

**OPTIMIZATION OF GLYCEROL RECOVERY ON EFFECT OF WASTE
VOLUME AND PH USING RESPONSE SURFACE METHODOLOGY (RSM)**

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ABSTRACT

Biodiesel waste or glycerol residue is a byproduct from transesterification of vegetable oil to biodiesel. These wastes contain high percentage of glycerol and other impurities such as salt and ash produced during production of biodiesel. Recovery of glycerol from biodiesel waste can give positive impact to the environment and very economical. The main objective of this experiment is to optimize the effect of glycerol residue (waste) volume and effect of pH on the glycerol production using Response Surface Methodology (RSM) based on central composite design (CCD). Pretreatment of glycerol residue is using sulphuric acid and then follow by neutralization using sodium hydroxide and evaporation process to concentrate the recovered glycerol. Every steps in pretreatment process, the glycerol recovered is filtered in order to remove the impurities. The experiment had been run with nine different pH from pH 1 to pH 9 and different volume of sample from 80 ml to 160 ml of glycerol residue. The optimized condition for highest recovery of glycerol is 138.78 ml of waste volume and pH at 4.71. The glycerol recovered at optimum condition is 8.656 g/l. for conclusion, the effect of pH and waste volume give significant effect to the concentration of glycerol recovered.

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ABSTRAK

Sisa biodiesel atau sisa glycerol adalah hasil daripada proses pentransesteran daripada minyak sayuran kepada biodiesel. Sisa- sisa ini mengandungi kandungan gliserol yang tinggi dan bendasing seperti garam dan abu yang dihasilkan sepanjang penghasilan biodiesel. Mendapatkan gliserol dari sisa biodiesel boleh memberi impak yang positif kepada alam sekitar dan sangat ekonomis. Tujuan utama kajian ini adalah untuk mengoptimumkan kesan sisa gliserol dan kesan pH terhadap penghasilan gliserol menggunakan kaedah tindakbalas permukaan (RSM) berdasarkan desain komposit pusat (CCD). Prarawatan sisa gliserol menggunakan asid sulfuric dan diikuti oleh neutralisasi menggunakan natrium hidroksida dan proses pengewapan untuk memekatkan gliserol yang dirawat. Setiap langkah didalam proses prarawatan, glycerol terawat. Hendaklah ditapis supaya bendasing dapat dikeluarkan. Kajian telah dilakukan sebanyak Sembilan pH yang berbeza dari pH1 kepada pH 9 dan berbeza jumlah sisa dari 80 ml kepada 160 ml sisa gliserol. Keadaan optimum bagi mendapatkan konsentrasi tertinggi gliserol terawat adalah pada 138.78 ml jumlah sisa dan pada pH 4.71. Gliserol yang terhasil pada keadaan optimum adalah 8.656 g/l. Untuk kesimpulan, kesan pH dan jumlah sisa memberi pengaruh yang signifikan terhadap konsentrasi gliserol terawat.

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LIST OF SYMBOLS/ABBREVIATIONS

ANOVA	-	Analysis of variance
CCD	-	Central composite design
GP		Glycerol pitch
H ₂ SO ₄		Sulphuric acid
NaOH		Sodium hydroxide
g/L	-	Gram per litre
M	-	Molar
ml	-	Mililitre
OFAT	-	One factor at time method
RSM	-	Response surface methodology
°C	-	Degree Celsius
%	-	Percentage

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CHAPTER 1

INTRODUCTION

1.1 Background of study

Glycerol also known as propan-1, 2, 3- triol is a side product that produced from biodiesel and oleo-chemical plant. Biodiesel is one of the alternative fuels that blend with diesel with certain percentage in order to reduce the usage of diesel from crude petroleum. Biodiesel is free from sulfur and aromatic as it is obtained from renewable sources, it reduces the lifecycle of carbon dioxide emissions by almost 70% compared to conventional diesel fuel. Moreover, recent European regulations have restricted sulfur content in diesel fuel to no more than 50 ppm in year 2005 (Bournay *et al.*, 2005).

