Intermediate Biodiesel Purification by Refined Glycerin Wash

by

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
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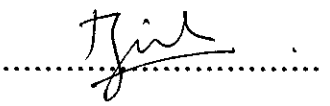
May 2012

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgments, and that the original work contained herein have not been undertaken or done by unspecified sources or person.



NAZIRAH BINTI ABD RAHMAN

ABSTRACT

Biodiesel has attracts worldwide attention due to its potential of replacing fossil-based fuel. In order to conform the stringent international standard, downstream purification is an essential section in the overall process. The feasibility of crude glycerin as biodiesel purifier was investigated. Crude biodiesel was washed with refined glycerin under conditions that have been close to commercial operating practice possible. The correlation of the extraction variables; temperature, glycerin concentration and weight ratio of glycerin to biodiesel were investigated. Three basic parameters were investigated; glycerin concentration, extraction temperature and ratio of glycerin to biodiesel. Experiments were performed in order to determine the optimum condition of the glycerin-wash using Taguchi method. The pretreated biodiesel was further purified with water. Characterization on the biodiesel was done to ensure the standard requirement was fulfilled. The result show that glycerin wash can significantly remove the soap content. The integrated glycerin wash (60% glycerin purity, 85°C and 15wt% ratio of glycerin to biodiesel) followed by 15wt% water wash is proved to be a better method for biodiesel purification.

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First and foremost, I would like to praise God the Almighty for His guidance. Though difficulties occurred, His guidance and blessing gave me the chance to complete this challenging Final Year Project successfully. Here, I would like to use this special opportunity to express my heartfelt gratitude to everyone that has contributed in order to complete the project.

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Finally, I really appreciate and pleased to all the hands given to us. I enjoyed completing this project even though I had faced a lot of obstacles throughout my journey. The experience gained throughout this project was so meaningful and I hope that this project could contribute some valuable things to the education field as well as commercialize field so that besides of me getting knowledge, I could give something back to the society and restored humanity. Thank you.

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CHAPTER 1

INTRODUCTION

1.1. Background

Modernization, urbanization and rapid growth in human population lead to drastic increment in global demand for energy. Currently, 80% of the global energy demands is met by petroleum based fuels where renewable energy and nuclear power contribute only 13.5% and 6.5%, respectively (Asif and Muneer, 2007). The world's biggest energy consumers are China, India, Russia, UK and USA where these countries account to 49% of the total energy consumption in the world (Asif and Muner, 2007). The enormous amount of energy being consumed has brings adverse implications to ecosystem including climate change, emission of greenhouse gases and environmental pollutions. According to a report by Intergovernmental Panel on Climate Change (IPCC, 2007), the world's temperature is increases of 2-6°C by 2100. In addition, sea level is rises of 1-1.5m by 2100 where snow cover shrinks with increases in thaw depth (IPCC, 2007).

However, depletion of reservoirs and price hiking of petroleum based fuels has becomes the major factors to search for alternative sources of energy (Klass, 1998). In 2004, Malaysia was ranked 24th in terms of world's oil reserves and 13th in natural gas (Cha and Oh, 2010). Nevertheless, as per current production rate, Malaysia is projected to be able to produce oil up to 18 years and gas for another 35 years only (Cha and OH, 2010). On top of that, public concerns on human health, quality of life and also ecological balance have growth interest to explore green, clean and sustainable energy. Biofuels, particularly biodiesel is a fuel that has great potential in replacing fossil fuels; specifically petro-diesel. Presently, several countries such as USA, Germany, Australia, Italy, and Austria are already using such

biofuels (Atadashi *et al.*, 2011a) since it has been found to have similar properties and offer similar engine performance as petro-diesel (Atadashi *et al.*, 2011a; Atadashi *et al.*, 2011b; Haas *et al.*, 2006).

1.2. Problem Statement

It has been proven that biodiesel possesses several advantages in term of biodegradability, sustainability and environmentally friendly as well as its capability to be used as fuel for automotive. Despite of the advantages, the most challenging part in biodiesel production is the purification technology where purity level of biodiesel must meet stringent international standard specification provided by European Standard (EN14214) and American Standard (ASTM D6751). Purification of biodiesel is a process of removing undesirable byproduct, unreacted reactant and residual catalyst from biodiesel. It is the most crucial part in biodiesel production where residual impurities will affect engine performance and its lifespan including corrosion, depositions at pistons, valves and injection nozzles and deterioration of gaskets (Atadashi, 2011; Xue, 2011; Berrios, 2008). In addition to that, the impurities may lower the quality of the biodiesel itself by lowering the viscosity, density and reduce heat of combustion (Atadashi *et al.*, 2011b; Xue *at al.*, 2011; Berrios and Skelton, 2008).

1.3. Significant of the project

This project work proposed the use of glycerin extraction method for intermediate biodiesel purification. Glycerin that has been produced as a byproduct in the reaction section will be refined and at the later stage will be used in the purification section. Refined glycerin is also marketable thus can be a value added product. Due to glycerin polar affinity, it is seems that glycerin-wash is a promising technique where it can reduce a significant amount of wastewater, cost saving and able to eliminate emulsification to occur.

1.4. Objective

- To demonstrate the feasibility of refined glycerin as intermediate biodiesel purifier
- To determine the optimal condition for intermediate biodiesel purification by glycerin wash and the parametric analysis

1.5. Scope of Study

As outline in the objectives, the main aim of this project is to demonstrate the feasibility of crude glycerin to be used as intermediate biodiesel purifier. The experiment will be conducted using Taguchi L9 Orthogonal Array computed by Design-Expert® Software. Parametric analysis will be carried out in order to comprehend the correlation between the parameters. The treated biodiesel will then be further purified by water wash. The treated biodiesel will be characterized to ensure the standard requirement is upholds. Besides, the findings will be compared to the existing commercialized method and studies.

CHAPTER 2

LITERATURE REVIEW AND THEORY

2. Biodiesel

2.1. Production of biodiesel

Biodiesel can be produced from four primary ways; direct use and blending, microemulsion, thermal cracking or pyrolysis, or transesterification (Ma and Fangrui, 1999). Biodiesel produced by direct use is not applicable to most of diesel engines due to its high viscosity (Borges & Díaz, 2012). On the other hand, biodiesel obtained from microemulsion and thermal cracking will lead to incomplete combustion as it has low cetane number (Borges & Díaz, 2012). Thus, among those methods, transesterification of vegetable oils and animal fats has become preferred method of choice for commercialization (Ma and Fangrui, 1999). Vegetable oils and animal fats are extracted to obtain crude oil and fat which contain free fatty acid, glycerides, water, odorants, sterols and other impurities. Amount of free fatty acids and water in the feedstocks will give significant effects on the yield of biodiesel.

