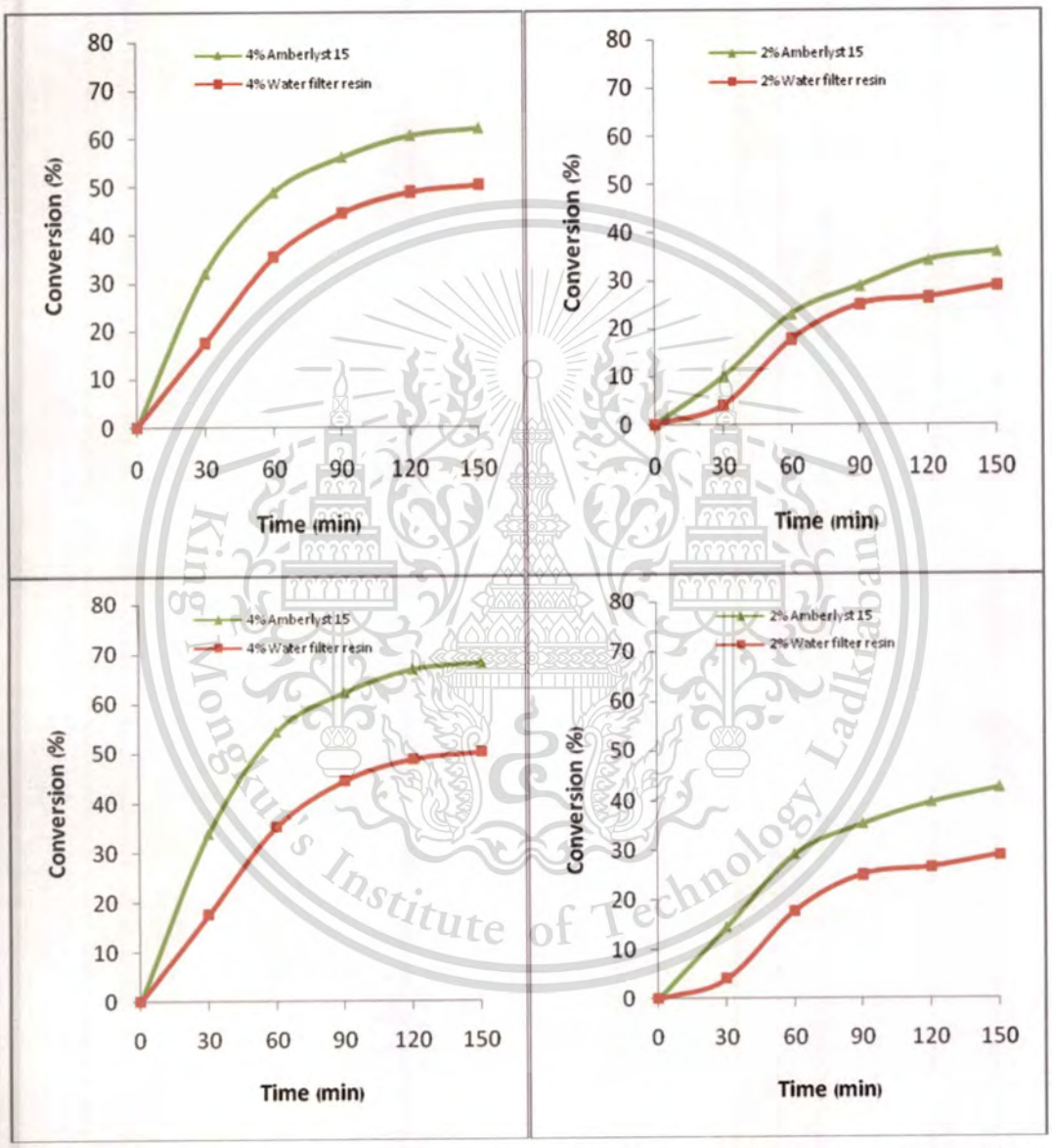


Figure 4-10. Comparison of different type of catalyst, (a) 50 °C, 4 wt% catalyst, (b) 50 °C, 2 wt% catalyst, (c) 60°C, 4 wt% catalyst, (d) 60 °C, 2 wt% catalyst.