The use of vegetable oils, such as palm, soya bean, sunflower, peanut, and olive oil, as alternative fuels for diesel engines dates back almost nine decades, but due to the rapid decline in crude oil reserves, it is again being promoted in many countries (Barnwal *et al.*, 2005). Glycerol waste is a largely waste in Malaysia. It is classified as a waste under Schedule S181 of the Environmental Regulations in Malaysia, and stored in drums and disposed off in landfills (Yong *et al.*, 2001). Currently in Malaysia, Kualiti Alam Waste Management Centre is the only body handling these scheduled wastes where disposal and its treatment are carried out at prescribed premises only with a certain amount of charges imposed for every tonne of waste disposed off. The cost for landfill is about RM 500 and incineration cost RM 810 to RM 3600 t⁻¹ (Hazimah *et al.*, 2003).

In general, the production of every 10 kg of biodiesel yields approximately 1 kg of crude glycerol (10% (w/w)), and currently the world's capacity for biodiesel production is increasing dramatically including within Thailand, where the recent yearly increase is 40% from less than 1.5×10^6 liters/day in 2007 to an expected 2.1×10^6 liters/day in 2008 (Kongjao *et al.*, 2010). When the demand biodiesel is increased, the production of biodiesel also increased. Thus the waste that produced also increased due to the production of biodiesel.

Purification of glycerol residue to glycerol can give positive impact to both of economic and environmentally. As most of this residue is dumped in landfills, it would be advantageous if its valuable components can be recovered for use (Ooi *et al.*, 2001). Glycerol is a trivalent alcohol widely used in the pharmaceutical, food, cosmetic, and chemical industries and it is produced from soaps which are obtained by saponification of triglycerides from vegetable oils or animal fats (Hajek and Skopal, 2010).

Converting the glycerol to other value-added product also provides alternative way in order to overcome the glycerol price problem. Glycerol can be converted into propylene glycol which used as antifreeze and acetol (Dasari *et al.*, 2005). It also can used as carbon sources for fermentation process to produced other various product such as succinic acid, acetic acid, ethanol and hydrogen. According to Dharmadi *et al.*, (2006), the anaerobic fermentation of glycerol by *E.coli* also can generate ethanol, lactate, succinate and hydrogen. Mu *et al.*, (2006) have use crude glycerol as raw material for production of 1,3-propanediol by using *Klebsiella pneumonia*.

1.2 Problem statement

By product from biodiesel and oleochemical industries are increasing. In Malaysia, glycerol residue is dumped into landfill and can causes effect to the environmental especially water pollution because this wastes easily to mix with water. The lower glycerol phase (GP) consists of glycerol and many other chemical substances such as water, organic, and inorganic salts, a small amount of esters and alcohol, traces of glycerides, and vegetable colors (Hajek and Skopal, 2010). To obtain the high quality of glycerol, these impurities must be removed at the end of pretreatment process. The effect of pH from pretreatment process can give significant effect to the glycerol purification and by study the effect of glycerol residue amount, it useful for plant upscale which can utilize optimum volume of glycerol residue to obtain higher glycerol production.

1.3 Research objective

The main objective of this experiment is to optimize the effect of glycerol residue (waste) volume and effect of pH on the glycerol production.

1.4 Research scope

There are mainly three scopes in this research:

- a. Effect of pH range (from pH 1 to pH 9) toward glycerol production.
- b. Effect of glycerol residue (waste) volume toward glycerol production
- c. To optimize the effect of pH and glycerol residue volume for glycerol production.

1.5 Rational and significant

Glycerol residue contains 20.2% glycerol, 6.6% fatty acids (as soap) and 64.3% salt (Yong *et al.*, 2001). Recovery glycerol from glycerol residue can give advantages to the operation cost because the price for glycerol residue is cheaper compared to commercial glycerol. From this research also can reduce amount of glycerol residue dumped into landfill. Recovery of glycerol from waste also can give value added to company income. If high purity of glycerol is obtains, the price of glycerol in market also increase. Glycerol also can be converted into other chemical that have high demand in market such as propylene glycol, and which can export to other country with high price due to money currency.