There are two possible ways in producing biodiesel; esterification and transesterification. The free fatty acid will be esterified with an alcohol of lower molecular weights typically methanol in a present of catalyst. For esterification reaction, it can be catalyzed by inorganic acid such as sulfuric acid and hydrochloric acid or organic acid such as para-toluene sulfonic acid (PTSA) and methane sulfonic acid (MSA) to form methyl ester and water. Esterification reaction is affected by reaction temperature and reactants ratio while catalyst amount has minimal effect to the whole reaction.

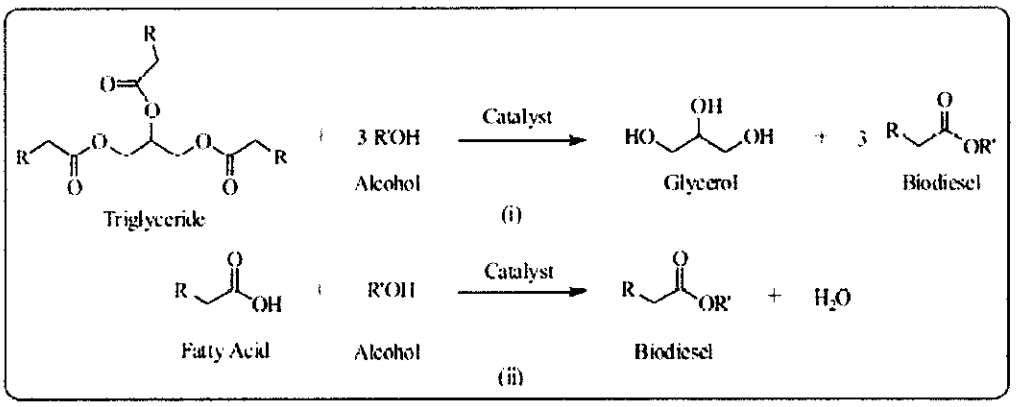

Fig. 2.1 : Schematic representation of transesterification (i) and esterification reactions (ii)

Biodiesel by transesterification reaction is made possible by involving triglyceride and alcohol of low molecular weight with the present of homogeneous or heterogeneous catalyst. Besides of biodiesel, glycerol will be produced from this chemical reaction as the byproduct. The homogeneous catalyst can be alkali or acid where the most commonly used are sodium hydroxide and potassium hydroxide due its solubility in methanol forming methoxide solution (Borges & Díaz, 2012). Furthermore, it gives higher yield and faster reaction time as compared to acid catalyst such as sulfuric acid, sulfonic acid and hydrochloric acid (Borges & Díaz, 2012). The reaction are affected by molar ratio of the alcohol to glycerides, catalyst, reaction temperature, reaction time, free fatty acids and water content of oils or fats (Ma & Hanna, 1999).

The major challenge in biodiesel production is the downstream section which account for 60-80% of the total processing cost (Taishung, 2007). By catalyzed reactions, the impurities that may present will be unreacted alcohol, unreacted glycerides (tri-, di- and mono-), water, free glycerin, free fatty acid and others. Impurities may cause severe implication to the quality of biodiesel and engine performace (Buyukkaya, 2010; Lapuerta, Armas, & Rodríguez-Fernández, 2008; Xue, Grift, & Hansen, 2011). Hence, stringent standards provided by European standard (EN14214) and American standard (D6751) must be met.

Table 2.4 : Negative implication of impurities on biodiesel and engines

Impurities	**Implications**
Methanol	Lower viscosity, density and flash point, corrosion of pieces of Aluminum and Zinc, deterioration of natural rubber seals and gaskets
Catalyst/soap	Corrosion, damage injectors, plugging of filters and weaken the engine
Glycerides	Crystallization, turbidity, higher viscosity and depositions
Water	Hydrolysis, bacterial growth, corrosion, reduces heat of combustion and gelling of residual fuel
Glycerol	Decantation, shorten engine durability, deposition of fuel
Free Fatty Acid	Corrosion, less oxidation stability

(Atadashi *et al.*, 2011b; Buyukkaya, 2010; Lapuerta *et al.*, 2008; Xue *et al.*, 2011)

In transesterification reaction, the presence of free fatty acid may cause the formation of saponified product. This is due to saponification reaction associated with alkaline catalyst in transesterification reaction (Balat and Balat, 2010; Van Gerpen *et al.*, 2004). The formation of soap will cause a significant difficulty in downstream separation and purification since it will solidify and form semi solid substance; as well as reduces biodiesel yield by increasing the biodiesel solubility in the glycerin phase (Balat and Balat, 2010).

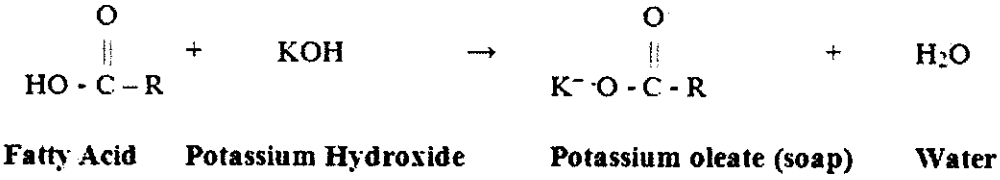

Fig.2.5 Soap formation

2.2. Biodiesel separation technologies

Numerous researchers reported that when suitable biodiesel separation process is employed, high quality biodiesel with economically viable can be achieved. Conventionally, biodiesel is separated via gravitational settling or centrifugation at the end of transesterification section since there is a significant density difference between biodiesel (880kg/m^3) and glycerin (1050kg/m^3). Due to its polarity, where 'like dissolves like', most of the excess methanol, water, and most importantly undesired formed soap will remain in the glycerin phase. Two immiscible layers will be formed thus made the separation by gravity separation is possible. However, some trace of these impurities will be carry over in biodiesel phase where the separation efficiency is influenced by factors such as amount of water, catalyst, soap and methanol present, intense mixing, side reaction of emulsification and solubility of biodiesel with glycerin (Van Gerpen *et al.*, 2004). Thus, for process rectification, intensive researches on heterogeneous catalyst for transesterification reaction have been carried out since it seems to have a bright future as a potential solution; which subsequently will lower the cost of biodiesel separation and purification process (Borges and Díaz, 2012; Lam *et al.*,2010).

2.3. Biodiesel purification technologies

After the physical separation, biodiesel phase with leftover impurities will be routed to purification section. In the purification section, it is mainly intended to remove free glycerol, excess methanol, and residual catalyst including dissolved soap. Otherwise, the quality of the biodiesel is reduced and more severely will bring negative implications to engine performance and its lifespan. Few researchers have carried out studies on the effects of these contaminants on diesel engines where it was found that ineffective biodiesel purification will lead to plugging of filters, coking on injectors, carbon depositions, corrosion and engine durability (Buyukkaya, 2010; Lapuerta *et al.*, 2008; Xue *et al.*, 2011). As for the quality of the biodiesel itself, contaminants will lower the flash point, viscosity and also density value (Buyukkaya, 2010; Lapuerta *et al.*, 2008; Xue *et al.*, 2011).

