PURIFICATION OF CRUDE GLYCERINE FROM BIODIESEL PRODUCTION

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ABSTRACT

The present invention is directed to a method for purification of crude glycerol contaminated with alkaline salts. The method comprises steps of: a) combining the crude glycerol with acid; b) separating a glycerol layer; c) treating the glycerol layer to decolorize it. This experiment including the comparison of percent purity, yield and time required for all process of purified glycerol by 4 different kind of concentrate acid. Purified glycerol was investigated by Nuclear Magnetic Resonance Spectroscopy (NMR) and refractometer. From the resulted of NMR spectroscopy and refractometer, it is represent that the purity of glycerol was enhanced from 74% to 96%.

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Chapter 1

Introduction

The global increase in biodiesel production has led to a marked increase in world glycerol production. Glycerol is a by-product of biodiesel produced by Transesterification and is contained in the glycerol phase together with many other materials such as soaps, remaining catalyst, water, and esters formed during the process. The content of glycerol is approximately 30–60 wt. %. Purification is required to transform crude glycerin to a usable state for existing or emerging uses. In addition to glycerol, crude glycerol from biodiesel production using alkaline catalysts typically comprises methanol, water, inorganic salts, salts of fatty acids and fatty acid esters (typically methyl esters, referred to as "FAME"). Salts usually are sodium and/or potassium salts. Levels of fatty acid salts and esters typically are from 5% to 50%. Levels of inorganic salts are from 1% to 5%. These levels typically are expressed together in terms of total cat-ion concentration, which usually is from 0.2% to 5%. [1]

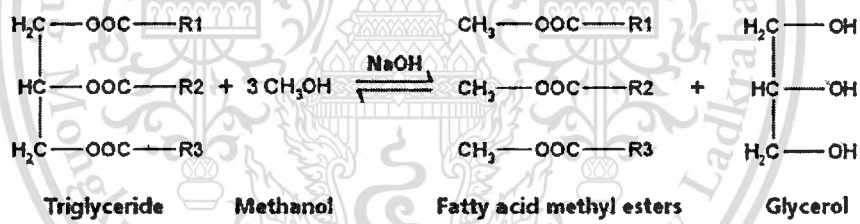
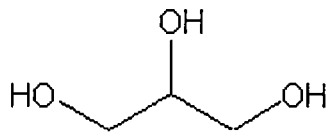


Figure 1.1 Transesterification reaction.

The purity requirements for the emerging applications of glycerin vary, and are often intermediate to the crude and refined grades previously established for the classical applications. The glycerin produced in the transesterification of triglycerides reaction is a crude grade. Almost all biodiesel production today involves homogeneous alkaline catalysts such as sodium methylate. The transesterification of triglycerides with methanol generates a methyl-ester phase and a glycerin phase. Impurities such as catalyst, soap, methanol and water are preferentially concentrated in the glycerin phase. The glycerin phase is typically neutralized with acid and the cationic component of the catalyst is incorporated as a salt.

Glycerol is an organic compound, also commonly called glycerin or glycerol. It is a colorless, odorless, viscous liquid that is widely used in pharmaceutical formulations. Glycerol

has three hydrophilic hydroxyl groups that are responsible for its solubility in water and its hygroscopic nature. The glycerol substructure is a central component of many lipids. Glycerol is sweet-testing and of low toxicity. It also is a by-product of the product of biodiesel via Transesterification. The formula of glycerol was $CH_2OHCHOHCH_2OH$. [2]



Glycerol

Figure 1.2 Structure of Glycerol [3]

Glycerol is used in nearly every industry. With dibasic acids, such as phathalic acid, it reacts to make the important class of products known as alkyd resins, which are widely used as coating and in paints. It is used in innumerable pharmaceutical and cosmetic preparations; it is an ingredient of many tinctures, elixirs, cough medicines, and anesthetics; and it is a basic medium for toothpaste. In foods, it is an important moistening agent for baked goods and is added to candies and icing to prevent crystallization. It is used as a solvent and carrier for extracts and flavoring agents and as a solvent for food colors. Many specialized lubrication problems have been solved by using glycerin or glycerin mixtures. Many millions of pounds are used each year to plasticize various materials. In foods and beverages, glycerol serves as a humectants, solvent and sweetener, and may be help preserve foods. It is also used as filter in commercially prepared low-fat foods, and as a thickening agent in liqueurs. Glycerol also serves as a way, along with water, to preserve certain types of leaves. Glycerol is also used as a sugar substitute. In this regard, it has approximately 27 calories per teaspoon and is 60% as sweet as sucrose. Although it has about the same food energy as table sugar, it does not raise blood sugar levels, nor does it feed the bacteria that form plaques and dental cavities. As a food additive, glycerol is also known as E number E422. [4] In nowadays glycerol can be usage in many industries, medical, pharmaceutical and personal care applications mainly as a means of improving smoothness, providing lubrication and as humectants. It found in cough syrups, elixirs and expectorants, hair care products, soaps and water based personal lubricants. In this project the way to purify the glycerol from biodiesel production by using 4 different types of concentrates acids were studies. The possibilities of this experiment for apply to the industrial method, decrease production cost, procedure time, were investigated.

Motivation

We are interested to make a purified glycerol from waste glycerol obtained as by-product in biodiesel production process. As an increasing of biodiesel production, the amount of waste glycerol as by-product is increased also. Most of waste glycerol has been discarded. The way to value added the glycerin is using simple methods; acidification, extraction, precipitation and decolorization. We are interested to find the answer why many research in the past mostly uses concentrate H_2SO_4 in acidification step and can we uses another type of concentrate acid.

Objective

1. To study, the way to purify the glycerol from biodiesel production by using 4 different types of concentrates acids.
2. To study, the possibilities of this experiment for apply to the industrial method.
3. To study, the way to gain the value of glycerol obtained as by-product from biodiesel production process.
4. To study, the way to decrease production cost and time in the procedure in industries.

Scope of study

1. To prepare and purify glycerol, in addition, the purification steps were also studied for 2 steps as the evaporation of methanol and hexane extraction of residue lipid.
2. To perform experiment on the best condition to make the highest yield of pure glycerol.
3. To perform the experiment on characteristic of glycerol gains from the experiment.

Expected results

1. To obtain purified glycerol with increased purity.
2. To gained information about the optimum type of concentrate acid to gain the highest %yield and the highest purity with lowest time and cost required.
3. To archive the possible way to apply this experiment to industry or to business.

Chapter 2

Literature reviews and involve articles

2.1 Glycerol

2.1.1 Glycerol Categorization and Usages [5-6]

As used in foods, glycerol is categorized by the American Dietetic Association as a carbohydrate. The U.S. FDA carbohydrate designation includes all caloric macronutrients excluding protein and fat. Glycerin has a caloric density similar to table sugar, but a lower glycemic index and different metabolic pathway within the body, so some dietary advocates accept glycerin as a sweetener compatible with low carbohydrate diets. In foods and beverages, glycerol serves as a humectants, solvent and sweetener, and help preserve foods. It is also used as filler in commercially prepared low-fat foods. As a sugar substitute, it has approximately 27 calories per teaspoon and is 60 percent as sweet as sucrose. Although it has about the same food energy as table sugar, it does not raise blood sugar levels, nor does it feed the bacteria that form plaques and cause dental cavities. As a food additive, glycerol is labeled as E number E422. Glycerol is also used to manufacture mono- and di-glycerides for use as emulsifiers, as well as poly-glycerol esters going into shortenings and margarine.

Glycerol is used in medical and pharmaceutical and personal care preparations, mainly as a means of improving smoothness, providing lubrication and as humectants. For human consumption, glycerol is classified by the U.S. FDA among the sugar alcohols as a caloric macronutrient.

Glycerol was historically used as an anti-freeze for automotive applications before being replaced by ethylene glycol, which has a lower freezing point. While, the minimum freezing point of a glycerol-water mixture is higher than an ethylene-glycol mixture, glycerol is not toxic and is being re-examined for use in automotive applications.

2.1.2 Physical Properties of Glycerol

The Physical Properties of Glycerol was shown in table 2.1. The Glycerol (or called glycerin) is a colorless, odorless, viscous liquid with a sweet taste. It is completely soluble in water and alcohol but it is slightly soluble in ether, ethyl acetate, and dioxane and insoluble in hydrocarbons. Glycerol has useful solvent properties similar to those of water and simple aliphatic alcohols because of its three-hydroxyl groups. Glycerol is a useful solvent for many solids, both

organic and inorganic which is particularly important for the preparation of pharmaceuticals. The solubility of gases in glycerol, like other liquids is temperature and pressure dependent.

Glycerol is a trivalent alcohol. It melts at 17.8°C, boils with decomposition at 290°C, and is miscible with water and ethanol. It is hygroscopic; i.e., it absorbs water from the air; this property makes it valuable as a moistener in cosmetics.

PHYSICAL PROPERTIES	MEASURING
Molecular weight	92.09
Melting point	18.17°C
Boiling point (760mm Hg)	290°C
Density (20°C)	1.261 g/cm3
Vapor pressure	
at 50°C	0.0025 mm Hg
at 100°C	0.195 mm Hg
at 150°C	4.3 mm Hg
at 200°C	46 mm Hg
Refractive index	1.474
Surface tension at 20°C (100% glycerol)	63.4 dyne/cm
Compressibility (28.5°C)	2.1×10 MPa
Viscosity at 20°C (100% glycerol)	1499 c.p.
Specific heat at 26°C (99.94%glycerol)	0.5779 cal/gm
Heat of vaporization	
at 55°C	21060 cal/mole
at 195°C	18170 cal/mole
Heat of formation	159.6 Kcal/gm mole
Heat of combustion	1662 KJ/mole
Heat of fusion	18.3 KJ/mole
Thermal conductivity	0.29 w/°K
Flash point	177°C
Fire point	204°C

Table 2.1 The physical properties of glycerol [6]

2.1.3 Chemical properties of glycerol [6]

Glycerol is a reactive molecule that undergoes all the usual reactions of alcohols. The two terminal primary hydroxyl groups are more reactive than the internal secondary hydroxyl group. Under neutral or alkaline conditions, glycerol can be heated to 250°C without formation of acrolein.

Reactions with glycerol are therefore best carried out under alkaline or neutral conditions at 180°C, Alkaline glycerol begins to dehydrate forming ether-linked polyglycerols. At room temperature glycerol rapidly absorbs water. When dilute it is attacked by microorganism. On oxidation, glycerol yields variety of product depending upon the reaction conditions. By the use of mild oxidizing agent it is possible to oxidize only one hydroxyl group to yield Glyceraldehyde. These compounds may be considered very simple aldose and simplest ketoses respectively and mixture of two compounds obtained from glycerol as well as glyceraldehyde has been called glycerose. Nitric acid converts glycerol to glyceric acid $CH_2CHCHOHCOOH$ melting at 134-135°C when pure, but usually obtained as syrupy. Oily liquid soluble in water and alcohol, but it is insoluble in ethers. Some industrially important reaction products of glycerol include: Mono-,di-,and tri esters of inorganic and organic acids

Mono and diglycerides of fatty acids formed by transesterification of triglycerides (from fats) Aliphatic and aromatic esters formed by reactions with alkylating agents respectively. Polyglycerols formed by the intermolecular alienation of water with alkaline catalyst. Cyclic 1,2- or 1,3-acetals or ketals formed by the reaction with aldehyde or ketons respectively.