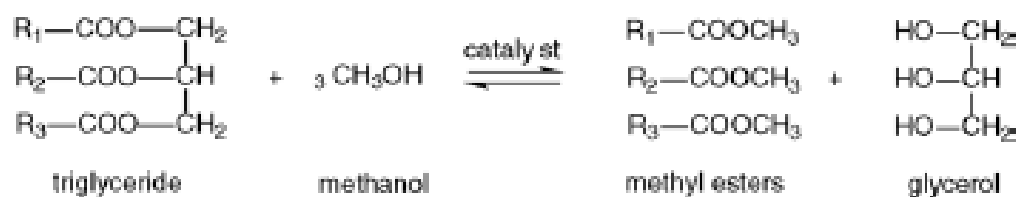
CHAPTER 2

LITERATURE REVIEW

2.1 Biodiesel production

Biodiesel is one of alternative fuel solution to overcome the energy crisis problems. Nowadays, the production of biodiesel has recently received much attention worldwide. The biodiesel market is expected to grow rapidly to meet the new European Directive target of 5.75% volume biofuels in the transport sector by 2010 (Bournay *et al.*, 2005). In general, the production of every 10kg of biodiesel yields approximately 1 kg of crude glycerol (10% (w/w), and currently the world's capacity for biodiesel production is increasing dramatically including within Thailand, where the recent yearly increase is 40% from less than 1.5×10^6 liters/day in 2007 to an expected 2.1×10^6 liters/day in 2008 (Kongjao *et al.*, 2010). The oleochemicals industry in Malaysia also is expanding strongly and producing an increasing array of products (Ooi *et al.*, 2001).

To produced biodiesel, the vegetable oil must undergo process known as transesterification. Transesterification (Figure 2.1)is process whereby the triglycerides with addition of excess methanol to produce methyl ester and glycerol. For conventional biodiesel industries, methanolysis of vegetable oil is achieved by using homogenous catalyst system which is usually using sodium hydroxide and sodium methyllate operated in either batch or continuous mode (Bournay *et al.*, 2005).



with R1, R2, R3 = hydrocarbon chain from 15 to 21 carbon atoms

Figure 2.1 : Biodiesel reaction

In conventional industrial biodiesel processes, vegetable oil methanolysis is achieved using a homogeneous catalyst system operated in either batch or continuous mode. Sodium hydroxide or sodium methylate is often used as catalyst. Sodium is recovered after the transesterification reaction as sodium glycerate, sodium methylate, and sodium soaps in the glycerol phase. An acidic neutralization step with, for example, aqueous hydrochloric acid is required to neutralize these salts. In that case, glycerol is obtained as an aqueous solution containing sodium chloride. Depending on the process, the final glycerol purity is about 80–95%. When sodium hydroxide is used as catalyst, side reactions forming sodium soaps generally occur. This type of reaction is also observed when sodium methylate is employed and traces of water are present. The sodium soaps are soluble in the glycerol phase and must be isolated after neutralization by decantation as fatty acids. The loss of esters converted to fatty acids can reach as high as 1% of the biodiesel production (Bournay *et al.*, 2005). Figure 2.2 show the typical operation for biodiesel production plant.

