Purification of Glycerin By-product from Biodiesel Production Using Electrolysis Process

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Abstract

High-purity glycerin is one of the most important industrial feedstocks. Its applications are found in food, pharmaceuticals, cosmetics, oleochemicals and tobacco industries. With increasing popularity of biodiesel, the amount of crude glycerin by-product has dramatically increased. The oversupply of glycerin has flooded the market and driven the prices of crude and refined glycerins down. Hence, the margin of refined glycerin depends largely on the purification cost. Therefore, this study proposes a cost-effective alternative to purify crude glycerin by using electrolysis, as well as obtaining the technical and economical feasibility. We found that, by using five pretreatment steps together with the electrolysis process, the glycerin content has increased from 75-80% up to meet pharmaceutical grade (> 95 %) without using the expensive vacuum distillation. This is because the electrolysis process could remove inorganic salts and other contaminants by electrolysis and electro-coagulation reaction.

Keywords*:* Refined Glycerin, Electrolysis, Purification, Biodiesel

1. Introduction

Crude Glycerin is the by-product of biodiesel production via transesterification[1] of triglyceride as shown in figure 1. In this process, triglycerides (1) are reacted with an alcohol such as methanol (2) with base catalyst to give alkyl esters of fatty acids (3) and glycerol (4). This crude glycerol obtained from biodiesel production is not pure as it contained large amount of contaminants including fatty acid soap, methanol, inherent contaminants from unclean raw material and other degraded glycerine products.

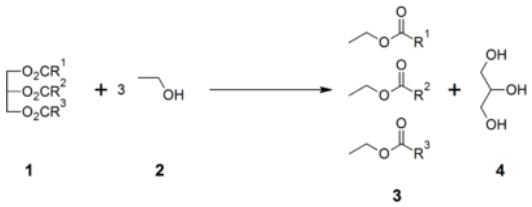

Figure 1: Transesterification of triglyceride

Adverse reactions that cause degradation of glycerin to other products includes polymerization into polyglycerol at temperature higher than 200 ^{o}C, dehydration in slightly acidic conditions at temperature above 160 ^{o}C, and oxidation of glycerine into glycerose, glyceraldehydes and di-hydroxylacetone.[2]

Therefore, purification of glycerin by distillation has to be done under vacuum, where pH, temperature and pressure must be controlled to prevent degeneration of glycerin. The general pretreatment of crude glycerine includes removal of methanol, fatty acid soap, and color.

With increasing popularity of biodiesel, the amount of crude glycerin by-product has increased. The oversupply of glycerin has flooded the market and driven the price of crude and refined glycerin down[3]. As a result, the margin of refined glycerin depends largely on the purification cost. Although vacuum distillation is widely used for purifying glycerine[4], the investment cost of vacuum distillation unit is not feasible for most small to medium-scale biodiesel producers.

Nevertheless, by purifying glycerine using vacuum distillation, Yong, K.C., OOI, T.L., Dzulkefly, K., Wanyunus, W.M.Z., and Hazamah, A.H., (2001) found that the weight of solid residue at the bottom of the distillation tower is 41.8% of the total weight of crude glycerin. This bottom solid consists mainly of salt and MONG (17% salt, 24% MONG (polyglycerol, sugar components, FFAs and glycerides)). This information implies that major fractions of high-boiling-point contaminants in crude glycerine are salt and MONG.