From Figure. 4-10, the reduction of free fatty acid in waste cooking oil by using Amberlyst-15 is higher than water filter resin in the same condition because of the result from exchange capacity. The exchange capacity of Amberlyst-15 is equal to 7.23 meq/g, which is higher than the exchange capacity of water filter resin. This is because that makes Amberlyst-15 higher activity than water filter resin. So the conversion of free fatty acid in waste cooking oil by using Amberlyst15 is better than water filter resin.

4.3.6 Comparison between the optimum condition of Amberlyst-15 and water filter resin

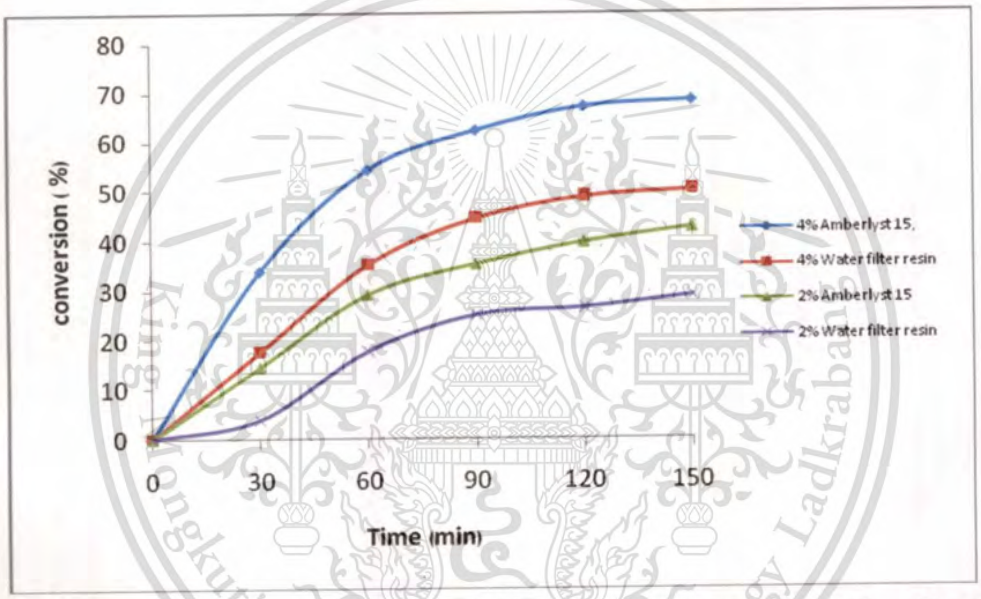


Figure 4-11. The graph of Comparison between the optimum condition of Amberlyst-15 and water filter resin

From figure 4-11 it can be conclude that 4% of Amberlyst-15 at 60 °C gives the highest conversion of free fatty acid which is equal to 68.44%. For the conversion of free fatty acid of 4% water filter resin, 2% Amberlyst-15, 2% water filter resin are equal to 50.41, 42.73, 29.08 respectively.

So the conversion of free fatty acid of 2% Amberlyst-15 can be take place by 4% water filter resin to reduce the cost of catalyst since the Amberlyst-15 has high cost.