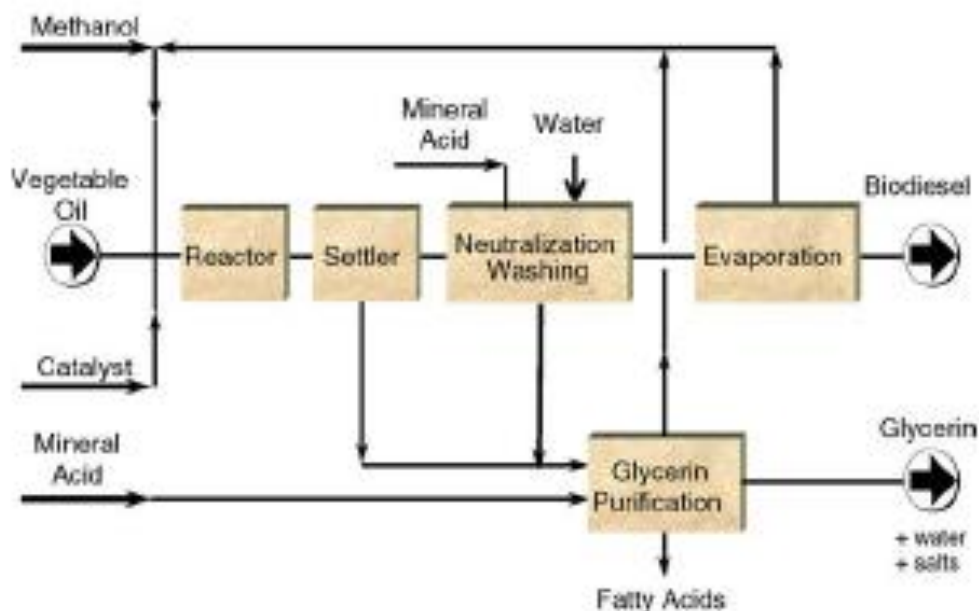


Figure 2.2 : Conventional biodiesel plant for continuous homogeneous catalyzed process (Bournay *et al.*, 2005)

Barnwal and Sharma (2005) show the properties of different sources of biodiesel from various vegetable oil and diesel. From Table 2.1 there is many similarity of properties between diesel and biodiesel from vegetable oil, thus biodiesel can become alternative fuel to diesel. This is due to the fact that the conversion of triglycerides into methyl or ethyl esters through the transesterification process reduces the molecular weight to one-third, reduces the viscosity by about one eighth, and increase the volatility marginally. Biodiesel contains 10–11% oxygen (w/w), thereby enhancing the combustion process in an engine. It has also been reported that the use of tertiary fatty amines and amides can be effective in enhancing the ignition quality of the biodiesel without having any negative effect on its cold flow properties. However, starting problems persist in cold conditions. Further, biodiesel has low volumetric heating values (about 12%), a high cetane number and a high flash point. The cloud points and flash points of biodiesel are 15–25 °C higher than those of diesel.

Table 2.1 : Properties of biodiesel from vegetable oil(Barnwal and Sharma,2005)

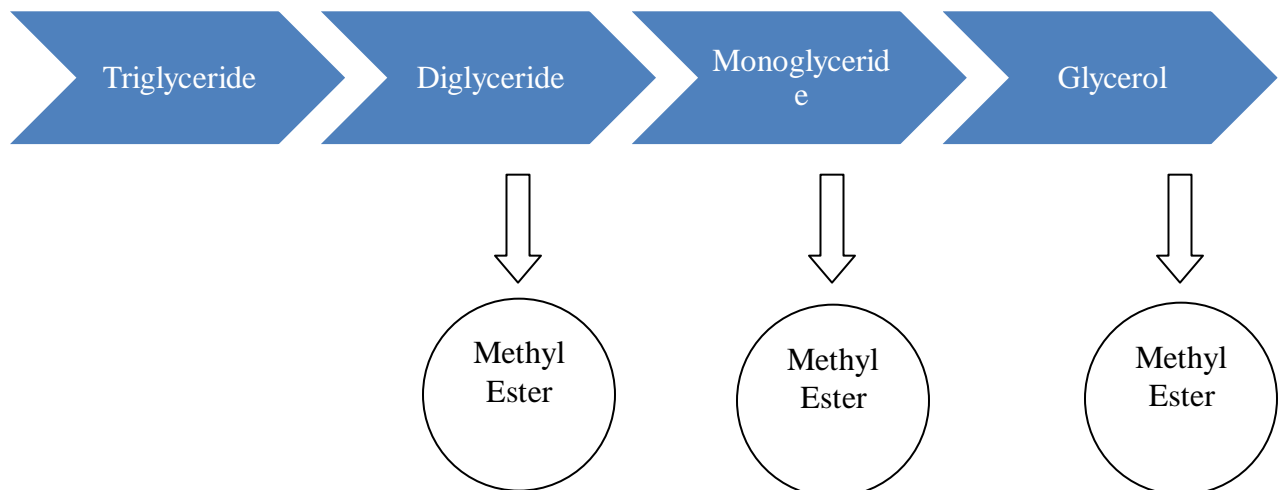
Vegetable oil methyl esters (biodiesel)	Kinematic viscosity (mm ² /s)	Cetane no.	Lower heating value (MJ/kg)	Cloud point (°C)	Pour point (°C)	Flash point (°C)	Density (kg/l)
Peanut	4.9	54	33.6	5	–	176	0.883
Soya bean	4.5	45	33.5	1	–7	178	0.885
Babassu	3.6	63	31.8	4	–	127	0.875
Palm	5.7	62	33.5	13	–	164	0.880
Sunflower	4.6	49	33.5	1	–	183	0.860
Tallow	–	–	–	12	9	96	–
Diesel	3.06	50	43.8	–	–16	76	0.855
20% biodiesel blend	3.2	51	43.2	–	–16	128	0.859