The purification technique can be classified into two techniques; wet and dry washing where conventionally, wet washing is the most employed technique in commercial plants (Berrios and Skelton, 2008). Among the solvent used in wet washing technique is water, acid, and ether.

2.3.1. Water washing technology

Preheated water at 60-80°C is added to wash the biodiesel phase which later is allowed to settle where it will form two immiscible phase. Suprihastuti and Aswati (2007) had investigated biodiesel washing by water where they reported that to achieved standard limitation of glycerol content in biodiesel, multistage washing process is required. In addition, water by 300% of biodiesel volume is managed to achieve glycerol content of less than 0.05% as compared to > 0.02% of the standard requirement. In another study, approximately 28% of water by the volume of oil which account to 10L of wastewater is produced for each liter of biodiesel (Karaosmanoglu *et al.*, 1996). Berrios and Skelton (2008) claimed that both methanol and free glycerol content can be lowered to the standard by water washing where the condition is; water needed is 50% of biodiesel volume. However, glycerides (mono-, di- and tri-) were not be effected. Another research by Berrios *et al.*, (2011) reported that either distilled water or tap water, no significant different results were found. Hence, it was concluded that 2 steps water washing process of 10 wt% of water will be efficient enough in removing the soap, glycerol and methanol (Berrios *et al.*, 2011).

Apart from the volume ratio of solvent to biodiesel, it is found that the rate of mass transfer of contaminants from biodiesel is also affected by temperature of the extraction (Suprihastuti and Aswati, 2007). On the other hand, FFA will be found to be increased resulting from the partial hydrolysis as high as 25% increment as reported by Berrios *et al.* (2011). The major drawback of water washing technique is due to large wastewater discharge which later incurs cost of wastewater treatment plant; not to mention that the wet biodiesel need to be dry further by distillation column which acquires high energy cost.

2.3.2. Acid washing technology

Acids such as phosphoric acid, sulfuric acid and hydrochloric acid are among the most acid used in the purification of biodiesel. Technically, this process is followed by the use of distilled water for complete removal of biodiesel impurities. A study by Predojević (2008) where 5% of phosphoric acid is used to help the process neutralizing the base catalyst in the transesterification section and converting the soap formed back to free fatty acid so that emulsification tendency is eliminated. In another study, Berrios and Skelton (2008) reported soap can be completely removed by acidified water where agitation had influenced the soap removal at some extent. Faccini *et al.* (2006) used 10% phosphoric acid followed by three time water wash in 10% (v/v). It was found that successive rinses are successfully removed contaminants to the required standards. However, the spent acid requires specified neutralization treatment facilities before it is discharged to common wastewater plant.

2.3.3. Ether washing technology

Organic solvents such as petroleum ether have been used to purify crude biodiesel. This process also followed by massive amount of demineralized water to remove residual soap and catalyst. Wang *et al.* (2007) has purified crude biodiesel using petroleum ether and washed with hot water until the washing reached neutral pH. N-Hexane of ratio 1:1 was also used to extract the crude biodiesel at room temperature where the final yield obtained was 93 wt. %. In another study, Karaousmanoglu (1996) added petroleum ether at ratio 1:1 to biodiesel volume and distilled water at ratio twice of biodiesel volume. The washing time was repeated three times where the final yield obtained was 82.6%.

2.4. Dry washing technologies

On the other hand, dry washing technique is made possible through the use of ion exchange resins, magnesium silicates powder, cellulosic, activated clay, activated carbon activated fiber, etc. (Atadashi *et al.*, 2011a; Atadashi *et al.*, 2011b). Such adsorbents consists of acidic and basic adsorption sites and have strong affinity for

polar compounds such as methanol, glycerol, metals and soap which make the purified biodiesel is able to meet the standard specification. The use of dry washing technique is typically followed by filtration which made the technique is effective and efficient. The schematic diagram for biodiesel purification by dry washing process is shown the Fig. 2.3.

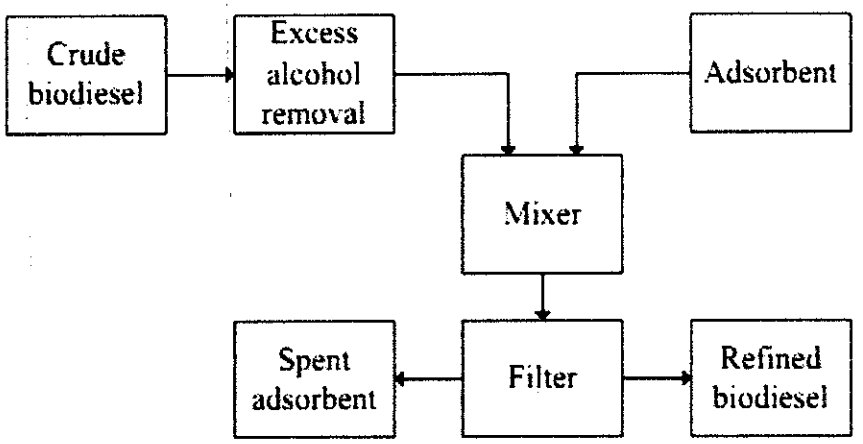

Fig. 2.3: Schematic diagram of biodiesel dry washing process

Two commercial ion exchange resins available in current market are manufactured by Rohm & Haas (BD10 Dry) and Purolite (PD206). Due to commercial confidential reason, it has not been possible to obtain any information on the chemical composition of either of the resins. As for magnesium silicate powder, Magnesol ® is commercialized by Hydrotechnik in UK and Dallas Corpororation in US. Both ion exchange resins and magnesium silicate powder are purely adsorbent where the spent material has to be disposed of to landfill or other applications for instance compost, potential animal feed additive or fuel (Berrios and Skelton, 2008). According to Berrios and Skelton (2008), these techniques have advantages of being waterless, easy to integrate into existing plant, significantly lower the purification time and cost, wastewater free, smaller equipment's footprint and most importantly improve biodiesel quality. The major limitation in the use of silicate is due to limited knowledge on the process while for ion exchange, feed composition is the major constrain since the capability to adsorb soap is very little (Berrios and Skelton, 2008).

Dry washing media such as activated carbon, activated clay, activated fiber and activated carbon are proven effective in removing color, alkalinity as well as odor (Hayafuji, 1999). A study has been conducted recently to investigate the feasibility of spent tea waste activated carbon as biodiesel purification media (Fadhil *et al.*, 2012). The purified biodiesel is being compared to other purification method which are silica gel and conventional method of water washing. It was found that the yield of biodiesel purified by spent tea waste activated carbon is higher while the fuel properties are better (Fadhil *et al.*, 2012). From the research, it is proven that spent tea waste activated carbon has higher surface area where the present of oxygen group in the carbon adsorbent will enhance the adsorption. Furthermore, the activated carbon used can be regenerated and reuse for the same purpose. However, since the cost for regeneration facilities is not economically practical, it seems not viable for large scale production.