Chapter 5

Conclusion and Discussion

5.1 Conclusion

This project is the reduction of free fatty acid in waste cooking oil: study between Amberlyst-15 and Water filter resin. The aim of this study is to compare the activity of Amberlyst-15 and Water filter resin for reduction of free fatty acid in waste cooking oil and examine the effect of catalyst amount (0, 2, 4%), reaction temperature (50°C, 60°C), and reaction time on the esterification process. Fourier Transform –Infrared Spectrometer (FT-IR) was used to characterize the structure of Amberlyst-15 and Water filter resin, the pattern of functional group of Water filter resin and Amberlyst-15 are the same. Determined the exchange capacity of catalysts, the result of exchange capacity of Amberlyst-15 and Water filter resin are 7.23 meq/g and 6.06 meq/g respectively. Free fatty acid was determined by titration method, initial free fatty acid in waste cooking oil is 8.620%, the result indicate that, both of Amberlyst-15 and Water filter resin can be reduced free fatty acid in waste cooking oil. However, at the same condition, the results of Amberlyst-15 are better than Water filter resin. For the highest free fatty acid conversion (68.44%) was obtain over Amberlyst-15 at 60°C with 4% wt catalyst amount. Even though Amberlyst-15 is better than Water filter resin, but if compare between the amounts of catalyst, 4% wt Water filter resin give the higher conversion than 2% wt Amberlyst-15. So 2% wt Amberlyst-15 can be replaced by 4% wt Water filter resin, to reduce the cost of catalyst.

5.2 Recommendation

1) Should be tried to increase the reaction time and amount of catalyst to improve the efficiency of reduction of free fatty acid.
2) Be carefully when titrating to determine the end point because the color is closely.
3) Should be treated the color of the waste cooking oil before do the experiment.

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Appendix A

Example of calculation

A-1 Standardization of exactly 0.05M sodium hydroxide

Standardization of sodium hydroxide by titrated with KHP

1. Weigh 0.2 g of KHP (4 decimal digits) into 250 ml Erlenmeyer flask.
2. Dissolved with distillated water and added 2-3 drops of Phenolphthalein.
3. Titrate with prepared NaOH until slightly pink occurs.
4. Record volume of NaOH used.
5. Repeat 2 times.
6. Calculated and average the concentration of NaOH.

Table A-1: The result of standardization of exactly 0.05M sodium hydroxide

KHP (g)	Mole of KHP (mol)	Volume of NaOH (L)	[NaOH] (M)
0.2015	9.867×10^{-4}	1.95×10^{-2}	0.0505
0.2012	9.905×10^{-4}	1.96×10^{-2}	0.0505
0.2046	1.002×10^{-3}	1.98×10^{-2}	0.0506
Average			0.0505

Note: Prepared NaOH solution 0.05M by weigh NaOH 2 g dissolve in distillation water 1000 ml and titrate with KHP.

Example of calculation

- Concentration of KHP

From Mole of KHP = weight of KHP / Molecular weight of KHP

Mole of KHP = (0.2019 g) / (204.22 g/mol)

Mole of KHP = 9.867×10^{-4} mol

- Exactly concentration of NaOH

Mole NaOH = Mole KHP

[NaOH] = mole of KHP / Volume of NaOH

[NaOH] = $(9.867 \times 10^{-4}$ mol) / $(1.95 \times 10^{-2}$ L)

[NaOH] = 0.0505 M

Exactly concentration of NaOH = (0.0505 + 0.0506 + 0.0505)/3 = 0.0505M

A-2 Standardization of Exactly 0.1M sodium hydroxide

Table A-2: The result of standardization of exactly 0.1M sodium hydroxide

KHP (g)	Mole of KHP (mol)	Volume of NaOH (L)	[NaOH] (M)
0.2018	9.886×10^{-4}	9.2×10^{-3}	0.1074
0.2012	9.852×10^{-4}	8.9×10^{-3}	0.1106
0.2047	1.0268×10^{-3}	9.4×10^{-3}	0.1066
Average			0.1082

Note: Prepared NaOH solution 0.1M by weigh NaOH 4 g dissolve in distillation water 1000ml and titrate with KHP.