2.1.4 Purification of Glycerol [7]

2.1.4.1 Glycerol Purification Method

Purification is required to transform crude glycerin to a usable state for existing or emerging uses. The purity requirements for the emerging applications of glycerin vary, and are often intermediate to the crude and refined grades previously established for the classical applications. The salt content in crude glycerin, stemming from the use of homogeneous alkaline catalysts, often ranges from 5 percent to 7 percent, which makes conventional techniques cost intensive. This suggests that for future glycerin markets a new low-cost purification strategy may be more cost-effective than conventional routes.

2.1.4.2 Simple purification method

Crude glycerol obtained as by-product from biodiesel production process can be purified by simple purification method. This method compromise 3 main steps which consist of glycerol-acidification, glycerol phase extraction and decolorization by adding an activated carbon.

Neutralization of basic salts in crude glycerol with acid results in three layers: (i) an upper layer rich in fatty acids and fatty acid esters; (ii) a middle layer rich in glycerol; and (iii) a bottom layer rich in salts. These layers are separated using standard equipment used for this purpose, e.g., a gravity settler or centrifuge. Preferably, the crude glycerol and acid are mixed and then the mixture is passed directly into the separation equipment. A solution of sodium borohydride and sodium hydroxide is combined with the glycerol layer to neutralize sulfuric acid and reduce colored impurities. Residual water and methanol can be removed via standard evaporation techniques, and borate salts and other solids removed by filtration. Optionally, the upper layer, which typically contains fatty acid esters, fatty acids and glycerides, can be recycled to a biodiesel process.

2.1.4.3 Distillation method

Distillation is the most commonly practiced method for purifying glycerin. The advantages of the distillation process are well known. Namely, it is an established technology that produces high-purity glycerin in high yield. However, the distillation of glycerin is an energy-intensive process. Glycerin has a high heat capacity, which demands a high-energy input for vaporization.

There are three possible reactions that may reduce the yield of glycerol in the distilled glycerine:

(a) Polymerization of the glycerol at high pH (in excess NaOH and high temperature, >200oC) to form polyglycerol (Garti *et al.*, 1981; Ikuya*et al.*, 1990; Lutz *et al.*, 1998), which concentrates in the distilled bottom.

(b) Dehydration of the glycerol at low pH (Hedtke, 1996; Monick, 1960) to form acrolein (bp. 52oC), which is then lost in the cold trap.

(c) Moderate oxidation of the glycerol to formglycerose, a mixture of glyceraldehyde and dihydroxyacetone (Jungermann, 1991; Monick, 1960).

However, by proper control of the pH of the crude glycerine, and the temperature and pressure of distillation, these unwanted reactions can be minimized. Vacuum distillation was used so that the glycerine distilled over at a lower temperature and pressure than would otherwise have been necessary.

2.1.4.4 Ion-Exchange method

Classical ion-exchange techniques have long been applied to glycerin purification. It is an attractive alternative to vacuum distillation for smaller capacity plants. The ion-exchange system uses cation, anion and mixed bed exchangers to remove catalyst and other impurities. The glycerol is first diluted with soft water to a 15 to 35 percent glycerol-to-water solution. The ion-exchange is followed by vacuum distillation or flash drying. As a result, water removal often results in a partially refined glycerol of 85 percent. However, the high salt content of glycerin issued from biodiesel production makes classical ion-exchange uneconomical for this application. Specifically, the chemical regeneration cost for the resins becomes exceedingly high when salt contents approach the 5 percent- to 7 percent-range commonly found in the biodiesel industry.

2.2 Sulfuric acid [8]

Sulfuric acid (alternative spelling **sulphuric acid**) is a strong mineral acid with the molecular formula H_2SO_4. Its historical name is **vitriol**. The salts of sulfuric acid are called sulfates. Sulfuric acid is soluble in water at all concentrations. Sulfuric acid has many applications, and is a central substance in the chemical industry. Principal uses include lead-acid batteries for cars and other vehicles, ore processing, fertilizer manufacturing, oil refining, wastewater processing, and chemical synthesis.

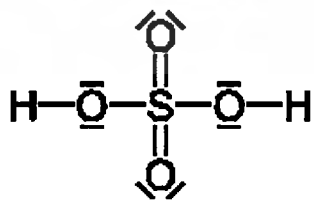


Figure 2.1 Structure of sulfuric acid.

2.2.1 Physical properties

Pure sulfuric acid is a viscous clear liquid, like oil, and this explains the old name of the acid ('oil of vitriol'). Commercial sulfuric acid is sold in several different purity grades. Technical grade H_2SO_4 is impure and often colored, but is suitable for making fertilizer. Pure grades such as United States Pharmacopoeia (USP) grade are used for making pharmaceuticals and dyestuffs. Analytical grades are also available.

Physical Properties	
Molecular formula	H_2SO_4
Molar mass	98.086 g/mol
Appearance	Clear, colorless, odorless liquid
Density	1.84 g/cm3, liquid
Melting point	10 °C, 283 K, 50 °F
Boiling point	337 °C, 610 K, 639 °F
Solubility in water	miscible
Acidity (pKa)	−3
Viscosity	26.7 cP (20 °C)

Table 2.2 Physical properties of Sulfuric acid.

2.2.1.1 Grades of sulfuric acid

Although nearly 100% sulfuric acid can be made, this loses SO_3 at the boiling point to produce 98.3% acid. The 98% grade is more stable in storage, and is the usual form of what is described as "concentrated sulfuric acid." Other concentrations are used for different purposes. Some common concentrations are:

Mass fraction H_2SO_4	Density (kg/L)	Concentration (mol/L)	Common name
10%	1.07	~1	dilute sulfuric acid
29–32%	1.25–1.28	4.2–5	battery acid (used in lead–acid batteries)
62–70%	1.52–1.60	9.6–11.5	*chamber acid* *fertilizer acid*
78–80%	1.70–1.73	13.5–14	*tower acid* *Glover acid*
95–98%	1.83	~18	concentrated sulfuric acid

Table 2.3 Grades of sulfuric acid.

2.2.2 Chemical properties

The hydration reaction of sulfuric acid is highly exothermic. One should always add the acid to the water rather than the water to the acid. Because the reaction is in an equilibrium that favors the rapid protonation of water, addition of acid to the water ensures that the *acid* is the limiting reagent. Because the hydration of sulfuric acid is thermodynamically favorable, sulfuric acid is an excellent dehydrating agent, and is used to prepare many dried fruits. The affinity of sulfuric acid for water is sufficiently strong that it will remove hydrogen and oxygen atoms from other compounds. The effect of this can be seen when concentrated sulfuric acid is spilled on paper; the cellulose reacts to give a burnt appearance, the carbon appears much as soot would in a fire. A more dramatic reaction occurs when sulfuric acid is added to a tablespoon of white sugar in a beaker; a rigid column of black, porous carbon will quickly emerge. The carbon will smell strongly of caramel due to the heat generated. Although less dramatic, the action of the acid on cotton, even in diluted form, will destroy the fabric.

As an acid, sulfuric acid reacts with most bases to give the corresponding sulfate. Sulfuric acid can also be used to displace weaker acids from their salts. Reaction with sodium acetate, for example, displaces acetic acid, CH_3COOH, and forms sodium bisulfate. Similarly, reacting

sulfuric acid with potassium nitrate can be used to produce nitric acid and a precipitate of potassium bisulfate. When combined with nitric acid, sulfuric acid acts both as an acid and a dehydrating agent, forming the nitronium ion NO^{+2}, which is important in nitration reactions involving electrophilic aromatic substitution. This type of reaction, where protonation occurs on an oxygen atom, is important in many organic chemistry reactions, such as Fischer esterification and dehydration of alcohols. Concentrated sulfuric acid reacts with sodium chloride, and gives hydrogen chloride gas and sodium bisulfate.

Concentrated sulfuric acid also dehydrates sugar, leaving a porous black carbon mass behind. Sulfuric acid does not take part in this reaction, but it decomposes the sugar. During this reaction heat is produced and water vapor is given off.

2.2.3 Usages

Sulfuric acid is a very important commodity chemical, and indeed, a nation's sulfuric acid production is a good indicator of its industrial strength. World production in 2001 was 165 million tons, with an approximate value of US$8 billion. The major use (60% of total production worldwide) for sulfuric acid is in the "wet method" for the production of phosphoric acid, used for manufacture of phosphate fertilizers as well as trisodium phosphate for detergents. Sulfuric acid is used in large quantities by the iron and steel making industry to remove oxidation, rust and scale from rolled sheet and billets prior to sale to the automobile and white goods (appliances) industry. Used acid is often recycled using a Spent Acid Regeneration (SAR) plant. These plants combust spent acid with natural gas, refinery gas, fuel oil or other fuel sources. This combustion process produces gaseous sulfur dioxide (SO_2) and sulfur trioxide (SO_3) which are then used to manufacture "new" sulfuric acid.

2.2.4 Safety

2.2.4.1 Laboratory hazards

The corrosive properties of sulfuric acid are accentuated by its highly exothermic reaction with water. Burns from sulfuric acid are potentially more serious than those of comparable strong acids (e.g. hydrochloric acid), as there is additional tissue damage due to dehydration and particularly secondary thermal damage due to the heat liberated by the reaction with water. The danger is greater with more concentrated preparations of sulfuric acid, but even the normal

laboratory "dilute" grade (approximately 1 M, 10%) will char paper by dehydration if left in contact for a sufficient time. Therefore, solutions equal to or stronger than 1.5 M are labeled "CORROSIVE", while solutions greater than 0.5 M but less than 1.5 M are labeled "IRRITANT". Fuming sulfuric acid (oleum) is not recommended for use in schools as it is quite hazardous.

The standard first aid treatment for acid spills on the skin is, as for other corrosive agents, irrigation with large quantities of water. Washing is continued for at least ten to fifteen minutes to cool the tissue surrounding the acid burn and to prevent secondary damage. Contaminated clothing is removed immediately and the underlying skin washed thoroughly. Preparation of the diluted acid can also be dangerous due to the heat released in the dilution process. The concentrated acid is always added to water and not the other way round, to take advantage of the relatively high heat capacity of water. Addition of water to concentrated sulfuric acid leads to the dispersal of a sulfuric acid aerosol or worse, an explosion. Preparation of solutions greater than 6 M (35%) in concentration is most dangerous, as the heat produced may be sufficient to boil the diluted acid: efficient mechanical stirring and external cooling (such as an ice bath) are essential.

On a laboratory scale, sulfuric acid can be diluted by pouring concentrated acid onto crushed ice made from de-ionized water. The ice melts in an endothermic process while dissolving the acid. The amount of heat needed to melt the ice in this process is greater than the amount of heat evolved by dissolving the acid so the solution remains cold. After all the ice has melted, further dilution can take place using water.

Figure 2.2 Concentrate 98% sulfuric acid burning tissue paper.