2.2 Biodiesel manufacturing waste

As the biodiesel demand is increased, the waste that produced from this process also will increasing rapidly. For each gallon of biodiesel produced, approximately 0.3 kg (0.66 lb) of crude glycerol accompanies (Thomson *et al.*, 2006). In Malaysia, Palm kernel oil methyl ester plants generate large amounts of glycerol residue from glycerol refining which about 1 t day⁻¹ by a particular plant alone. It is classified as a waste under Schedule S181 of the Environmental Regulations in Malaysia, and stored in drums and disposed off in landfills (Yong *et al.*, 2001). Treatment of crude glycerol depends on the parent feedstock and the biodiesel production. Before considering glycerine as positive value added, it is necessary to characterize the crude glycerol on its physical, chemical, and nutritional properties.

2.3 Production Process Factor

To complete the transesterification process in biodiesel, understanding of basic chemical process is necessary. The chemical process that occurs during the reaction is dedicated by the following sequence of event:



From this process, firstly the triglycerides are converted to diglycerides, which at the end of reaction the monoglycerides is converted into glycerol. Each step within this process will produce methyl ester of a fatty acid. If the reaction is not complete, the triglyceride, diglyceride and monoglycerides still exist within the reaction mixture and these compound still contain a glycerol molecule that has not been released. The glycerol portion of these is referred to as bound glycerol. When the bound glycerol is added to the free glycerol, the sum is known as total glycerol.

2.4 Source of glycerol

2.4.1 Chemical synthesis

Glycerol can be synthesis from propylene by chlorinated in high yields to allyl chloride. Since allyl chloride could be converted to glycerol by several routes, the synthesis of glycerol from propylene became possible. Propylene can also be oxidized in high yields to acrolein. Several routes for conversion of acrolein to glycerol are shown in Figure 2.3.

In the traditional allyl chloride route, the allyl chloride may be converted into glycerol by two processes. The allyl chloride may be treated with aqueous chlorine, and the resulting mixture of glycerol dichlorohydrins dehydrochlorinated to epichlorohydrin, which is then hydrolyzed to glycerol. In the second process, allyl chloride is hydrolyzed to allyl alcohol. The allyl alcohol is chlorohydrinated with aqueous chlorine solution to yield a mixture of monochlorohydrins which are hydrolyzed to glycerol in 90% yield based on allyl alcohol. The product from either of the above procedures is a dilute aqueous solution containing 5% or less of glycerol. High purity glycerol is obtained in several steps: the crude glycerol is concentrated to ca 80% in multiple-effect evaporators and salt is removed by centrifuging; additional concentration of the product, followed by desalting, yields 98% glycerol; colored substances are removed by solvent extraction; and the product is refined by steam-vacuum distillation. (Kirk, 2005)