In this study, the technique of interest for purifying crude glycerine is electrolysis process. Electrolysis is the technique for decomposition of chemical species by using electrical power to induce chemical reactions. In addition, the oxidation of anode material could serve as coagulant for particle agglomeration by electro-coagulation process. The electro-chemical reactions at the cathode and anode are as follows[5]:

Anode:

$Al_{(s)} \longrightarrow Al^{3+}_{(aq)} + 3e^-$

(lose electrons)

$Al^{3+}_{(aq)} + 3H_2O \longrightarrow Al(OH)_3 + 3H^+$

$nAl(OH)3 \longrightarrow Al_n(OH)_{3n}$

Cathode:

$2H_2O + 2e^- \longrightarrow H_{2(g)} + 2OH^-$

$Al^{3+} + 3e^- \longrightarrow Al_{(s)}$

(gain electrons)

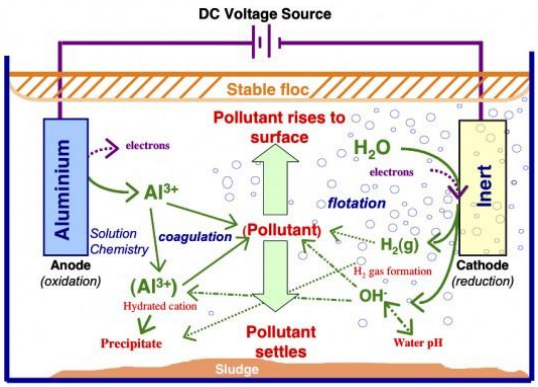

Figure 2: Electro-coagulation process

At the cathod, the reduction reaction occurs and releases hydroxyl ions (OH^-), whereas at the anode, the oxidation reaction occurs and releases metal ions such as Al^{3+}. The ions released will attract the opposite charge contaminants and also neutralize electrically charge of the contaminant particles. Particles are then combined by a van der waals force, and form large agglomerates that could be separated out.

In addition, information about the use of "Integrated electro-pressure membrane deionization system" (US Patent 1130542, EET Corporation, Filed Jan 6,2005) to purify glycerin

show that the High Efficiency Electro-Pressure Membrane processes (HEEPM) can remove the salt and MONG from crude glycerin[6].

Parameter	Treated Crude Glycerin	Product
Glycerol (wt%)	70-88 / 85	99.7
Water (wt%)	5-15 / 7	<1
Sodium Chloride (ppm)	50,000-100,000 / 80,000	<10
Sodium Sulfate (ppm)	<1,000	<20
APHA Color	NA	<20
Methanol (wt%)	<1	<0.01
FFA (wt%)	<1-5 / 2	<0.002
MONG (wt%)	<1-5 / 2	<0.002

Table 1 : Refined Glycerin from HEEPM

So it is interesting that simple electrolysis process can eliminate the rest salt and MONG from pretreatment crude glycerin or not.

This research is study the technical feasibility of purifying crude glycerin, by-product from biodiesel processing by using pretreatment steps together with the electrolysis process.

This study proposes the incorporation of electrolysis process a cost-effective alternative to purify crude glycerin, as well as obtaining the technical and economical feasibility.

2. Experimental

2.1. Material

Crude Glycerin used in this study is derived from the production of palm oil biodiesel donated by Pratum Oil Co. Ltd.

2.2. Glycerin Purification

Crude glycerin has dark color and usually contains large amount of soap, free fatty acids and MONG. In this study crude glycerin was purified by using forth pretreatment step combined with electrolysis process and evaporation. The sequence of processes is showed in figure 3.