2.2.4.2 Industrial hazards

Although sulfuric acid is non-flammable, contact with metals in the event of a spillage can lead to the liberation of hydrogen gas. The dispersal of acid aerosols and gaseous sulfur dioxide is an additional hazard of fires involving sulfuric acid.

Sulfuric acid is not considered toxic besides its obvious corrosive hazard, and the main occupational risks are skin contact leading to burns (see above) and the inhalation of aerosols. Exposure to aerosols at high concentrations leads to immediate and severe irritation of the eyes, respiratory tract and mucous membranes: this ceases rapidly after exposure, although there is a risk of subsequent pulmonary edema if tissue damage has been more severe. At lower concentrations, the most commonly reported symptom of chronic exposure to sulfuric acid aerosols is erosion of the teeth, found in virtually all studies: indications of possible chronic damage to the respiratory tract are inconclusive as of 1997. In the United States, the permissible exposure limit (PEL) for sulfuric acid is fixed at 1 mg/m^3: limits in other countries are similar. Interestingly there have been reports of sulfuric acid ingestion leading to vitamin B12 deficiency with sub acute combined degeneration. The spinal cord is most often affected in such cases, but the optic nerves may show demyelination, loss of axons and gliosis.

2.3 Nitric acid [9]

Nitric acid (HNO_3), is also known as ***aqua fortis*** and **spirit of nitre**, is a highly corrosive and toxic strong acid. Colorless when pure, older samples tend to acquire a yellow cast due to the accumulation of oxides of nitrogen. If the solution contains more than 86% nitric acid, it is referred to as **fuming nitric acid**. Depending on the amount of nitrogen dioxide present, fuming nitric acid is further characterized as white fuming nitric acid or red fuming nitric acid, at concentrations above 95%. At room temperature, nitric acid tends to rapidly develop a yellow color due to decomposition. Nitric acid is also commonly used as a strong oxidizing agent.

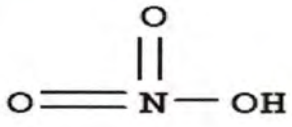


Figure 2.3 Structure of Nitric acid.

2.3.1 Physical properties

Pure anhydrous nitric acid (100%) is a colorless mobile liquid with a density of 1.512 g/cm^3 which solidifies at −42 °C to form white crystals and boils at 83 °C. Nitric acid is miscible with water and distillation gives a maximum-boiling azeotrope with a concentration of 68% HNO_3 and a boiling temperature of 120.5 °C at 1 atm, which is the ordinary concentrated nitric acid of commerce. Two solid hydrates are known; the monohydrate ($HNO_3 \cdot H_2O$) and the trihydrate ($HNO_3 \cdot 3H_2O$).

Physical Properties	
Molecular formula	HNO3
Molar mass	63.01 g mol^{-1}
Exact mass	62.995642903 g mol^{-1}
Appearance	Colourless liquid
Density	1.5129 g cm^{-3}
Melting point	-42 °C, 231 K, -44 °F
Boiling point	83 °C, 356 K, 181 °F
Solubility in water	Completely miscible
Acidity (pKa)	-1.4
Refractive index (nD	1.397 (16.5 °C)
Dipole moment	2.17 ± 0.02 D

Table 2.4 Physical properties of Nitric acid.

2.3.1.1 Grades of Nitric acid

The concentrated nitric acid of commerce consists of the maximum boiling azeotrope of nitric acid and water. Technical grades are normally 68% HNO_3, (approx 15 molar), while reagent grades are specified at 70% HNO_3. The density of concentrated nitric acid is 1.42 g/mL. An older density scale is occasionally seen, with concentrated nitric acid specified as 42° Baumé.

White fuming nitric acid, also called 100% nitric acid or WFNA, is very close to anhydrous nitric acid. One specification for white fuming nitric acid is that it has a maximum of 2% water and a maximum of 0.5% dissolved NO_2. Anhydrous nitric acid has a density of 1.513 g/mL and has the approximate concentration of 24 molar. A commercial grade of fuming nitric acid, referred to in the trade as "strong nitric acid" contains 90% HNO_3 and has a density of 1.50 g/mL. This grade is much used in the explosives industry. It is not as volatile nor as corrosive as the anhydrous acid and has the approximate concentration of 21.4 molar.

Red fuming nitric acid, or RFNA, contains substantial quantities of dissolved nitrogen dioxide (NO_2) leaving the solution with a reddish-brown color. One formulation of RFNA specifies a minimum of 17% NO_2, another specifies 13% NO_2. Because of the dissolved nitrogen dioxide, the density of red fuming nitric acid is lower at 1.490 g/mL.

An *inhibited* fuming nitric acid (either IWFNA or IRFNA) can be made by the addition of 0.6% - 0.7% hydrogen fluoride (HF). This fluoride is added for corrosion resistance in metal tanks. The fluoride creates a metal fluoride layer that protects the metal.

2.3.2 Chemical properties

Nitric acid is normally considered to be a strong acid at ambient temperatures. There is some disagreement over the value of the acid dissociation constant, though the pK_a value is usually reported as less than –1. This means that the nitric acid in solution is fully dissociated except in extremely acidic solutions. The pK_a value rises to 1 at a temperature of 250 °C.

2.3.3 Usages

The main use of nitric acid is for the production of fertilizers; other important uses include the production of explosives, etching and dissolution of metals, especially as a component of aqua regia for the purification and extraction of gold, and in chemical synthesis

2.3.4 Safety

Nitric acid is a powerful oxidizing agent, and the reactions of nitric acid with compounds such as cyanides, carbides, and metallic powders can be explosive. Reactions of nitric acid with many organic compounds, such as turpentine, are violent and hypergolic (i.e., self-igniting). Due to its properties it is stored away from bases and organics. Concentrated nitric acid dyes human skin yellow due to a reaction with the keratin. These yellow stains turn orange when neutralized.

Figure 2.4 The effect of nitric acid on human skin.

2.4 Hydrochloric acid [10]

Hydrochloric acid is a solution of hydrogen chloride (HCl) in water, which is a highly corrosive, strong mineral acid with many industrial uses. It is found naturally in gastric acid. Historically called "muriatic acid or spirits of salt", hydrochloric acid was produced from vitriol (sulfuric acid) and common salt. It first appeared during the Renaissance, and then it was used by chemists like Glauber, Priestley and Davy in their scientific research.

With major production starting in the Industrial Revolution, hydrochloric acid is used in the chemical industry as a chemical reagent in the large-scale production of vinyl chloride for PVC plastic, and MDI/TDI for polyurethane. It has numerous smaller-scale applications, including household cleaning, production of gelatin and other food additives, descaling, and leather processing. About 20 million tones of hydrochloric acid are produced annually.

2.4.1 Physical properties

Hydrochloric acid is a clear, colorless, fuming, poisonous, highly acidic aqueous solution of hydrogen chloride, HCl, used as a chemical intermediate and in petroleum production, ore reduction, food processing, pickling, and metal cleaning. It is found in the stomach in dilute form.

2.4.2 Chemical Properties.

Hydrogen chloride (HCl) is a monoprotic acid, which means it can dissociate (*i.e.,* ionize) only once to give up one H^+ ion (a single proton). In aqueous hydrochloric acid, the H^+ joins a water molecule to form a hydronium ion, H_3O^+. The other ion formed is Cl^-, the chloride ion. Hydrochloric acid can therefore be used to prepare salts called *chlorides*, such as sodium chloride. Hydrochloric acid is a strong acid, since it is essentially completely dissociated in water.

Monoprotic acids have an acid dissociation constant, K_a, which indicates the level of dissociation in water. For a strong acid like HCl, the K_a is large. Theoretical attempts to assign a K_a to HCl have been made. When chloride salts such as NaCl are added to aqueous HCl they have practically no effect on pH, indicating that Cl^- is an exceedingly weak conjugate base and that HCl is fully dissociated in aqueous solution. For intermediate to strong solutions of hydrochloric acid, the assumption that H^+ molarity (a unit of concentration) equals HCl molarity is excellent, agreeing to four significant digits.

2.5 Acetic acid [11]

Acetic acid is one of the simplest carboxylic acids. It is an important chemical reagent and industrial chemical, used in the production of polyethylene teraphthalate mainly used in soft drink bottles; cellulose acetate, mainly for photographic film; and polyvinyl acetate for wood glue, as well as synthetic fibers and fabrics. In households, diluted acetic acid is often used in descaling agents. In the food industry, acetic acid is used under the food additive code E260 as an acidity regulator and as a condiment.

The global demand of acetic acid is around 6.5 million tons per year (Mt/a), of which approximately 1.5 million tons per year is met by recycling; the remainder is manufactured from petrochemical feedstock or from biological sources. Dilute acetic acid produced by natural fermentation is called vinegar. Acetic acid is produced industrially both synthetically and by bacterial fermentation. Acetic acid is also a component of the vaginal lubrication of humans and other primates, where it appears to serve as a mild antibacterial agent.

2.5.1 Physical Properties

Acetic acid, CH_3COOH is an organic acid that gives vinegar its sour taste and pungent smell. It is a weak acid, in that it is only a partially dissociated acid in an aqueous solution. Pure, water-free acetic acid (*glacial acetic acid*) is a colorless liquid that absorbs water from the environment (hygroscope), and freezes at 16.5 °C (62 °F) to a colorless crystalline solid. The pure acid and its concentrated solutions are very corrosive.

Physical Properties	
Molecular formula	C2H4O2
Molar mass	60.05 g mol−1
Appearance	Colourless liquid
Density	1.049 g/cm^3 (Liquid)
	1.266 g/cm3 (Solid)
Melting point	16.5 °C, 290 K, 62 °F
Boiling point	118.1 °C, 391 K, 245 °F
Solubility in water	miscible
Acidity (pKa)	4.76
Viscousity	1.22 mPa·s at 25 °C

Table 2.5 Physical properties of Acetic acid.

2.5.2 Chemical Properties

The hydrogen (H) atom in the carboxyl group (−COOH) in carboxylic acids such as acetic acid can be given off as an H^+ ion (proton). For this reason these compounds have an acidic character. Acetic acid is a weak monoprotic acid. In aqueous solution, it has pK_a value of 4.75. Its conjugate base is acetate (CH_3COO^-).

Liquid acetic acid is a hydrophilic (polar) protic solvent, similar to ethanol and water. With a moderate relative static permittivity (dielectric constant) of 6.2, it can dissolve not only polar compounds such as inorganic salts and sugars, but also non-polar compounds such as oils and elements such as sulfur and iodine. It readily mixes with other polar and non-polar solvents such as water, chloroform, and hexane. With higher alkanes (starting with octane) acetic acid is not completely miscible anymore, and its miscibility continues to decline with longer n-alkanes. This dissolving property and miscibility of acetic acid makes it a widely used industrial chemical.

The crystal structure of acetic acid shows that the molecules pair up into dimers connected by hydrogen bonds. The dimers can also be detected in the vapour at 120 °C. They also occur in the liquid phase in dilute solutions in non-hydrogen-bonding solvents, and a certain extent in pure acetic acid, but are disrupted by hydrogen-bonding solvents. The dissociation enthalpy of the dimer is estimated at 65.0–66.0 kJ/mol, and the dissociation entropy at 154–157 J mol^{-1} K^{-1}. This dimerization behaviour is shared by other lower carboxylic acids.