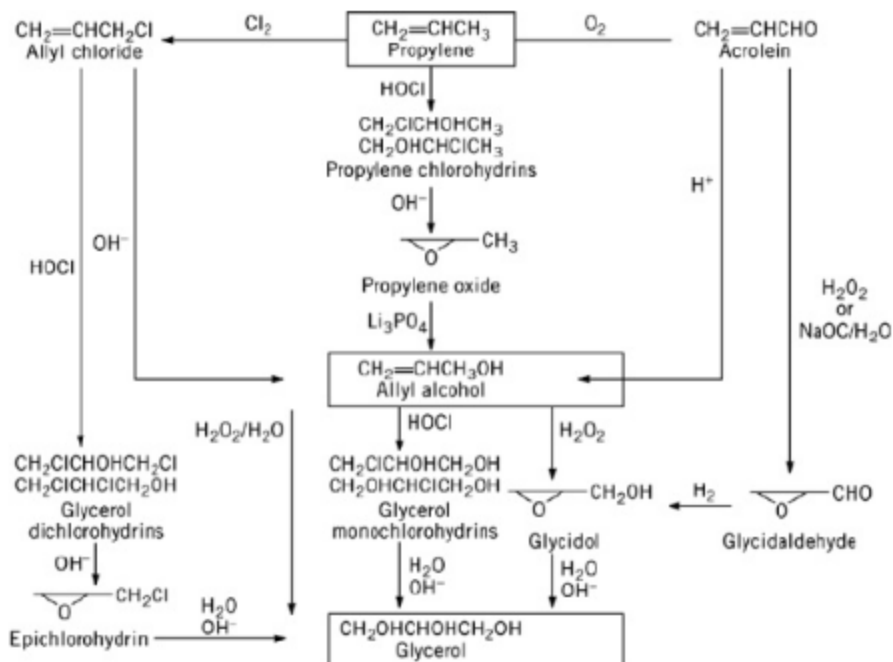


Figure 2.3 : Process flow of Glycerol synthesis from propylene (Kirk, 2005)

2.4.2 Biodiesel waste

Glycecol is the side product from the transesterification of vegetable oil to produced biodiesel. Transesterification (Figure 2.4) is an equilibrium reaction in which excess alcohol is required to drive the reaction close to completion. Fortunately, the equilibrium constant favors the formation of methyl esters such that only a 5:1 molar ratio of methanol:triglycerides is sufficient for 95–98% yield of ester. It might be anticipated that in such a system, glycerol would play a major role in achieving conversions close to 100%. Several catalysts were tried for the purpose of transesterification by several workers, e.g. magnesium, calcium oxides and carbonates of basic and acidic macro-reticular organic resin, alkaline alumina, phase transfer catalysts, sulphuric acids, p-toluene sulphonic acid, and dehydrating agents as co catalysts (Barnwal, 2005).

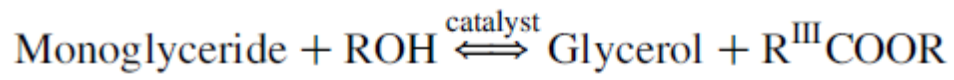
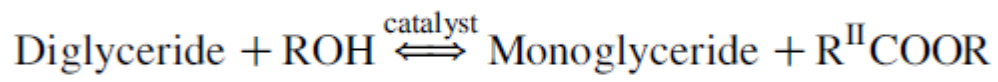
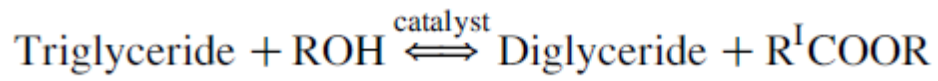


Figure 2.4 : Transesterification of vegetable oil in biodiesel production

2.5 Properties of glycerol

Glycerol, or propan-1, 2, 3-triol is an organic compound, also called glycerin or glycerine. Glycerol is colorless, odorless, viscous liquid that widely used in the pharmaceutical, food, cosmetic, and chemical industries (Hajek, 2009). Glycerol has three hydrophilic hydroxyl groups that are responsible for its solubility in water and its hygroscopic nature.

Glycerol has a specific gravity of 1.261, a melting point of 18.2°C and a boiling point of 290°C under normal atmospheric pressure, accompanied by decomposition. At low temperatures, glycerol may form crystals which melt at 17.9°C. Table 2,2 show the properties of glycerol.

Table 2.2 : Properties of glycerol at 20°C

Item	Description
Chemical Formula	$\text{C}_3\text{H}_4(\text{OH})_3$
Molecular mass	92.09382 g mol ⁻¹
Density	1.261 g cm ⁻³
Viscosity	1.5 Pa.s
Melting point	18.2°C
Boiling point	290°C
Food energy	4.32 kcal.g ⁻¹
Flash point	160°C
Surface tension	64 mNm ⁻¹
Temperature coefficient	-0.0598 mN(mK) ⁻¹