2.5. Emerging membrane technologies

Membrane technology is seems as a promising alternative for biodiesel purification. Several researches have conducted studies on various type of membrane namely organic and inorganic membrane. Among of the advantages of this technology including high selectivity and high purity of biodiesel, moderate temperature and pressure condition, low energy consumption, elimination of wastewater treatment and high mechanical, thermal and chemical stability (Atadashi *et al.*, 2011b; Saleh and Jehad, 2010). Initially, most of the membranes were cellulosic in nature. However, polymers for instance polyamide, polysulphone, polycarbonate and ceramic have big potential in replacing the organic membrane (Atadashi *et al.*, 2011b). Nevertheless, further development of membrane technology is necessary before adopting the technology in the existing plant.

Table 2.5 Various biodiesel purification techniques

TECHNIQUES	ADVANTAGES	DISADVANTAGES
WET WASHING		
Water Acid Ether	Excellent methanol, fatty acid soap and free glycerin removal Purity up to 99%	Massive wastewater Loss of product due to emulsion and soap formation Chemical treatment More time and high cost
DRY WASHING		
Resin Ion exchange Adsorbent	Effectively remove water, fatty acid soap and catalyst Save time Lower energy Less wastewater discharge	Expensive Limited information Require regeneration facilities Disposal of spent adsorbent
MEMBRANE		
Inorganic Organic Polymeric	High purity, good yield Less energy and environmental benefits No waste discharge	No large scale industrial application

Table 2.6: International biodiesel standard specification

Properties	Units	ASTM	EN 14214
Ester content	%(m/m)	-	96.5
Flash point	°C	130 min.	>101
Water and sediment	vol.%	0.050 max.	0.05
Kinematic viscosity. 40°c	mm^2/s	1.9-6.0	3.5-5
Sulfated ash	%(m/m)	0.020 max.	0.02
Sulfur	Mg/kg	-	≤10
S 15 grade	ppm	15 max.	-
S 500 grade	-	500 max.	-
Copper strip corrosion	rating	No. 3 max.	class1
Cetane	-	47min	≥51
Cloud point	°C	report	-
Carbon residue 100% sample	%(m/m)	0.050 max.	-
Acid number	mg KOH/gm	0.50 max.	0.50
Triglyceride	%(m/m)	0.20 max.	0.20
Free glycerin	%(m/m)	0.020 max.	0.02
Total glycerin	%(m/m)	0.240 max.	0.025
Phosphorus content	mass%	0.001 max.	0.001
Methanol content	%(m/m)		0.20
Distillation temperature, atmospheric equivalent temperature. 90% recovered	°C	360 max.	-
Sodium/potassium	ppm	5 max. combined	5 max

Max. : Maximum.
Min. : Minimum.

2.6. Theory

Glycerin is seems to have a great potential to be used in intention to remove impurities from biodiesel which consist of soap, excess methanol, residual catalyst, and water. Glycerin is categorized as a polar compound since its positive and negative charges are not distributed evenly. So does water, methanol and soap. On the other hand, biodiesel is categorized as non-polar compound where the majority of biodiesel molecule is neutral. Applying a basic chemistry where 'like dissolves like' molecules with a charge dissolve other molecules with a charge. This fact describes the biodiesel will not dissolve in water or glycerin in fact these contaminants will be extracted from biodiesel phase and two immiscible layer will be formed.

For an operation which a material dissolved in one liquid phase is transferred to a second liquid phase, it is called liquid-liquid extraction. In biodiesel washing process, there are two phases, the aqueous phase and the ester phase. The solute which in this project is specifically concerned on soap is transferred from diluent (ester phase) to solvent (glycerin phase).

The main objective of this paper work has been to look the feasibility and efficiency of refined glycerin to be used as intermediate biodiesel purification. Hence, the proposed scheme of this purification method is shown in Fig. 2.4.

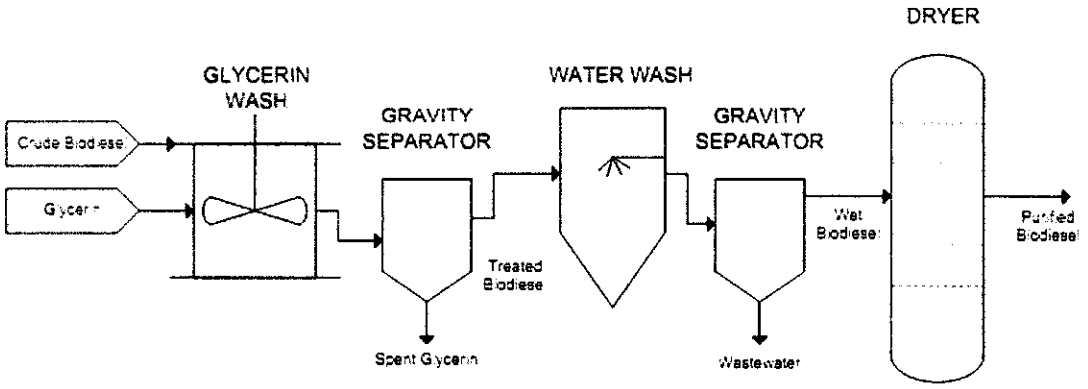

Fig. 2.4: Proposed scheme of biodiesel purification using glycerin wash

Following the effective phase separation between biodiesel and produced glycerin in transesterification section, the crude biodiesel will be washed with refined glycerin before being separated by gravity. The good mixing will allow efficient extraction of methanol, water, catalyst, and most extensively discussed in this paper work; soap. Subsequently, the pretreated biodiesel will be further purified with warm water by 10 wt% of biodiesel. Phase separation will be employed followed by final polish perhaps by dryer or distillation column.

Such scheme is seems able to reduce the consumption of water during the washing process which eventually significantly reduce the discharge of the wastewater. In addition, less water used is preferable since it will save the cost of chemical treatment at wastewater treatment section, less load to final polish section and most importantly eliminate the event of loss of product by emulsion. This study will compare the intermediate glycerin wash scheme to other conventional methods which currently commercially adopted.