2.5.3 Usages

Acetic acid is a chemical reagent for the production of chemical compounds. The largest single use of acetic acid is in the production of vinyl acetate monomer; this application consumes approximately 40% to 45% of the world's production of acetic acid, closely followed by acetic anhydride and ester production. The reaction is of ethylene and acetic acid with oxygen over a palladium catalyst. Vinyl acetate can be polymerized to polyvinyl acetate or to other polymers, which are applied in paints and adhesives.

The volume of acetic acid used in vinegar is comparatively small. Acetic acid comprises typically 4 to 18% of vinegar, with the percentage usually calculated by mass. Vinegar is used directly as a condiment, and also in the pickling of vegetables and other foods. Table vinegar tends to be more diluted (4% to 8% acetic acid), while commercial food pickling, in general, employs more concentrated solutions. The amount of acetic acid used as vinegar on a worldwide scale is not large, but is by far the oldest and best-known application. Glacial acetic acid is an

excellent polar protic solvent, as noted above. It is frequently used as a solvent for recrystallization to purify organic compounds.

Acetic acid is used as a solvent in the production of terephthalic acid (TPA), the raw material for polyethylene terephthalate (PET). Acetic acid is often used as a solvent for reactions involving carbocations, such as Friedel-Crafts alkylation. Glacial acetic acid is used in analytical chemistry for the estimation of weakly alkaline substances such as organic amides. Glacial acetic acid is a much weaker base than water, so the amide behaves as a strong base in this medium. It then can be titrated using a solution in glacial acetic acid of a very strong acid, such as perchloric acid.

2.5.4 Safety

Concentrated acetic acid is corrosive and must, therefore, be handled with appropriate care, since it can cause skin burns, permanent eye damage, and irritation to the mucous membranes. These burns or blisters may not appear until hours after exposure. Latex gloves offer no protection, so specially resistant gloves, such as those made of nitrile rubber, are worn when handling the compound. Concentrated acetic acid can be ignited with difficulty in the laboratory. It becomes a flammable risk if the ambient temperature exceeds 39 °C (102 °F), and can form explosive mixtures with air above this temperature (explosive limits: 5.4–16%).

The hazards of solutions of acetic acid depend on the concentration. The following table lists the EU classification of acetic acid solutions:

Concentration by weight	Molarity	Classification	R-Phrases
10–25%	1.67–4.16 mol/L	Irritant (Xi)	R36/38
25–90%	4.16–14.99 mol/L	Corrosive (C)	R34
>90%	>14.99 mol/L	Corrosive (C) Flammable (F)	R10, R35

Table 2.6 Classification of acetic acid solutions.

Solutions at more than 25% acetic acid are handled in a fume hood because of the pungent, corrosive vapors. Dilute acetic acid, in the form of vinegar, is harmless. However, ingestion of stronger solutions is dangerous to human and animal life. It can cause severe damage to the digestive system, and a potentially lethal change in the acidity of the blood. Due to

incompatibilities, it is recommended to keep acetic acid away from chromic acid, ethylene glycol, nitric acid, perchloric acid, permanganates, peroxides and hydroxyls.

2.6 Activated Carbon [12]

Activated carbon, also called activated charcoal or activated coal is a form of carbon that has been processed to make it extremely porous and thus to have a very large surface area available for adsorption or chemical reactions. The word *activated* in the name is sometimes replaced with *active*. Due to its high degree of micro porosity, just 1 gram of activated carbon has a surface area in excess of 500 m^2 (about one tenth the size of a football field), as determined typically by nitrogen gas adsorption. Sufficient activation for useful applications may come solely from the high surface area, though further chemical treatment often enhances the absorbing properties of the material. Activated carbon is usually derived from charcoal. A gram of activated carbon can have a surface area in excess of 500 m^2, with 1500 m^2 being readily achievable. Carbon aerogels, while more expensive, have even higher surface areas, and are used in special applications. Physically, activated carbon binds materials by van der Waals force or London dispersion force. Activated carbon is used in gas purification, gold purification, metal extraction, water purification, medicine, sewage treatment, air filters in gas masks and respirators, filters in compressed air and many other applications. One major industrial application involves use of activated carbon in the metal finishing field. It is very widely employed for purification of electroplating solutions. For example, it is a main purification technique for removing organic impurities from bright nickel plating solutions. A variety of organic chemicals are added to plating solutions for improving their deposit qualities and for enhancing properties like brightness, smoothness, ductility, etc. Due to passage of direct current and electrolytic reactions of anodic oxidation and cathodic reduction, organic additives generate unwanted break down products in solution. Their excessive build up can adversely affect the plating quality and physical properties of deposited metal. Activated carbon treatment removes such impurities and restores plating performance to the desired level.

Traditionally, active carbons are made in particular form as powders or fine granules less than 1.0 mm in size with an average diameter between .15 and .25 mm. Thus they present a large surface to volume ratio with a small diffusion distance. PAC is made up of crushed or ground carbon particles, 95–100% of which will pass through a designated mesh sieve or sieve. Granular activated carbon is defined as the activated carbon being retained on a 50-mesh sieve (0.297 mm) and PAC material as finer material, while ASTM classifies particle sizes corresponding to an 80-

mesh sieve (0.177 mm) and smaller as PAC. PAC is not commonly used in a dedicated vessel, owing to the high head loss that would occur. PAC is generally added directly to other process units, such as raw water intakes, rapid mix basins, clarifiers, and gravity filters.

2.7 Analysis

2.7.1 Refractive Index Analysis

The refractive index (or index of refraction) of a medium is a measure of how much the velocity of a wave is reduced inside that medium. For example, typical soda-lime glass has a refractive index close to 1.5, which means that in glass, light travels at 1 / 1.5 = 2/3 the speed of light in a vacuum. Two common properties of glass and other transparent materials are directly related to their refractive index. First, light rays change direction when they cross the interface from air to the material, an effect that is used in lenses. Second, light reflects partially from surfaces that have a refractive index different from that of their surroundings.

2.7.1.1 Refractometer

A refractometer is a laboratory or field device for the measurement of an index of refraction. The index of refraction is calculated from Snell's law and can be calculated from the composition of the material using the Gladstone-Dale relation.

2.7.1.2 Types of Refractometer

There are four main types of refractometer;

1) Traditional handheld refractometer.
2) Digital handheld refractometer.
3) Laboratory or Abbe refractometer.
4) Inline process refractometer.

There is also the Rayleigh Refractometer used (typically) for measuring the refractive indices of gases.

2.7.1.3 The using steps of traditional handheld Refractometer.

Figure 2.5 Picture of traditional handheld refractometer [14]

1) Aim the front end of the refractometer in the direction of a bright, and adjust the adjusting ring of diopter until the reticle can be seen clearly.

2) Adjustment of null: Open the cover plate and put one or two drops of distilled water on the prism. Close the cover plate and press it lightly, then adjust the correcting screw (3) to make the light/dark boundary coincide with the null line. (ATC model should be adjusted at an environmental temperature of 20°C)

3) Open the cover plate clean the surface of prism with a piece of soft cotton flannel, drop 1~2 drops of the solution to be measured. Close the cover plates, press it lightly, and then read the corresponding scale of light and dark boundary, the reading is the data of measured solution.

4) After measurement, clean the surface of prism and cover plate with moist gauze. After drying it, it should be stored carefully. [13]

2.7.1.4 The using steps of Digital Refractometer.

Figure 2.6 Picture of Digital Refractometer [15]

1). Press the ON/OFF key, then release. Fill the sample well with distilled or deionized water. Make sure the prism is completely covered. Press the ZERO key. If no error messages appear, your unit is calibrated.

2). Gentle absorbs the ZERO water standards with a soft tissue. Use care not to scratch the prism surface. Dry the surface completely. The instrument is ready for sample measurement.

3). Wipe off prism surface located at the bottom of the sample well. Make sure the prism and sample well are completely dry. Drip sample onto the prism surface. Fill the well completely. Press the READ key. The results are displayed in unit of interest.

4). Remove sample from the sample well by absorbing with a soft tissue. Rinse prism and sample well with distilled or deionized water. Wipe dry. The instrument is ready for the next sample.

2.7.2 NMR spectroscopy

Nuclear magnetic resonance spectroscopy, most commonly known as NMR spectroscopy, is the name given to a technique which exploits the magnetic properties of certain nuclei. This phenomenon and its origins are detailed in a separate section on nuclear magnetic resonance. The most important applications for the organic chemist are proton NMR and carbon-13 NMR spectroscopy. In principle, NMR is applicable to any nucleus possessing spin. Many types of information can be obtained from an NMR spectrum. Much like using infrared spectroscopy to identify functional groups, analysis of a 1D NMR spectrum provides information on the number and type of chemical entities in a molecule. However, NMR provides much more information than IR.

The impact of NMR spectroscopy on the natural sciences has been substantial. It can, among other things, be used to study mixtures of analytes, to understand dynamic effects such as change in temperature and reaction mechanisms, and is an invaluable tool in understanding protein and nucleic acid structure and function. It can be applied to a wide variety of samples, both in the solution and the solid state.

Nuclear Magnetic Resonance (NMR) spectra database is an electronic repository of information concerning NMR spectra. The repository can be stored as a complete self contained data set or as an online repository that can be accessed and searched remotely. The form in which

the data is stored ranges from line lists that can be graphically displayed to raw free induction decay (FID) data. The data is usually annotated in a way that correlates the spectral data with the related molecular structure. [16]

2.8 Literature Review

Wannaporn B. and Kriangkrai A. Residues from biodiesel production processes have a compound of glycerine incurred by chemical reactions. Such "crude" glycerine can be purified and, then, used as a raw material for several products such as soap, pharmaceutical, and cosmetic.. Based on 30 liter glycerin purification equipment, four main procedures are studied. The methanol removal process requires the heating temperature of 95oC. After 9 hours, 2.29% by volume of methanol is retrieved from crude glycerine. The crude glycerine is next neutralized by 1.44% by volume of acetic acid for 5 hours. The fatty acid is separated from glycerine solvent. The concentration of glycerine in the solvent is approximately 49.49%. Then, Color and odor of solvent glycerine are removed by using activated carbon at room temperature for 24 hours with the ratio of 1:4 and 1:6. Finally, it was heated to vaporize the remaining acetic acid and water at the temperature of 130 °C. The concentration of glycerine in the solvent or glycerin purity is finally 81.6%. However, the process is still not economically feasible because of the cost variation of glycerine in world market. [17]

Martin Hajek and František Skopal. Glycerol is a by-product of biodiesel produced by transesterification and is contained in the glycerol phase together with many other materials such as soaps, remaining catalyst, water, and esters formed during the process. The content of glycerol is approximately 30–60 wt.%. In this paper, treatments of the glycerol phase to obtain glycerol with a purity of 86 wt.% (without distillation) and a mixture of fatty acids with esters (1:1) or only a mixture of fatty acids with a purity of 99 wt.% are presented. Fatty acids were produced by saponification of the remaining esters and subsequent neutralization of alkaline substances by phosphoric, sulfuric, hydrochloric, or acetic acids. Salts are by-products and, in the case of phosphoric acid can be used as potash-phosphate fertilizer. The process of treatment is easy and environmentally friendly, because no special chemicals or equipment are required and all products are utilizable. [18]