A-3 Calculation the capacity of Amberlyst-15 and Water filter resin

Cation Exchange capacity

1. **Nitric acid** (65% of nitric acid , molecular weight = 63 g , density = 1.40 g/L)

- Calculate molarity

$$M = \frac{\% \times 10 \times d}{MW} = \frac{65\% \times 10 \times 1.40\ g/L}{63\ g/mol} = 14.4444 \text{ mol/L}$$

- Calculate volume of 14.4444 M HNO_3 needed to make 2 L of a dilute solution having a concentration of 1 mol/L

$$M_1V_1 = M_2V_2$$
$$14.4444 \text{ mol/L} \times V_1 = 1 \text{ mol/L} \times 2 \text{ L}$$
$$V_1 = 0.13846 \text{ L}$$

2. **Sodium hydroxide** (molecular weight = 40 g)

- Calculate the weight of NaOH to make 1 L of 0.1 M

1 M of NaOH : 40 g of NaOH dilute with distilled water until 1 L

0.1 M of NaOH : 4 g of NaOH dilute with distilled water until 1 L

Table A-3: The result of the exchange capacity of water filter resin and Amberlyst-15

	Water filter resins	**Amberlysts-15**
Weight before dry (g)	3.9942	-
Weight resin after dry (g)	1.9730	-
Sample weight (g)	1.0026	1.0238
Volume of NaOH (mL)	3.0	7.4
% solids	49.39	100

- Calculate cation exchange capacity

$$\frac{ml_{NaOH} \times N_{NaOH} \times 10}{\text{sample weight} \times \frac{\%\,\text{solid}}{100}} = \frac{\text{meq.of strong acid capacity}}{\text{gram of dry H-form resins}}$$

Resins : $$\frac{3.0 \times 0.1 \times 10}{1.0026 \times 0.4939} = 6.06 \ \frac{meq.of\ strong\ acid\ capacity}{gram\ of\ dry\ H-form\ resins}$$

Amblysts-15 : $$\frac{7.4 \times 0.1 \times 10}{1.0238 \times 1.0000} = 7.23 \ \frac{meq.of\ strong\ acid\ capacity}{gram\ of\ dry\ H-form\ resins}$$

A-4 Calculation percentage of free fatty acid

Calculation of percentage of free fatty acid (%FFA)

$$\%FFA = \frac{C \times V \times MW}{m \times 1000} 100(wt\%)$$

Percentage of free fatty acid = %FFA

Concentration of NaOH = C mol/L

Volume of NaOH used = V mL

Molecular weight of FFA = MW mol

Weight of sample used = m g.

For initial free fatty acid (Oleic acid)

Find initial %FFA :

- V_{NaOH} used = 30.95 mL
- Molecular weight of oleic acid = 282.46 g/mol
- Concentration of NaOH = 0.05 mol/L
- Weight of sample = 5.3413 g

$$\%FFA \text{ of oleic acid} = \frac{\left(0.05\frac{mol}{L}\right)\times(30.95\ mL)\times\left(282.46\frac{g}{mol}\right)\times 100(wt\%)}{(5.3413\ g)\times 1000}$$

= 8.620 wt%

A-5 Calculation conversion of free fatty acid

Calculation conversion of free fatty acid

$$\text{conversion of free fatty acid (\%)} = \frac{FFA_i - FFA_t}{FFA_i} \times 100$$

Initial acidity level (wt%) = FFA_i

Acidity at certain reaction time (wt%) = FFA_t

For conversion of free fatty acid at 60 °C, 150 min., Amberlyst-15 4 wt%

Find conversion:

- FFA_i = 8.620 (wt%)
- FFA_t = 2.672 (wt%)

$$\text{conversion of free fatty acid (\%)} = \frac{8.620 - 2.672}{8.620} \times 100$$

= 68.444 wt%

Appendix B

Result of experiment

B-1 Reduction of free fatty acid in waste cooking oil without using catalyst

Table B-1: Percentage of free fatty acid without using catalyst by reaction temperature and reaction time