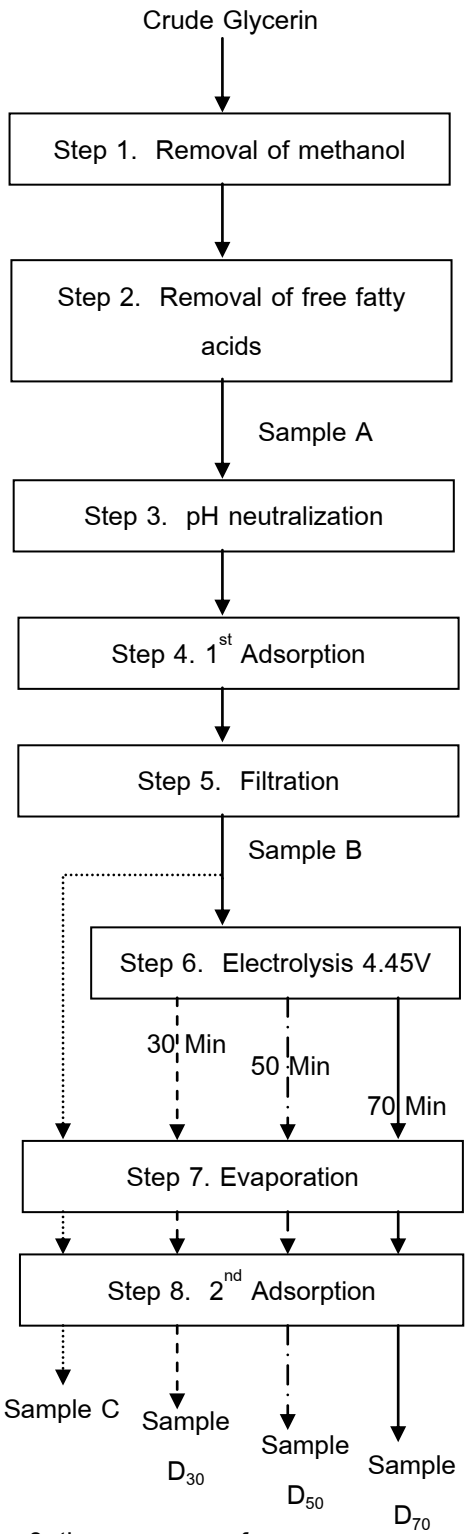

Figure 3: the sequence of processes

Removal of alcohol (Methanol) from crude glycerin is use evaporation process at 70 - 85 ^{o}C and crude glycerin passed alcohol removal process will be adjusted the pH to approximately 4.9 to 5.0 with 85% phosphoric aci and maintained the temperature between 50 - 60 ^{o}C over the length of time. When the pH is adjusted then dropped glycerin for make separation layer of glycerin, fatty acids and salt. Put a layer of glycerin, a clear yellow color used in the research (into the other processes).

Figure 4 Glycerin in the removal of free fatty acid step

The glycerine passed the removal of free fatty acids must be adjusted the pH to approximately 6.9 to 7.1 by using 50% sodium hydroxide (NaOH) solution. Before adsorption glycerin was heated to a temperature about 60 - 65 ^{o}C than Glycerin adsorbed by using 0.055 g. activated char coal per 1 ml of glycerin about 15 minutes. Then it was filtered with the filter paper number 0, 2 layers at a temperature of about 50 - 60 ^{o}C. This step is for absorb the contaminants and the color of the glycerin.

Then glycerin was put into a electrolysis cell that use aluminum electrode. During the process glycerin was stirred for good movement. The DC voltage was varied into 4.45 V, 7.01V and 9.20V respectively and retention times of electrolysis was varied into 30 minutes, 50 minutes and 70 minutes.

Water in glycerin was removed by evaporation process using heat from hot plate at 1.5 (low heating rate). During evaporation glycerin was stirred all the time, maintained temperature at about 110 - 125 ^{o}C. And boil until the temperature of glycerin rapidly increased and the vapor was reduced. After evaporation keep the glycerin in bottles sealed with rubber or plastic to prevent absorption of moisture in the air.

2.3. Characterization

In this study, the glycerol produced was analyzed by the following techniques.

The first is visualization. It is to examine the physical quality of the glycerin roughly by color and clarity.

Analyzing the concentration of glycerin was done by the titration according to ISO 2879-1975 and free fatty acid analysis was done by the titration according to AOCS. Ca 5a - 40.

Analyzing the water content of glycerin used Karl Fischer Titration technique follows on ASTM E203 with volumetric Karl Fischer titrator model Metrohm, KF 831.

The chemical bonding of produced glycerin was verified by using Fourier Transform Infrared Spectroscopy (FTIR), model Perkin Elmer System 2000R. The FTIR light source is used in the middle range infrared (4000 - 550 cm^{-1}), resolution 4 cm^{-1} and the detector is TGS. This analysis is referenced on standard ASTM: 1252-98.