Noppawan K. and Wattana P. Glycerine from biodiesel production of Palm oil (crude Palm oil, Palm stearin, and refined Palm oil) exhibits brown wax like. The glycerine content

yields only 55%. Hence, it is not useful in industry, except using as fuel. The way to value added the glycerine is using simple methods-acidification, extraction, precipitation and decolorization. It is found that after purification, 38-40% of glycerine is yielded. The glycerine content increases from 55% to 82-85%. However, centrifugal method (720 rpm) is used to assist separation, as a result, the glycerine content increases up to 92%. In other words, the centrifugal technique increases the purity of glycerine about 12%. With the simple methods to get a better quality, the glycerine increases its value and it can reduce the biodiesel production cost. [19]

Sangkorn Kongjao, Somsak Damronglerd and Mali Hunsom. The purification of crude glycerol from a biodiesel plant using waste used-oil as a raw material was carried out on a laboratory scale by using the combined chemical and physical treatments based upon repeated cycles of acidification to the desired pH within the range of 1–6 using 1.19 M H_2SO_4, allowing phase separation and harvesting of the glycerol-rich middle phase followed by neutralization of the harvested glycerol phase with 12.5M NaOH. Subsequently, the glycerol-enriched fraction was extracted by ethanol. The results indicated that increasing the pH of the acidification step led to an increased yield of the glycerol-rich layer and decreased amount of inorganic salt and free fatty acids phase. Under strong acid conditions, large quantities of fatty acid and salt in the glycerol-enriched fraction were eliminated and, at pH 1, high purity glycerol (~93.34%) with relatively low contaminant levels (0.00045% (w/w) ash and 5.16% (w/w) MONG) was obtained. [20]

Chapter 3

Experimental Details

3.1 Chemicals

3.1.1 Glycerol (waste from biodiesel production)

3.1.2 Concentrate 98% Sulfuric acid, H_2SO_4

3.1.3 37% Hydrochloric acid, HCl

3.1.4 Nitric acid, HNO_3

3.1.5 Acetic acid, CH_3COOH

3.1.6 Analytical grade Sodium Hydroxide, NaOH

3.1.7 Potassium hydrogen phthalate, KHP

3.1.8 Phenolphthalein indicator

3.1.9 Hexane

3.1.10 Activated carbon

3.1.11 Distilled water

3.2 Equipments & Instruments

3.2.1 50 mL, 250 mL and 600 mL Beaker

3.2.2 500 mL Separated Funnel

3.2.3 10 mL and 50 mL Graduated cylinder

3.2.4 100 mL, 250 mL and 500 mL Volumetric flask

3.2.5 250 mL Erlenmeyer flask

3.2.6 50 mL Burette

3.2.7 Heater and Magnetic stirrer

3.2.8 Magnetic Bar

3.2.9 Dropper

3.2.10 Thermometer

3.2.11 Stand with Clamp

3.2.12 Aluminium Foil

3.2.13 Watch glass

3.2.14 Spoon

3.2.16 Vacuum Filtration Set

3.3 Source of Waste Glycerol.

Waste glycerol of this experiment was obtained from biodiesel production of The Royal Thai Naval Dockyard.

3.4 Analysis Equipment

3.4.1 NMR analysis; Bruker AV-400

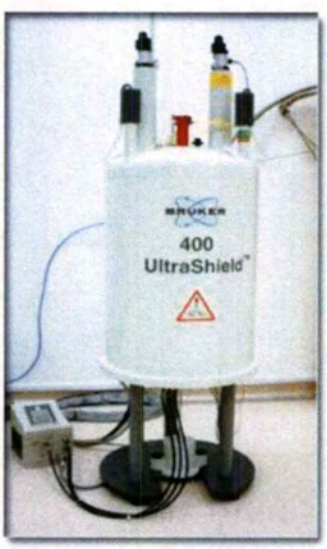


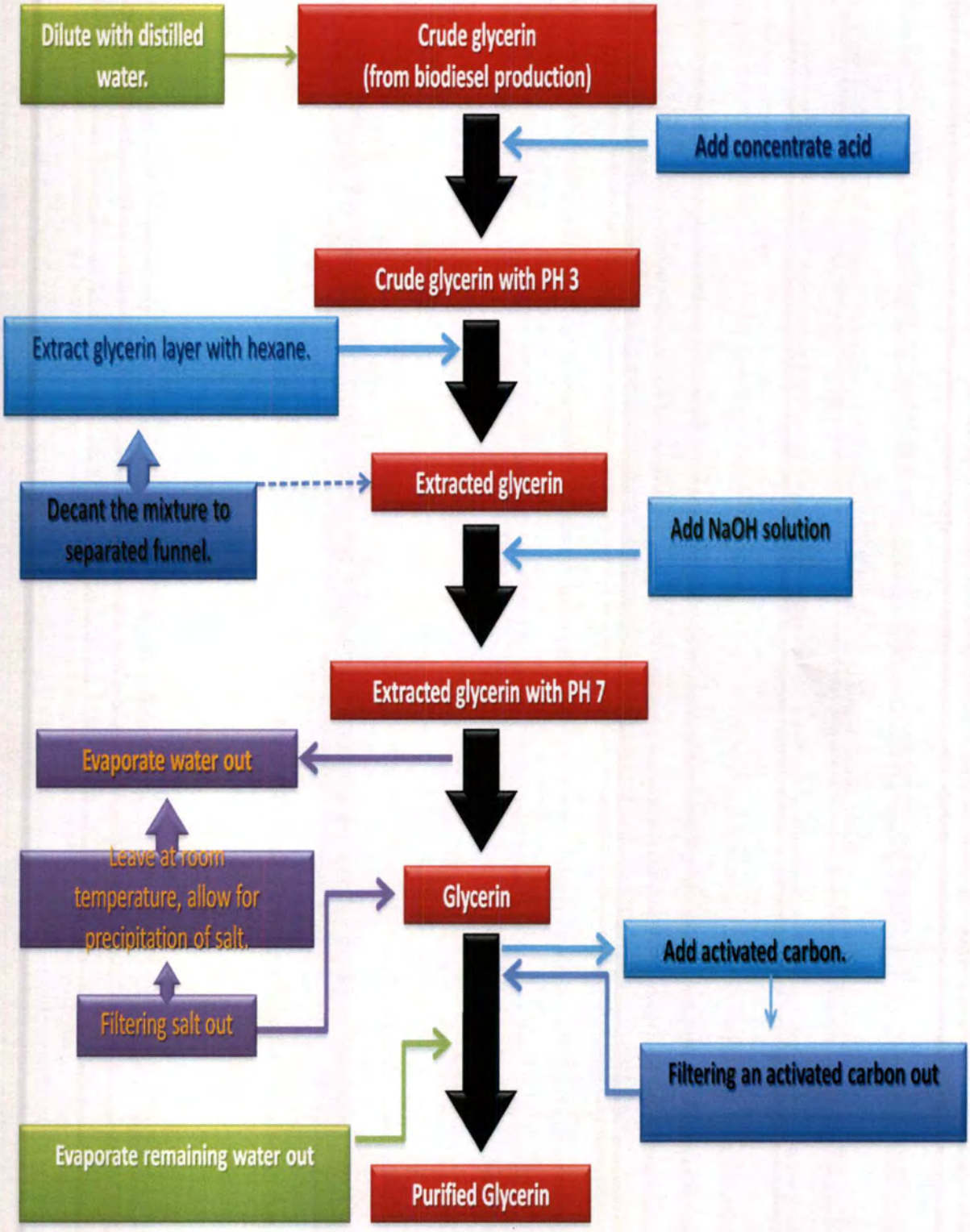
Figure 3.1 Bruker AV-400

3.4.2 Digital Refractometer

ATAGO Digital Refractive Index Refractometer PAL-RI – model 3850.

Figure. 3.2 ATAGO Digital Refractive Index Refractometer.

3.5 Experimental procedure.



Chapter 4

Results and Discussion

This experiment was study in sample of crude glycerol which part from transesterification process of biodiesel. Purification process of crude glycerol by used difference acid; sulfuric acid, nitric acid, and hydrochloric acid. The Nuclear Magnetic Resonance Spectroscopy (NMR) instrument and the measurement of an index of refraction were used to analyze the results of this experiment.

4.1 Standard Glycerol.

Standard glycerol with 99.5% purity is obtained from Oleo Chemicals Company. The standard glycerol was analyzed by Nuclear Magnetic Resonance Spectroscopy (NMR) and refractometer.

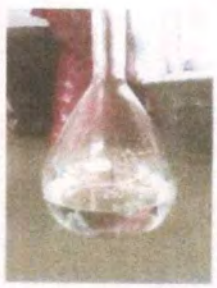


Figure 4.1 Standard glycerol was from Oleo Chemicals Company.

The refractive index of standard glycerol measured by digital refractometer in experiment was 1.4699. Thus the percentage of purity of glycerol from refractive index of glycerol-water solutions was 97%.

From the result of refractive index was shown 97% purity of standard glycerol which lower than the purity of an information obtained from Oleo Chemicals Company. However, the refractive index result can be able to indicate the percent purification trend of purified glycerol from our purification process.

4.2 Waste Glycerol.

Waste glycerol of this experiment was obtained from biodiesel production of The Royal Thai Naval Dockyard. The waste glycerol was analyzed by Nuclear Magnetic Resonance Spectroscopy (NMR) and Refractometer.

Figure 4.2 Waste glycerol left from biodiesel production.

The refractive index of waste glycerol is 1.4332, that corresponding to the percent purification of glycerol at 74% (+2.5% error).

4.3 Purified Glycerol.

The purified glycerol obtained from our experiment was carried out in 3 steps of purification; a) combining the crude glycerol with acid, separating a glycerol layer, and treating the glycerol layer to decolorize it. The percent purity of purified glycerol was first analyzed by refractometer.

Figure 4.3 Purified glycerol by purification process with sulfuric acid, nitric acid and hydrochloric acid respectively.

The characteristic of purified glycerol are light yellow, low viscosity and mild odor which shown in Figure 4.4. Thus, the physical characteristic of purified glycerol and standard glycerol is almost similar.

The refractive index of purified glycerol is measured at 20 ºC, by using digital refractometer. The refractometer was calibrated with distilled water and the result is showing in Table 4.1 below.