CHAPTER 3

METHODOLOGY

3. Methodology

3.1. Research Methodology

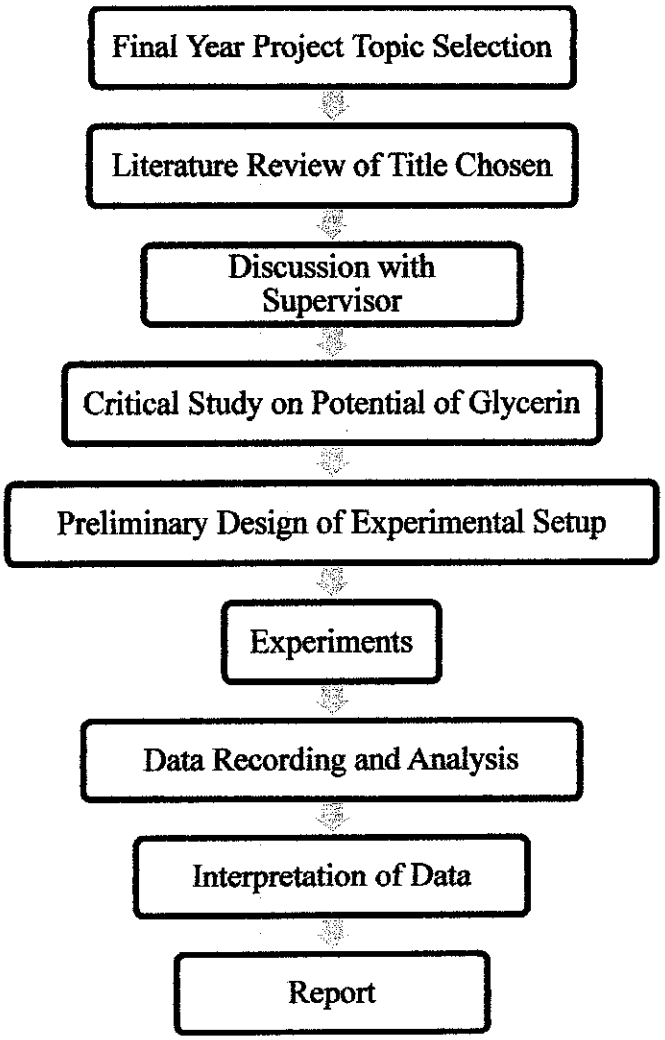

Fig.3.1: Flow Diagram of research methodology

3.2. Experimental Procedures

3.2.1. Experimental materials

The feedstock which is crude biodiesel was obtained from Platinum Nanochem Sdn Bhd, Negeri Sembilan; an existing biodiesel manufacturer in Malaysia. The crude biodiesel was made from palm free fatty acid distillate catalyzed by para-toluene sulfonic acid in continuous process. To produce biodiesel, the manufacturer employed combined process of esterification and transesterification since the free fatty acid of the raw material is high. The crude biodiesel was taken immediately after the gravity separation of transesterification section. Sodium methoxide was used as the catalyst during transesterification reaction. Spent glycerin is obtained from the transesterification section of the same plant.

The equipment used including three neck round bottom glass flask (250ml) equipped with magnetic stirrer, thermometer, condenser and heating jacket. For gravity separation, separating funnel (250ml) is used. For analytical equipment used are pH meter and burette for titration.

3.2.2. Analytical methods

All the properties of the samples were analyzed following Standard Methods. The water content was determined by the coulometric Karl Fisher titration method and acid value as well as free fatty acid was determined by titration with KOH in accordance with the EN14104 Standard. The free glycerol content was determined by titration with sodium metaperiodate in accordance with EN14105. Soap content was determined in accordance with a method from Biodiesel Analytical Methods. Methanol content was determined by a method in accordance with the EN14110 Standard as well as alkalinity and pH value.

3.2.3. Apparatus and Washing Procedures

A 1000cm^3 three neck flask equipped with stirrer and thermometer was attached to a condenser and a heating jacket. 200g of crude biodiesel was filled into

the flask. A certain amount of glycerin was poured while mixing at constant 750 rpm. After 10 minutes, the mixture is being transferred into a separating funnel and was kept in a warm water bath for 30 minutes. The sample was allowed to separate by gravity. The immiscible layer was separated after 30 minutes. Both layers are weighted and analyzed.

Pretreated biodiesel was further purified by water wash where 10wt% of warm water to biodiesel was used. Washing was carried out with sample size 100ml. the mixture was shaken vigorously and then left settles for 10 min. the sample analysis was the same as the glycerin wash experiment.

3.2.4. Determination of the optimal condition by Taguchi method

Taguchi method is a tool used to design the experiments using systematic approach by orthogonal array based on scientific and engineering knowledge.

Extraction temperature, volume ratio of glycerin to biodiesel, and concentration of glycerin were selected as independent variables. The experiments were designed using Taguchi technique. The level of independent variables was determined as given in Table 3.1.

Table 3.1: Independent variables and levels of L_9 (3^3) for Taguchi method

Parameters	Symbol	Level 1	Level 2	Level 3
Glycerin concentration (wt %)	C	60	70	80
Temperature (°C)	T	65	75	85
Ratio of glycerin to biodiesel (wt%)	R	5	10	15

3.3. Characterization and Properties Measurement

The characterization analysis was conducted in order to ensure the purified biodiesel met the standard requirement of both EN 14214 and ASTM D6751. Properties that have been analyzed throughout the experiment were:

- Soap content
- Free glycerol
- Methanol content
- Acid value

CHAPTER 4

RESULT AND DISCUSSION

4. Result and Discussion

The efficiency of glycerin extraction method in removing impurities in biodiesel specifically soap has been assessed as a function of the extracted percentage of soap calculated by the following equation:

$$\eta_i = \frac{x_0 - x_f}{x_0} \times 100$$

where η_i is the efficiency of the glycerin extraction methods and x_0 and x_f are the concentrations of soap at the beginning and at the end of the treatment.

4.1. Process optimization

The results from the experiments conducted based on the OA design experiments are shown is Table 4.1. Soap content had been reduced in all the runs; which is in the range of 68.58-95.79%. The highest extraction of soap was found to be in run #9; 95.79% of the original value. The free fatty acid content was analyzed to be 0.3005 and the pH value is 6.9. This result was recorded at the highest tested ratio of glycerin to biodiesel of 15% (wt/wt) with highest extraction temperature of 85°C and glycerin purity of 60%.

Table 4.1 Extracted soap obtained based on L9 OA design of experiments

Run	Concentration (%)	Temperature (°C)	Glycerin : Biodiesel (wt/wt)%	Extracted soap (%)
1	80	85	10	89.33
2	60	65	5	68.58
3	70	75	15	75.53
4	70	85	5	90.79
5	80	65	15	93.52
6	80	75	5	74.78

7	60	75	10	87.67
8	70	65	10	94.17
9	60	85	15	95.79

The optimal conditions predicted by the Design-Expert® Software at extraction temperature of 85°C, glycerin to biodiesel of 15wt% where the glycerin purity is 60%. The predicted extracted soap is 94.89%. These operating conditions were tested in duplicate obtaining 95.79% and 96.2% with the average of 96%. The standard deviation is 1.16% where the signal to noise ratio is 39.65.

4.2. Parametric analysis

Based on the data presented in Table 4.1, the signal of noise ratio were calculated and tabulated to investigate the effect of each parameter to the extraction of soap. The signal to noise ratio for each experiments showed in Table 4.2.