Temperature stability of the produced glycerin was analyzed by using Thermo Gravimetric Analysis (TGA) technique under nitrogen atmosphere and temperature increase rate is 5 ^{o}C per minute from room temperature to 900 ^{o}C. The model of TGA is Meltler Toledo TGA/SDTA 851.

Analyzing the amount of aluminum used the AAS model AA800 and auto sampler model As-90.

Figure 5 Electrolysis Cell

3. Results and Discussion

3.1. Effect of electrolysis condition to %Glycerin

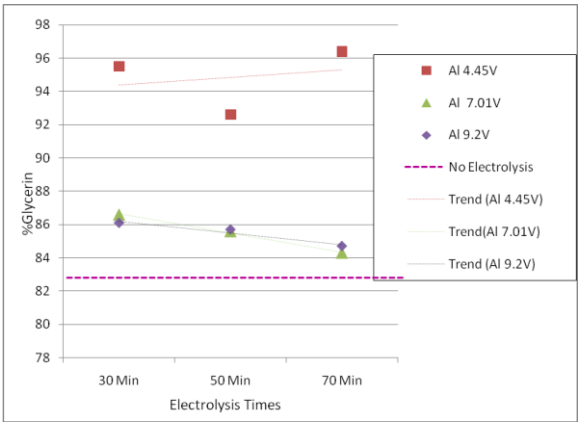

Figure 8: The graph shows % Glycerin from experiment

From Figure 8, the dot line is %glycerin from produced glycerin not passed electrolysis process (sample C).

From the comparison of %glycerin between the glycerin not passed electrolysis (sample C) and all glycerin passed electrolysis, glycerins that passed electrolysis will have a better %glycerin.

When considering the electrolysis process used Al-cell at any difference voltage found that the voltage is 4.45 V, the results are good and not break glycerin over time. However, when the voltage increased to 7.01V and 9.2 V showed that, the loss of glycerol occurred but not too much between two levels of voltage.

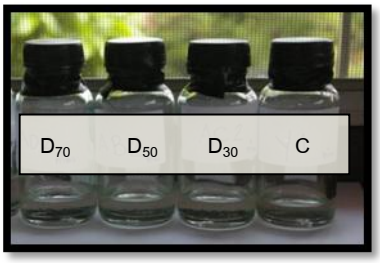

Figure 7: Glycerin from experiment

3.2. Effect of electrolysis on purity of glycerin

Comparing glycerin from the process, the most powerful examples D_{30}, D_{50}, D_{70} with sample C, not passed the electrolysis and standard glycerin 99.6% of the MAXWAY company has a results as follow.

sample	%Glyc-erin	%FFAs (wt)	%Water(wt)	Density
A	60.1	8.60	-	1.1706
B	75.4	3.80	13.0107	1.2446
C	83.2	2.95	1.0139	1.2711
D_{30}	95.5	2.14	1.2275	1.2683

D_{50}	92.6	2.21	0.7782	1.2609
D_{70}	96.4	2.16	0.6165	1.2626
Std.Gly -cerin	99.8	0.05	≤ 0.3	1.2613

Table 6: shows the results obtained with standard glycerin 99.7%

From table 6, When using electrolysis process %glycerin was increased from glycerin not passed electrolysis around 12.3% to 13.2%.

The %FFAs was greatly reduced in the process of absorption (around 55.81%). On comparing between samples C, not passed the electrolysis and the sample passed the electrolysis (D_{70}) found that the electrolysis process can reduce the amount of free fatty acids around 20.52%.

The produced glycerins have the water content exceeded the prescribed standard and have density close to pure glycerin.