Type of concentrate acid.	Refractive index		% Purity	
	Activated Carbon Ratio		Activated Carbon Ratio	
	1:05	1:10	1:05	1:10
conc. 98% Sulfuric acid	1.458	1.460	90	92
conc. 35.7% Hydrochloric acid	1.452	1.456	86	89
conc. Nitric acid	1.455	1.459	88	91
Acetic acid	x	x	x	x
STD Glycerol	1.4699	1.4699	97	97

Table 4.1 Table of results

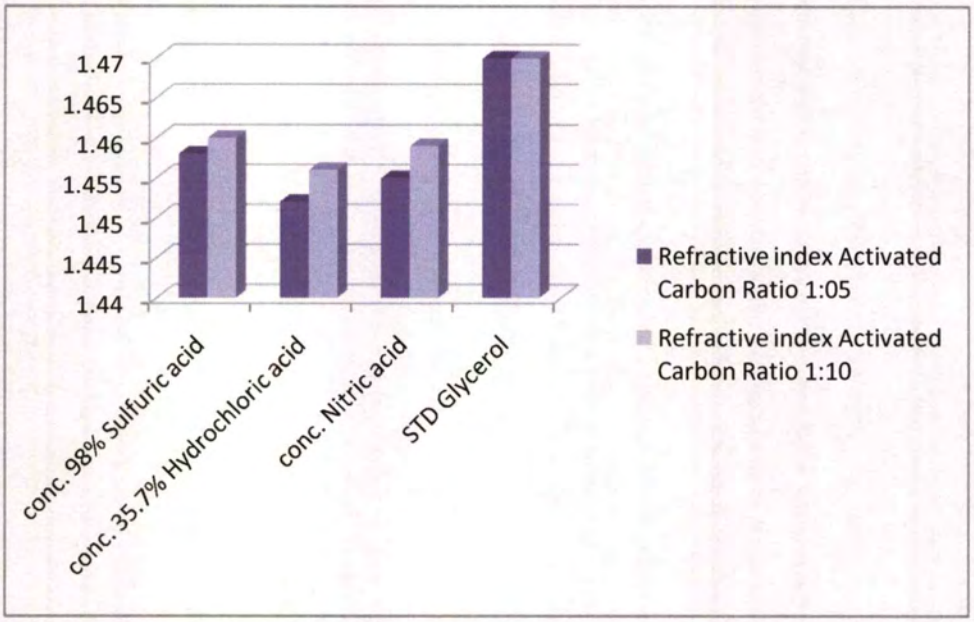


Figure 4.4 The comparison of Refractive index

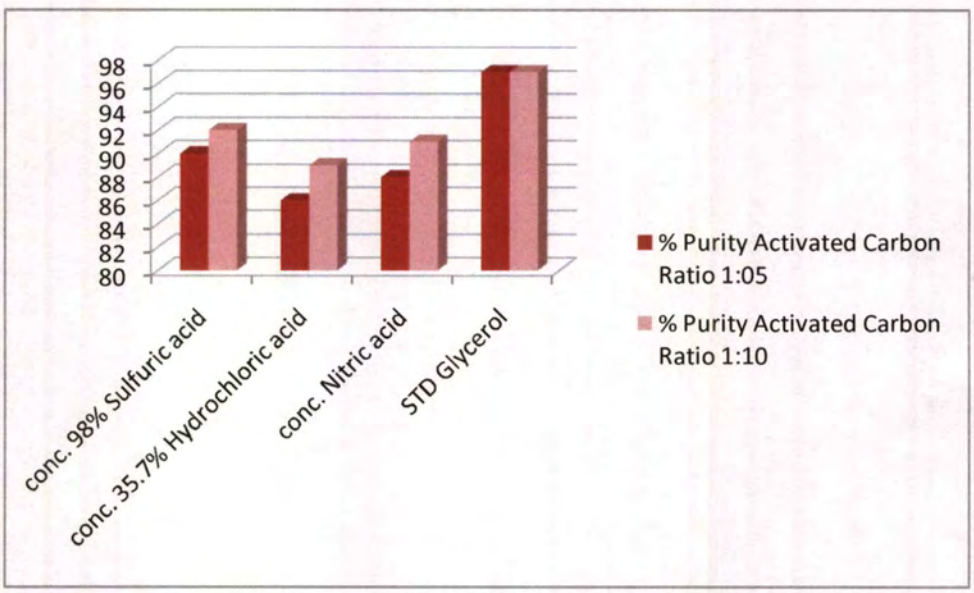


Figure 4.5 The comparison of % Purity

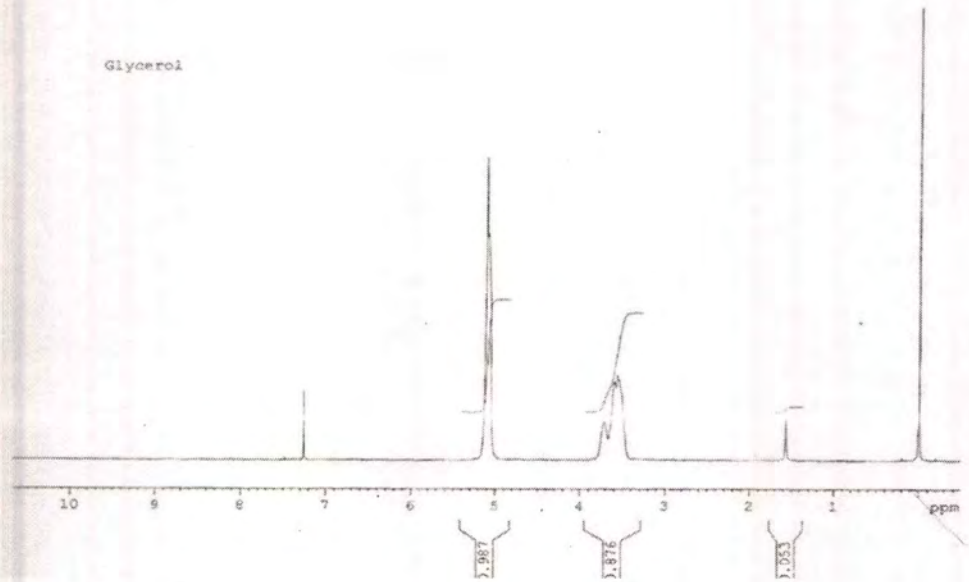


Figure 4.6 Standard glycerol was analyzed by Nuclear Magnetic Resonance Spectroscopy (NMR) instrument.

From the Figure 4.6, chemical structure of Standard glycerol was present NMR peak at;

1.) 1.6 ppm for ^{1}H of OH group.

2.) 3.4-3.9 ppm for ^{1}H of CH_2O at 3.7 ppm and CHO at 3.55 ppm.

3.) 5.1 ppm for ^{1}H of H_2O or MeOH

4.) 7.25 ppm for ^{1}H of CCl_4

The resulted from refractometer in experiment got n_D was 1.4699. So, the percentage of glycerol by weight that from refractive index of glycerol-water solutions was about 97%.

After the percent purity was determined by using the digital refractometer. The Nuclear Magnetic Resonance spectroscopy has been used to ensure that our product is purified glycerol. The NMR spectrum of purified glycerol was showing below.

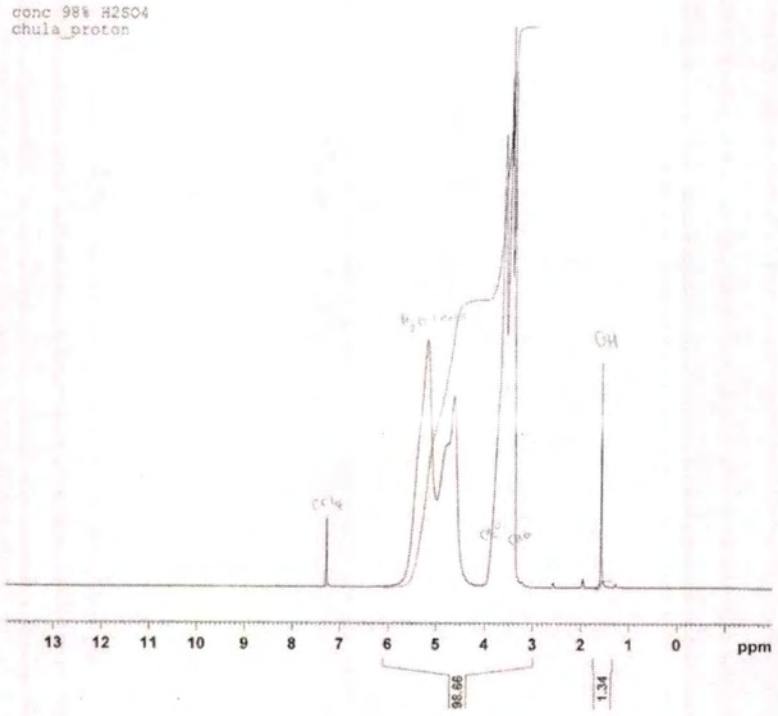


Figure 4.7 NMR spectrum of purified glycerin which acidified by concentrate 98% H_2SO_4

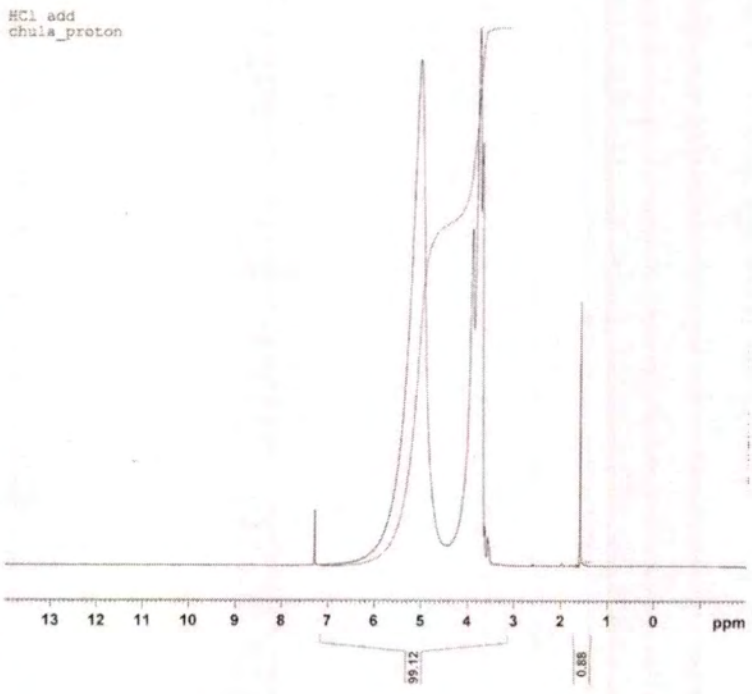


Figure 4.8 NMR spectrum of purified glycerin which acidified by concentrate 37% HCl.