Temperature (°C)	Time (min)	Wt. of oil (g.)	V_{NaOH} (ml)	Acidity (wt%)	Conversion (%)
50	0	-	-	8.620	-
	30	5.0572	30.4	8.660	0.534
	60	5.0116	30.1	8.567	0.614
	90	5.0059	29.9	8.520	1.163
	120	5.0121	29.9	8.509	1.286
	150	5.0026	29.75	8.483	1.595
60	0	-	-	8.620	-
	30	5.1201	30.7	8.553	0.781
	60	5.0264	30.1	8.542	0.907
	90	5.0045	29.8	8.494	1.467
	120	5.0147	29.75	8.462	1.833
	150	5.0068	29.6	8.433	2.175

B-2 Reduction of free fatty acid in waste cooking oil by using Water filter resin as catalyst

Table B-2: Percentage of free fatty acid when using water filter resin (2% wt.) as catalyst by varying reaction temperature and reaction time

Temperature (°C)	Time (min)	Wt. of oil (g.)	V_{NaOH} (ml)	Acidity (wt%)	Conversion (%)
50	0	-	-	8.620	-
	30	5.0112	29.3	8.340	3.220
	60	5.0244	26.3	7.467	13.273
	90	5.0077	24.15	6.879	20.034
	120	5.0049	23.5	6.698	22.122
	150	5.0157	23.1	6.569	23.597
60	0	-	-	8.620	-
	30	5.027	29.1	8.257	4.175
	60	5.0078	24.8	7.064	17.905
	90	5.0129	22.6	6.431	25.192
	120	5.0004	22.1	6.304	26.648
	150	5.0098	21.4	6.093	29.078

Table B-3: Percentage of free fatty acid when using water filter resin (4% wt.) as catalyst by varying reaction temperature and reaction time

Temperature (°C)	Time (min)	Wt. of oil (g.)	V_{NaOH} (ml)	Acidity (wt%)	Conversion (%)
50	0	-	-	8.620	-
	30	5.0122	25.7	7.314	15.029
	60	5.0097	21.3	6.065	29.404
	90	5.0064	18.85	5.371	37.391
	120	5.0044	17.4	4.960	42.122
	150	5.0141	17.05	4.850	43.378

60	0	-	-	8.620	-
	30	5.263	26.1	7.074	17.792
	60	5.1	19.8	5.538	35.467
	90	5.0184	16.65	4.733	44.734
	120	5.0064	15.3	4.359	49.030
	150	5.0135	14.9	4.239	50.411

B-3 Reduction of free fatty acid in waste cooking oil by using Amberlyst-15 as catalyst

Table B-4: Percentage of free fatty acid when using Amberlyst-15 (2% wt.) as catalyst by varying reaction temperature and reaction time

Temperature (°C)	Time (min)	Wt. of oil (g.)	V_{NaOH} (ml)	Acidity (wt%)	Conversion (%)
50	0	-	-	8.620	-
	30	5.0328	27.3	7.738	10.155
	60	5.0557	23.4	6.602	23.221
	90	5.0332	21.5	6.093	29.078
	120	5.0388	19.9	5.633	34.368
	150	5.0027	19.2	5.475	36.197
60	0	-	-	8.620	-
	30	5.0205	25.85	7.344	14.678
	60	5.0033	21.3	6.073	29.315
	90	5.0478	19.6	5.539	35.459
	120	5.0444	18.25	5.161	39.809
	150	5.0579	17.4	4.907	42.726

Table B-5: Percentage of free fatty acid when using Amberlyst-15 (4% wt.) as catalyst by varying reaction temperature and reaction time

Temperature (°C)	Time (min)	Wt. of oil (g.)	V_{NaOH} (ml)	Acidity (wt%)	Conversion (%)
50	0	-	-	8.620	-
	30	5.0011	20.4	5.819	32.238
	60	5.0831	15.5	4.350	49.141
	90	5.0792	13.25	3.721	56.374
	120	5.0094	11.7	3.332	60.857
	150	5.029	11.3	3.205	62.312
60	0	-	-	8.620	-
	30	5.0648	20.1	5.661	34.052
	60	5.0003	13.6	3.880	54.550
	90	5.0279	11.25	3.192	62.467
	120	5.0774	9.9	2.781	67.189
	150	5.0177	9.4	2.672	68.444