Table 4.2: Extracted soap and Signal to Noise Ratio

Run	Extracted Soap (%)	Signal / Noise
1	89.33	39.02
2	68.58	36.72
3	75.53	37.56
4	90.79	39.16
5	93.52	39.42
6	74.78	37.48
7	87.67	38.86
8	95.17	39.57
9	95.79	39.63

From Table 4.2, average signal to noise ratio were calculated as shown in Table 4.3. The difference between the highest and lowest average signal to noise ratio for each parameter will conclude their significance over the removal of soap from biodiesel depending on the difference magnitude. In order to verify the parametric analysis obtained from the fractional factorial experiments, additional experiments were conducted.

As shown in Table 4.3, temperature and ratio give fairly high effect to the extraction of soap by glycerin as compared to glycerin concentration.

Table 4.3: Average signal to noise ratio for each parameter

Level	Glycerin concentration	Temperature	Ratio
1	84.013	85.757	78.050
2	87.163	79.327	90.723
3	85.877	91.970	88.280
Δ	3.150	12.643	12.673

4.2.1. Effect of glycerin concentration

To study the dependency of glycerin concentration on intermediate glycerin wash method, additional experiments have been carried out at various glycerin purities while the glycerin to biodiesel weight ratio, temperature and mixing speed were kept constant at 15wt%, 85°C and 750rpm respectively. Fig.4.1 shows the extraction efficiency at different extraction temperature.

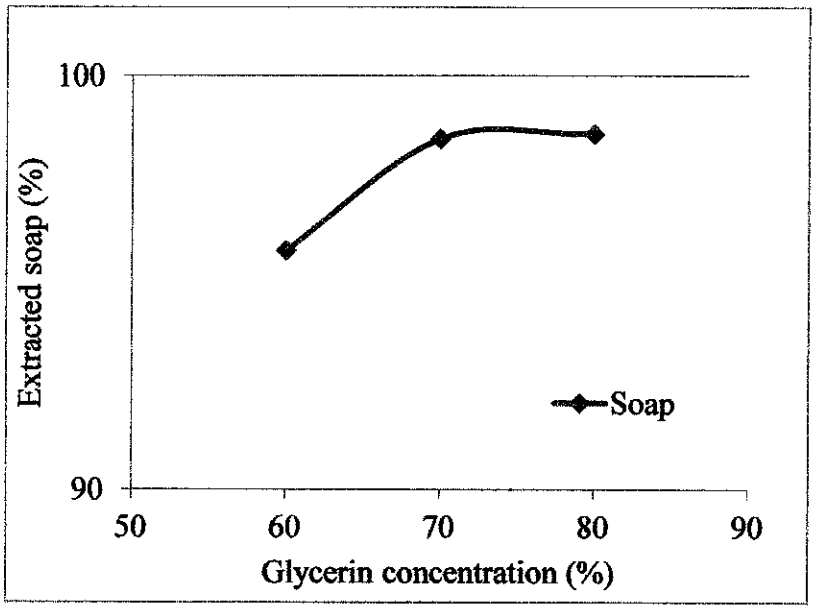

Fig.4.1: Effect of glycerin concentration

For the same washing time, it was found that higher concentration of glycerin used was resulting to the more amount of soap being extracted. As a polar solvent (glycerin), higher purity will provide greater glycerin molecules whose electric

charges are unevenly distributed leaving one end of the molecule positive and the other end negative. Thus more charges mean more soap will be extracted, subsequently improve the extraction efficiency. Based on Fig.4.1, it can be concluded that glycerin concentration does give effect to the extraction of soap up to certain point where above 70%, it gives least effect to the extraction efficiency.

Following the results, it is interesting to know that lower purity of extraction agent (glycerin) can be employed at even lower price without trading its performance. On the other hand, from industrial's economic point of view, low concentration of glycerin is preferable as it influence the operating cost.

4.2.2. Effect of temperature on glycerin wash

Experiment was done to study the dependency of intermediate glycerin wash method on temperature by manipulating the extraction temperature while the glycerin to biodiesel weight ratio, glycerin concentration and mixing speed were kept constant at 15, 60% and 750rpm respectively. Fig.4.2 shows the extraction efficiency at different extraction temperature.

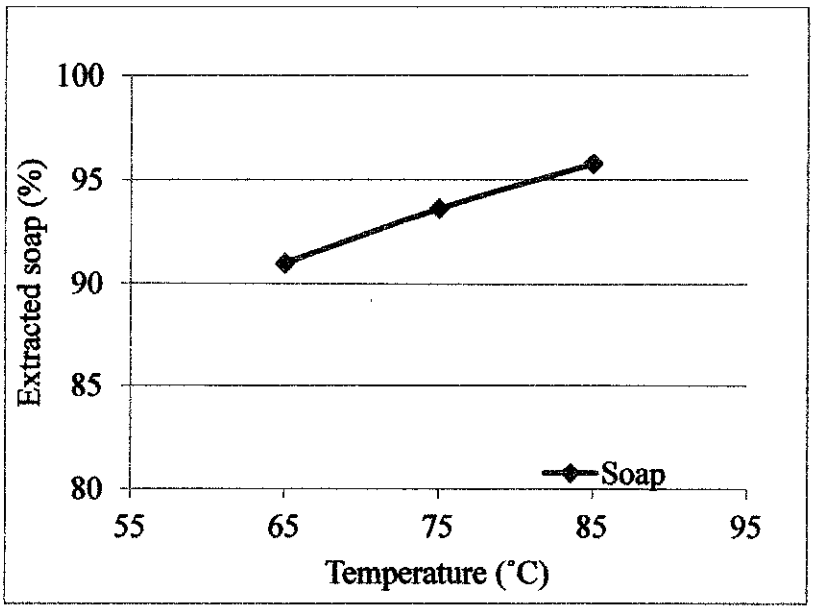

Fig. 4.2: Effect of extraction temperature

From the graph, for the same washing time, it can be seen that increasing the temperature will increase the amount of soap extracted where at 65°C the extracted

soap was 91.02% and it increased by 3% at 75°C to 93.62% followed by 95.79% at 85 °C. This observation in line with the work reported by Suprihastuti and Aswati (2007) where the amount of free glycerol extracted increased with the increasing of washing temperature of biodiesel by water. In addition, the principle of molecular kinetic explains that higher temperature gives higher collision and higher diffusivity of the molecules. In liquid-liquid extraction, better diffusivity will result in better molecules contact of solute into solvent thus improve the extraction efficiency.

4.2.3. Effect of weight ratio of glycerin to biodiesel

The weight ratio of glycerin to biodiesel was varied across the experiments to where glycerin concentration, temperature and mixing speed were kept constant at 70%, 85°C and 750rpm respectively. Fig.4.3 shows the extraction efficiency at different solvent ratio.