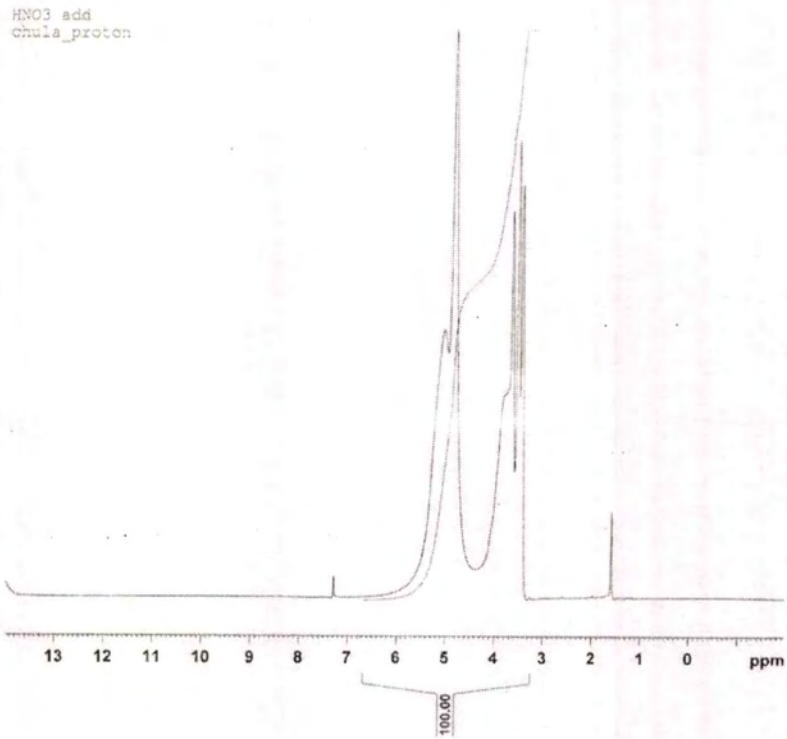


Figure 4.9 NMR spectrum of purified glycerin which acidified by concentrate HNO_3-

Chapter 5

Conclusions and Suggestions

5.1 Conclusions

In this experiment is the study about the purification process of waste glycerol obtained from biodiesel production of Royal Thai Naval Dockyard. The characteristic of waste glycerol are brown color, high viscosity and strongly smell. The way to value added the glycerol is using simple methods; acidification, extraction, precipitation and decolorization. The purity of waste glycerol is about 74%. After passes the purification process, it is found that the purity of glycerol has been increased from 74% to 89%-92%. The purified glycerol which is uses concentrate. 98% H_2SO_4 to acidify gave us the highest %purity, but it very similar to another purified glycerol which is uses concentrates 37% HCl and concentrates HNO_3 to acidify. The percent purity is 92%, 89% and 91% respectively. The purified glycerol which is uses concentrates HNO_3 gave us the highest percent yield. From that information, it can be concluded that concentrate HCl and concentrate HNO_3 can be used to acidify instead of concentrate 98% H_2SO_4. Even if the purified glycerol with highest percent purity is obtained from the glycerol acidified by concentrate 98% H_2SO_4.

An optimum ratio of weight of activated carbon added and weight of glycerol in decolorization step is 1:5. With this level of %purity, it can be used to make soap and used to reduce an amount of free fatty acid in palm oil.

5.2 Suggestions

From our experiment, this simple purification method is not recommended in the case of purification process that uses acetic acid to acidify waste glycerol. Because an acetic acid is weak acid, it required too much amount of acid used to acidified waste glycerol from pH 8 to pH 2. More over it is required too much time and energy.

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Appendix

Appendix-A

Experimental data

A.1 Data recorded

Table A.1 Crude glycerol + 98% H_2SO_4

	pH		
Added	Start	End	Volume used (ml)
H_2SO_4	9	2	6
NaOH	2	7	30

Pure glycerin 92 ml

Table A.2 Crude glycerol + 35.7% HCL

	pH		
Added	Start	End	Volume used (ml)
HCL	10	2	17
NaOH	2	7	230

Pure glycerin 89 ml

Table A.3 Crude glycerol + HNO_3

	pH		
Added	Start	End	Volume used (ml)
HNO_3	10	2	13
NaOH	2	7	169

Pure glycerin 91 ml

Appendix-B

Glycerol [21]

B.1) What is Glycerin?

Glycerin (Glycerol) is a clear, odorless, viscous liquid with a naturally sweet taste. It is derived from both natural and petrochemical feedstocks. Glycerin occurs in combined form (triglycerides) in animal fats and vegetable oils and is obtained from these fats and oils during transesterification, such as in biodiesel production.

Glycerin currently has over 1500 known uses in many different industries ranging from foods, pharmaceuticals, and cosmetics (USP grade glycerin) to paints, coatings and other industrial types of applications (technical grade glycerin). It continues to be one of the most versatile and valuable byproducts created during biodiesel production.

B.2) Glycerin in Biodiesel

Glycerin naturally occurs during the biodiesel production process and is specifically produced in the transesterification process. The glycerin produced at this stage is crude glycerin and is about 80% pure still containing contaminants like soap, methanol and water. In order to turn this crude glycerin into a usable state for existing or emerging uses, a purification process must take place.

During this refinement process residual organic matter, water, salt, methanol, and odors are removed.

There are many different types of glycerin grades ranging from crude glycerin to refined glycerin (pharmaceutical grade).

Other names for glycerin:

- glycerol
- 1,2,3-trihydroxypropane
- glycerine
- glyceritol
- propane-1,2,3-triol
- glycyl alcohol
- 1,2,3-propanetriol

B.3) Crude Glycerol

Crude glycerol can be purified to use in products such as cosmetics, pharmaceuticals, and a variety of food items. Purifacation of crude glycerol is a costly and energy intensive procedure; therefore, glycerol intended for livestock consumption is normally not purified.

B.4) Grade of glycerol

B.4.1) Crude Glycerol

Crude Glycerol contains a significant amount of methanol, water, soaps and salts. Typically has a glycerol content of anywhere between 40 to 88%. Crude glycerol is a natural by-product had produced during the biodiesel production process, specifically taking place during transesterification.

B.4.2) Technical Grade Glycerol

Technical Grade Glycerol is a refined, high purity product that is water white with most of its contaminants completely removed. Technical grade glycerol contains no methanol, soaps, salts, and other matter. Biodiesel plants purchased from SRS Engineering, unlike many of our competitor's plants, produce technical grade glycerol right from the start.

B.4.3) USP Grade Glycerol

USP Grade Glycerol is a pharmaceutical grade suitable for food, personal care, cosmetics, pharmaceuticals and other specially applications. All of these products have met the US Pharmacopeia specifications (USP 30).

B.4.3.1 What classifies glycerin as USP Grade?

To be called USP Grade Glycerin companies are closely regulated with regards to their manufacturing facility, testing methods, inspections, distribution, and warehousing. True USP Grade Glycerin follows strict rules and guidelines set forth by the FDA. The FDA requires that all domestic companies distributing USP Grade Glycerin must be registered and listed unless they qualify for exemption. The same applies for USP Glycerin originating from a foreign manufacturing facility going to an importer in the states. In this instance, FDA compliance by both parties is still a requirement.

FDA regulations also require systematic and complete record keeping by all USP glycerin manufacturers. They must have supporting documentation at all times for every shipment providing lot numbers and permits tracing back to the plant it was produced in.

USP Grade Glycerin assures buyers of the product's integrity which cannot be achieving through physical and chemical testing alone. On the flip side, Technical Grade Glycerin is not subject to such governmental regulatory control. Although produced by similiar processes, Technical Grade Glycerin does not need to comply with USP and FCC requirements or FDA regulations. This grade of glycerin only needs to conform to the specifications mutually agreed upon by the buyer and seller.

The differences between Crude Glycerin, Technical Grade Glycerin, and USP Grade

Properties	Crude Glycerin	Technical Grade Glycerin	99.7 -USP Grade Glycerin
Glycerol Content	40 - 88%	98.0 Min	99.70%
Ash	2.0% Max	N/A	N/A
Moisture Content	N/A	2.0% Max	0.3% Max
Chlorides	N/A	10 ppm Max	10 ppm Max
Color	N/A	40 Max (Pt - Co)	10 Max. (APHA)
Specific Gravity	N/A	1.262 (@25C)	1.2612 Min
Sulfate	N/A	N/A	20 ppm Max
Assay	N/A	N/A	99.0 - 101.0% (on dry basis)
Heavy Metals	N/A	5 ppm Max	5 ppm Max
Chlorinated Compounds	N/A	30 ppm Max	30 ppm Max
Residue on Ignition	N/A	N/A	100 ppm Max
Fatty Acid & Ester	N/A	1.00 Max	1.000 Max
Water	12.0% Max	5.0% Max	0.5% Max
pH (10% Solution)	4.0 - 9.0	4.0 - 9.1	N/A
DEG and Related Compounds	N/A	N/A	Pass
Organic Volatile Impurities	N/A	N/A	Pass
Organic Residue	2.0% Max	2.0% Max	N/A

Table B-1 Properties of Grade of Glycerol [22]

Appendix-C

Material Safety Data Sheet of Glycerol (MSDS) [23]

C.1) Product Identification

Synonyms: 1,2,3-propanetriol; glycerin; glycol alcohol; glycerol, anhydrous

CAS No.: 56-81-5

Molecular Weight: 92.10

Chemical Formula: C3H5(OH)3

Product Codes:

J.T. Baker: 2135, 2136, 2140, 2142, 2143, 2988, 4043, 5093, 72138, M778

Mallinckrodt: 0564, 5092, 5093, 5100

C.2) Composition/Information on Ingredients

Ingredient	CAS No	Percent	Hazardous
Glycerin	56-81-5	90 - 100%	Yes

Table C.1 Composition/Information on Ingredients

C.3) Hazards Identification

Emergency Overview SAF-T-DATA$^{(tm)}$ Ratings (Provided here for your convenience)

Health Rating: 2 - Moderate (Life)

Flammability Rating: 1 - Slight

Reactivity Rating: 0 - None

Contact Rating: 1 - Slight

Lab Protective Equip: GOGGLES; LAB COAT; VENT HOOD; PROPER GLOVES

Storage Color Code: Green (General Storage)

Potential Health Effects

Inhalation: Due to the low vapor pressure, inhalation of the vapors at room temperatures is unlikely. Inhalation of mist may cause irritation of respiratory tract.

Ingestion: Low toxicity. May cause nausea, headache, diarrhea.

Skin Contact: May cause irritation.

Eye Contact: May cause irritation.

Chronic Exposure: May cause kidney injury.

Aggravation of Pre-existing Conditions: Persons with pre-existing skin disorders or eye problems or impaired liver or kidney function may be more susceptible to the effects of the substance

C.4) First Aid Measures

Inhalation: Remove to fresh air. Get medical attention for any breathing difficulty.

Ingestion: Induce vomiting immediately as directed by medical personnel. Never give anything by mouth to an unconscious person. Get medical attention.

Skin Contact: Immediately flush skin with plenty of water for at least 15 minutes. Remove contaminated clothing and shoes. Wash clothing before reuse. Thoroughly clean shoes before reuse. Get medical attention if irritation develops.

Eye Contact: Immediately flush eyes with plenty of water for at least 15 minutes, lifting upper and lower eyelids occasionally. Get medical attention if irritation persists

C.5) Fire Fighting Measures

Fire: Flash point: 199C (390F) CC

Autoignition temperature: 370C (698F)

Slight fire hazard when exposed to heat or flame. Slight fire hazard when exposed to heat or flame.

Explosion: Above flash point, vapor-air mixtures may cause flash fire.

Fire Extinguishing Media: Use any means suitable for extinguishing surrounding fire. Water spray may be used to extinguish surrounding fire and cool exposed containers. Water spray will also reduce fume and irritant gases.

Special Information: In the event of a fire, wear full protective clothing and NIOSH-approved self-contained breathing apparatus with full facepiece operated in the pressure demand or other positive pressure mode.

C.6) Accidental Release Measures

Ventilate area of leak or spill. Wear appropriate personal protective equipment as specified in Section 8. Contain and recover liquid when possible. Collect liquid in an appropriate container or absorb with an inert material (e. g., vermiculite, dry sand, earth), and place in a chemical waste container. Do not use combustible materials, such as saw dust. Do not flush to sewer!

C.7) Handling and Storage

Keep in a tightly closed container, stored in a cool, dry, ventilated area. Protect against physical damage. Isolate from incompatible substances. Containers of this material may be hazardous when empty since they retain product residues (vapors, liquid); observe all warnings and precautions listed for the product.

C.8) Exposure Controls/Personal Protection

Airborne Exposure Limits: For Glycerin Mist:

- OSHA Permissible Exposure Limit (PEL):Total Dust: 15 mg/m3 (TWA); Respirable Fraction: 5 mg/m3(TWA).
- ACGIH Threshold Limit Value (TLV): 10 mg/m3

Ventilation System:

A system of local and/or general exhaust is recommended to keep employee exposures below the Airborne Exposure Limits. Local exhaust ventilation is generally preferred because it can control the emissions of the contaminant at its source, preventing dispersion of it into the general work area. Please refer to the ACGIH document, *Industrial Ventilation, A Manual of Recommended Practices*, most recent edition, for details.

Personal Respirators (NIOSH Approved):

If the exposure limit is exceeded and engineering controls are not feasible, a half facepiece particulate respirator (NIOSH type P95 or R95 filters) may be worn for up to ten times the exposure limit or the maximum use concentration specified by the appropriate regulatory agency or respirator supplier, whichever is lowest.. A full-face piece particulate respirator (NIOSH type P100 or R100 filters) may be worn up to 50 times the exposure limit, or the maximum use concentration specified by the appropriate regulatory agency, or respirator supplier, whichever is lowest. Please note that N filters are not recommended for this material. For emergencies or

instances where the exposure levels are not known, use a full-facepiece positive-pressure, air-supplied respirator. WARNING: Air-purifying respirators do not protect workers in oxygen-deficient atmospheres.

Skin Protection: Wear protective gloves and clean body-covering clothing.

Eye Protection: Use chemical safety goggles. Maintain eye wash fountain and quick-drench facilities in work area.

C.9) Physical and Chemical Properties

Appearance: Clear oily liquid.

Odor: Odorless. **Solubility:** Miscible in water. **Specific Gravity:** 1.26 @ 20C/4C

pH: (neutral to litmus)

% Volatiles by volume @ 21C (70F): 0

Boiling Point: 290C (554F)

Melting Point: 18C (64F)

Vapor Density (Air=1): 3.17

Vapor Pressure (mm Hg): 0.0025 @ 50C (122F)

Evaporation Rate (BuAc=1): No information found.

C.10) Stability and Reactivity

Stability: Stable under ordinary conditions of use and storage.

Hazardous Decomposition Products: Toxic gases and vapors may be released if involved in a fire. Glycerin decomposes upon heating above 290C, forming corrosive gas (acrolein).

Hazardous Polymerization: Will not occur.

Incompatibilities: Strong oxidizers. Can react violently with acetic anhydride, calcium oxychloride, chromium oxides and alkali metal hydrides.

Conditions to Avoid: Heat, flames, ignition sources and incompatibles.

C.11) Toxicological Information

Oral rat LD50: 12,600 mg/kg. Investigated as a mutagen, reproductive effector.

	---NTP Carcinogen---		
Ingredient	Known	Anticipated	IARC Category
Glycerin (56-81-5)	No	No	None

Table C.2 Toxicological Information

C.12) Ecological Information

Environmental Fate: When released into the soil, this material is expected to readily biodegrade. When released into the soil, this material is not expected to evaporate significantly. When released into water, this material is expected to readily biodegrade. This material is not expected to significantly bioaccumulate. When released into the air, this material may be moderately degraded by reaction with photochemically produced hydroxyl radicals. When released into the air, this material may be removed from the atmosphere to a moderate extent by wet deposition.
Environmental Toxicity: This material is not expected to be toxic to aquatic life.

C.13) Disposal Considerations

Whatever cannot be saved for recovery or recycling should be managed in an appropriate and approved waste disposal facility. Processing, use or contamination of this product may change the waste management options. State and local disposal regulations may differ from federal disposal regulations. Dispose of container and unused contents in accordance with federal, state and local requirements.

C.14) Other Information

NFPA Ratings: Health: **1** Flammability: **1** Reactivity: **0**

Label Precautions: Avoid breathing mist.

Avoid contact with eyes, skin and clothing.

Keep container closed.

Use with adequate ventilation.

Wash thoroughly after handling.

Label First Aid:

If inhaled, remove to fresh air. Get medical attention for any breathing difficulty. In case of contact, immediately flush eyes or skin with plenty of water for at least 15 minutes. Get medical attention if irritation develops or persists.

Product Use: Laboratory Reagent.

Revision Information: No Changes.

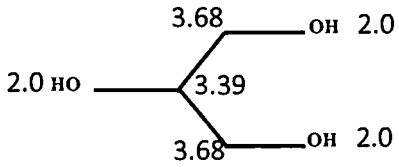
Appendix-D

Refractive Index of Glycerine-Water Solutions at 20°C (69°F)[24]

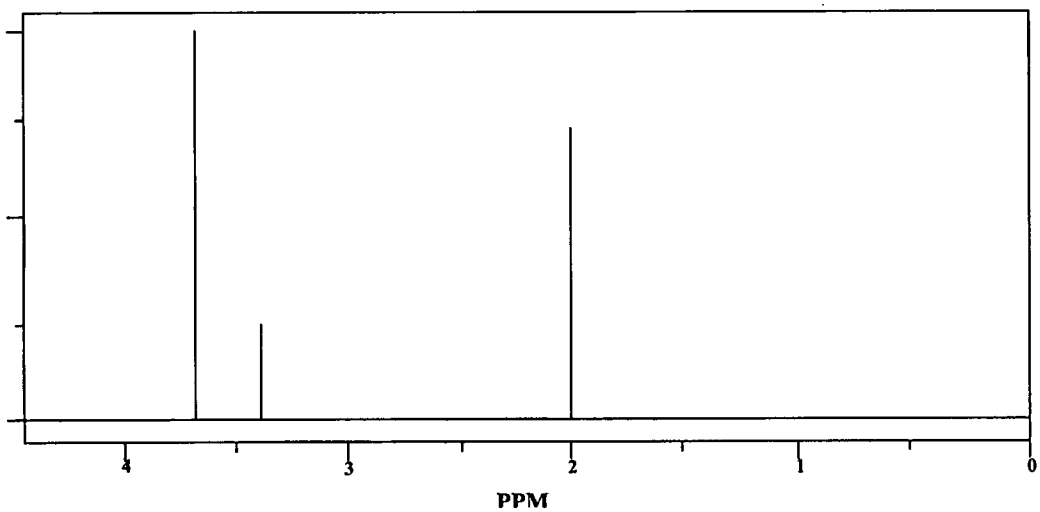
Glycerine % By Weight	Refractive Index n_D^{20}	Difference for 1%	Glycerine % By Weight	Refractive Index n_D^{20}	Difference for 1%
100	1.47399	0.00165	50	1.39809	0.00149
99	1.47234	0.00163	49	1.39660	0.00147
98	1.47071	0.00161	48	1.39513	0.00145
97	1.46909	0.00157	47	1.39368	0.00141
96	1.46752	0.00156	46	1.39227	0.00138
95	1.46597	0.00154	45	1.39089	0.00136
94	1.46443	0.00153	44	1.38953	0.00135
93	1.46290	0.00151	43	1.38818	0.00135
92	1.46139	0.00151	42	1.38683	0.00135
91	1.45989	0.00151	41	1.38548	0.00135
90	1.45839	0.00150	40	1.38413	0.00135
89	1.45689	0.00150	39	1.38278	0.00135
88	1.45539	0.00150	38	1.38143	0.00135
87	1.45389	0.00152	37	1.38008	0.00134
86	1.45237	0.00152	36	1.37874	0.00134
85	1.45085	0.00155	35	1.37740	0.00134
84	1.44930	0.00156	34	1.37606	0.00134
83	1.44770	0.00160	33	1.37472	0.00134
82	1.44612	0.00162	32	1.37338	0.00134
81	1.44450	0.00160	31	1.37204	0.00134
80	1.44290	0.00155	30	1.37070	0.00134
79	1.44135	0.00153	29	1.36936	0.00134
78	1.43982	0.00150	28	1.36802	0.00133
77	1.43832	0.00149	27	1.36669	0.00133
76	1.43683	0.00149	26	1.36536	0.00132
75	1.43534	0.00149	25	1.36404	0.00132
74	1.43385	0.00149	24	1.36272	0.00131
73	1.43236	0.00149	23	1.36141	0.00131
72	1.43087	0.00149	22	1.36010	0.00131
71	1.42938	0.00149	21	1.35879	0.00130
70	1.42789	0.00149	20	1.35749	0.00130
69	1.42640	0.00149	19	1.35619	0.00129
68	1.42791	0.00149	18	1.35490	0.00129
67	1.42342	0.00149	17	1.35361	0.00128
66	1.42193	0.00149	16	1.35233	0.00127
65	1.42044	0.00149	15	1.35106	0.00126
64	1.41895	0.00149	14	1.34980	0.00126
63	1.41746	0.00149	13	1.34854	0.00125
62	1.41597	0.00149	12	1.34729	0.00125
61	1.41448	0.00149	11	1.34604	0.00123
60	1.41299	0.00149	10	1.34481	0.00122
59	1.41150	0.00149	9	1.34359	0.00121
58	1.41001	0.00149	8	1.34238	0.00120
57	1.40852	0.00149	7	1.34118	0.00119
56	1.40703	0.00149	6	1.33999	0.00119
55	1.40554	0.00149	5	1.33880	0.00118
54	1.40405	0.00149	4	1.33762	0.00117
53	1.40256	0.00149	3	1.33645	0.00115
52	1.40107	0.00149	2	1.33530	0.00114
51	1.39958	0.00149	1	1.33416	0.00113
			0	1.33303	-

Appendix-E

ChemNMR H-1 Estimation [25]



Estimation Quality: blue = good, medium, red = rough



Protocol of the H-1 NMR Prediction

Node	Shift	Base + Inc.	Comment (ppm rel. to TMS)
OH	2.0	2.00	alcohol
CH_2	3.68	1.37	meyhylene
		2.20	1 alpha –O
		0.15	1 beta –O
		-0.04	1 beta –O
CH 3.39	1.50	methine	
		1.73	1 alpha –O
		0.08	1 beta –O
		0.08	1 beta –O
OH	2.0	2.00	alcohol
CH_2	3.68	1.37	meyhylene
		2.20	1 alpha –O
		0.15	1 beta –O
		-0.04	1 beta –O
OH	2.0	2.00	alcohol