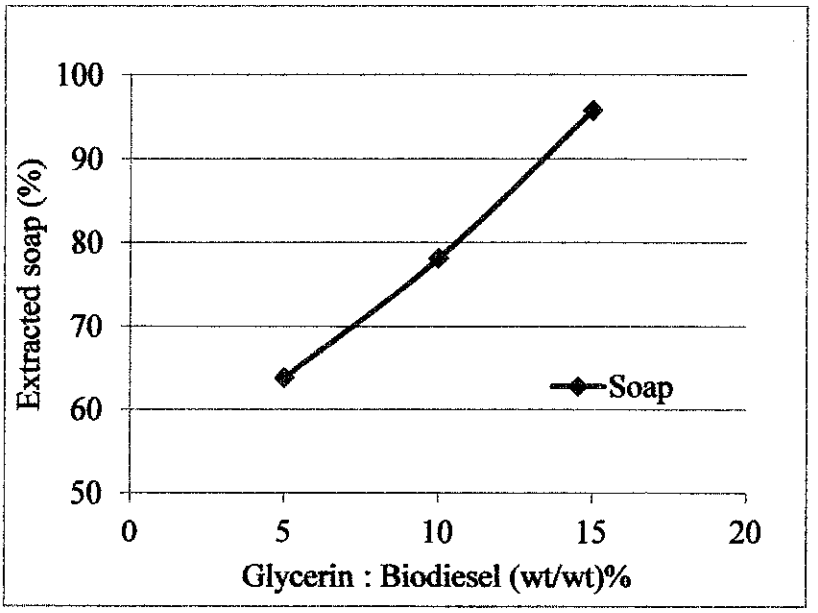

Fig.4.3: Effect of weight ratio of glycerin to biodiesel

The results show that ratio of glycerin to biodiesel will significantly affect the extraction of soap. Higher ratio will result to higher soap extraction. The presence of glycerin at higher ratio directly provided more glycerin molecules with polar charges. Hence, more soap with charge positive will be attached to the glycerin molecules. As reported by Suprihastuti and Aswati (2007), the higher ratio of extraction agent to the biodiesel, the more impurities will be extracted. Berrios *et al.*

(2011) studied the biodiesel purification by glycerin wash where it was reported that at 15wt% of pure glycerin to biodiesel ratio and two-step process will give best result. Corresponded to the work done by Berrios *et al.* (2007), the proposed ratio for glycerin wash is similar which is 15wt%; however adopting solely glycerin wash method require pure glycerin and two-step washing process.

On top of that, the free fatty acid content after glycerin treatment was found to reduce by 60%. The crude biodiesel collected from plant is alkaline where the base catalyst in the tranesterification section shall react with free fatty acid forming soap. This theory explains the significant reduction of free fatty acid from its initial value. An opposite observation found by Berrios *et al.* (2007) where it was reported that free fatty acid shall increase by 27.5% due to left side movement in the esterification reaction.

4.2.4. Comparative study

Glycerin washing shows significant impact to the extraction of soap in all operating conditions. The soap content after glycerin treatment was compared to the required level of EN 14214 and ASTM standard which is 5ppm max (g soap/g sample) as presented in Fig.4.4. The results show that none of the treated biodiesel fulfills the requirement, but the best results are reached with the minimum extraction temperature at 65°C (run 8). The amount of soap content after the glycerin treatment for each experiment was also corresponded to its initial soap content. Since the crude biodiesel were obtained directly from the plant, thus the soap content fluctuated where these data represented the actual plant performance.

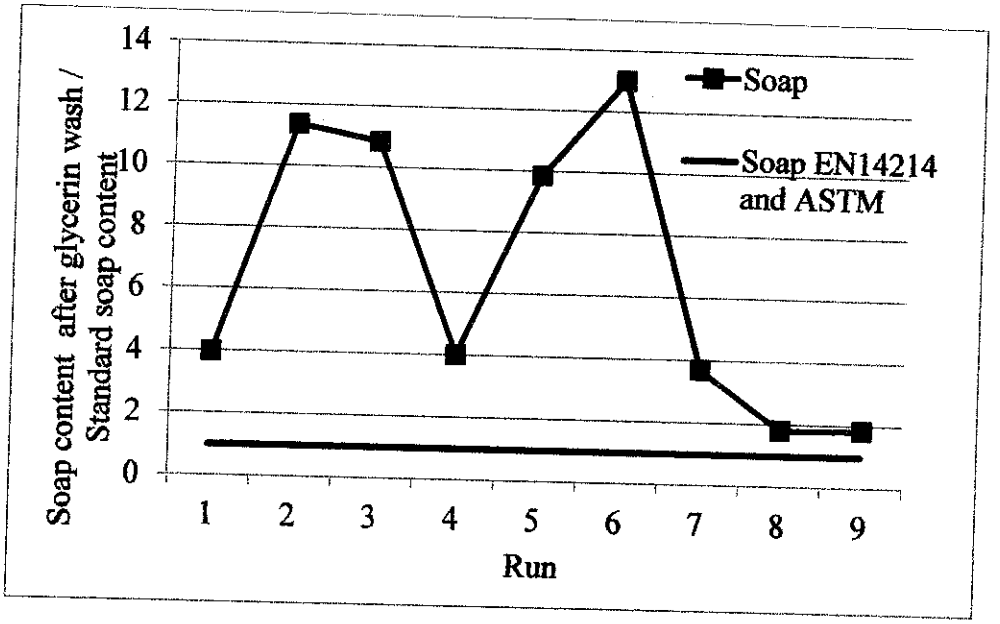

Fig.4.4: Soap content after glycerin wash

Table 4.4: Characterization of biodiesel after water wash treatment

Properties	This work	EN 14214	ASTM
Methanol content, %(m/m)	0	-	-
Soap content, (g soap/g sample)	0.02	5max. combined	5max.
Acid value, (mg KOH/g sample)	0.4	0.50 max	0.50 max.
Free glycerol, %(m/m)	0.005	0.02	0.05

The treated biodiesel were then being further purified by one step water wash where 10wt% of warm water is used. It was found that the soap content was successfully been reduced to the required standard when the ratio is 10 and below; regardless its operating conditions. Characterization of biodiesel for run 6 is shown in Table 4.4 (only run 6 is shown since its ratio approaching the limit of 10). Referring to Fig. 4.4, run 2, run 3 and run 6 are out of the soap specification where the ratios are 11.364, 10.846 and 13.014 respectively. It is interesting to observe that for such wide range of soap ratio, the maximum standard limit can still be fulfilled by only one step water wash process.

This observation has great advantage over the proposed conditions of solely water washing method as reported by few researchers. Berrios and Skelton (2008)

proposed the water wash condition to be 50wt% of water to biodiesel, 200rpm at ambient temperature where deionized water is reported to give similar performance as town water. On the other hand, Suprihastuti and Aswati (2007) proposed the optimization of water washing process to be 300vol.% of water to biodiesel and should be done in multistage while Demirbas (2008) reported 28vol.% of water to biodiesel is required to be added.

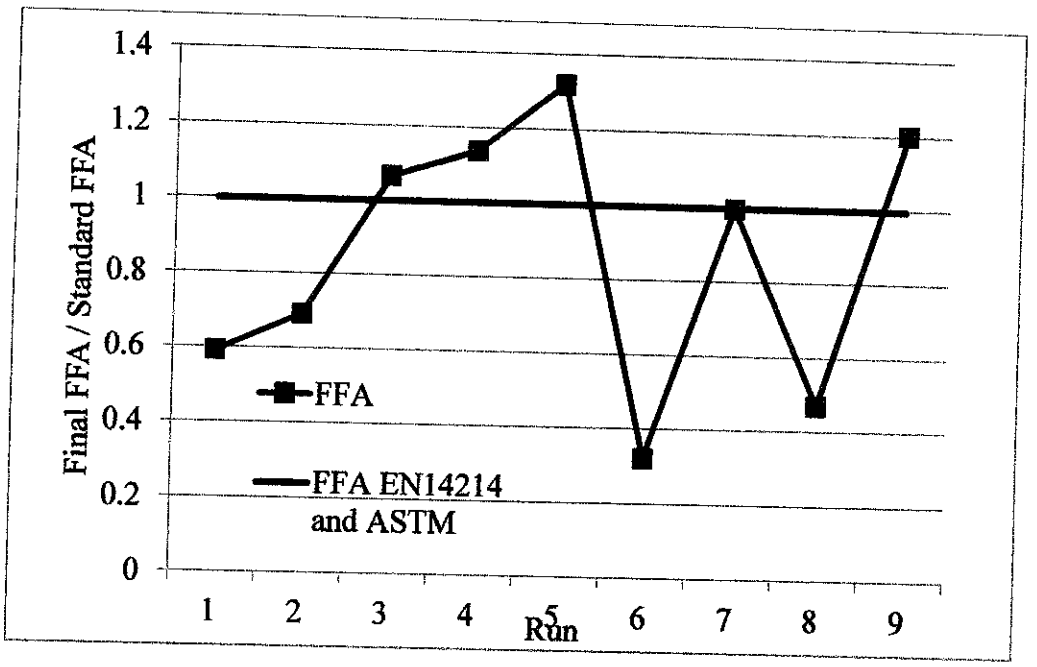

Fig. 4.6: Free fatty acid content after glycerin wash

Glycerin washing has given effect on free fatty acid content in biodiesel. The free fatty acid content after glycerin treatment were possible to increase and decrease even down to maximum level of EN 14214 and ASTM standard which is 0.25 (equivalent to 0.5 of acid value) as presented in Fig. 4.5. The results show that in most cases the free fatty acid will decrease. This happened due to the alkalinity of the crude biodiesel when it was collected after undergoing transesterification reaction. Prior to the presence of base catalyst (sodium methoxide), sodium will react with free fatty acid forming soap. Following the glycerin wash process, soap will be extracted from biodiesel phase and will be carried over in glycerin phase. Having relatively high polarity (0.812), glycerin will eventually attached to positive charge by sodium.

However, the increment of free fatty acid may result from the left side movement of esterification reaction. This phenomenon is made possible with the presence of water at acidic environment. The pH of refined glycerin used is around 4.5. This findings agreed by Berrios *et al.* (2011) where about 27.5% increment of free fatty acid over the initial content after washing with pure glycerin. On the other hand, after water wash, the free fatty acid content found to be under required specification in all experiments.

In order to remove soap from biodiesel, there are few commercial processes adopted by the biodiesel manufacturers around the globe while on going researches are taking place to intensify and rectify the current process. Rohm and Hass (R&H) and Purolite proposed the ion exchange technology, BD10Dry and PD206 respectively. It was reported by Berrios and Skelton (2008) that BD10Dry is able to reduce the soap content factor 10. However, it may not flexible to crude biodiesel containing high amount of soap. Hydrotechnick (UK) and Dallas Corporation, proposed the use of magnesium silicate, Magnesol® to reduce the soap content. However, Berrios and Skelton (2008) found that the amount of soap removal is less than BD10Dry. Another alternative media for soap removal is Bentonites where it able to reduced soap by 24-40%, slightly lower than Magnesol® (Berrios *et al.*, 2011).

Table 4.5: Comparison on different purification method for soap removal

Purification method	Soap removal efficiency (%)	References
Wet washing		
• Water	61-82	Berrios *et al.*, 2011
	Not studied	Suprihastuti and Aswati, 2007
	Not studied	Demirbas, 2008
• Pure glycerin	69.6-81.8	Berrios *et al.*, 2011
• Crude glycerin	68.58-95.79	This work
Dry washing		
• Magnesol®	67-92	Berrios *et al.*, 2011
• Bentonites	24-40	Berrios *et al.*, 2011
• Lewatit® GF202	52.2	Berrios *et al.*, 2011
• Eco2pure®	100	http://www.eco2pure.com

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5. Conclusions and Recommendations

Biodiesel purification by glycerin wash followed by water wash was studied to investigate the feasibility of crude glycerin as impurities extractor, mainly soap. It was proven that crude glycerin washing method is viable to be implemented in the real biodiesel production plant.

The optimum conditions for intermediate glycerin washing ware investigated using fractional factorial design of experiment based on Taguchi method. It was found that the best condition would be at 70% of glycerin purity, extraction temperature of 85°C and ratio of 15wt% of glycerin to biodiesel. Further analysis of extraction parameters concluded that the extraction temperature and ratio had great effect to the extraction efficiency while glycerin concentration had least effect.

Given the need to purify the biodiesel as required by EN14214 and ASTM standard, further water wash treatment is necessary where significantly lower consumption of water is adopted which is 10wt% of biodiesel. This much of water is able to reduce the soap content and free fatty acid content to the maximum standard level provided that the ratio of soap content after glycerin wash over standard soap level must be lower than 10 while the ratio of free fatty acid after glycerin wash to its standard must be lower than 2.

Comparing glycerin-water wash to the other conventional methods, it seems that this method can reduce significant number of wastewater discharge, cost saving and save time not to mention value added product since residual glycerin produced in the transesterification section can be refined by a basic treatment.

Mixing mechanism is a parameter that may influence the extraction of impurities by glycerin wash which is not covered in this research work. Optimum condition for glycerin wash's post (water wash) treatment must be carried out since this study covered the glycerin wash treatment only. Characterizations on the treated biodiesel for other properties are recommended to be further studied as to ensure it will meet both standards. Detailed economic analysis is worth to study to evaluate and justify the intermediate glycerin wash is commercially viable.

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