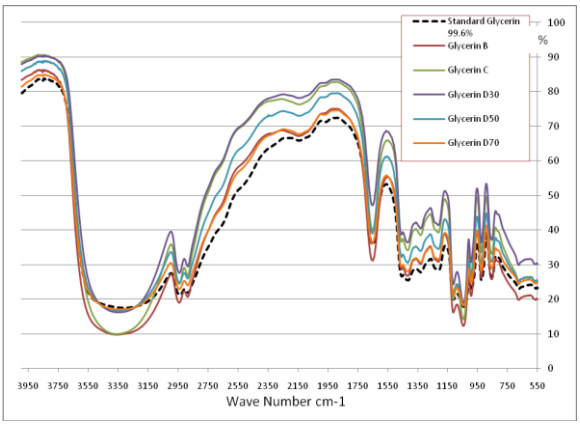

Figure 9: The graph shows the results of the analysis by FTIR.

Figure 9 showed that all the main elements of glycerin samples are consistent with the glycerin and water (OH stretching at 3358 cm^{-1}).

For AD2 (% Glycerin 96.4%) has a curve most close to the standard glycerin according with the results of %glycerin from titration.

Sample C, B have composition of the water more than glycerins that passed electrolysis.

Considering only the samples passed electrolysis, sample D_{30} has most deviations from the standard glycerin. So It is possible that in the titration result to find the %glycerin of D_{50} less than D_{30} has tolerances.

Glycerin samples are tested to determine the amount of aluminum (Al) residue in the product result in table 7.

sample	Al (mg/l) or ppm
B	8.041
C	7.798
D_{30}	6.647
D_{50}	7.521
D_{70}	5.704

Table 7: The amount of Aluminum (Al), using AAS

Table 7 shows that glycerin B and C not passed electrolysis have more amount of Al than glycerins that passed electrolysis. Show that in the crude glycerol has Al anyway and it seems that the glycerin passed electrolysis will decrease the amount of Al but it's not clear.

Therefore, the researcher can only conclude that the electrolysis with the Al-cell does not affect the amount of Al in the production of glycerin.

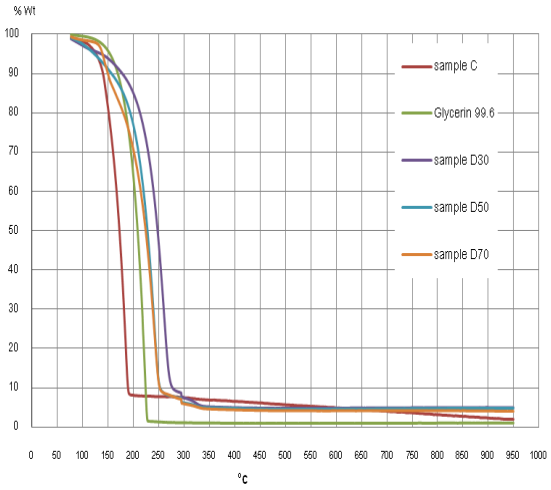

Figure 10: The graph shows the results of the analysis by TGA.

TGA results were analyzed from 100 °C temperature rise due to the glycerin is left longer and absorb moisture prior to analysis by the TGA and the researchers analyzed the water with the Karl Fischer Titration already.

The residual weight at the boiling point of standard glycerin (290 °C)[7] is 1.0537% and the weight is relatively constant to 900 °C. From the properties of standard glycerin this residual weight should not exceed 0.4% may be due to the precision of the TGA.

From the graph you can see a graph of the glycerin C the weight of the samples decreased rapidly in the range of 130 °C to 190 °C, which is different from the glycerol standards were in the range of 160 °C to 230 °C.

It is possible that sample C has a lower boiling point organic compound mixed with glycerin. At temperatures above 290°C, which is the boiling point of glycerin, weight of sample C is still decreasing. Indicates it has other organic compounds that have boiling point in the range of 290 °C to 900 °C. At over 290 °C the %weight contaminants, residues of glycerin is 7.6240%.

From the graph you can see a graph of the glycerins passed electrolysis (D_{30}, D_{50}, D_{70}) the weight of the samples decreased rapidly in the range that higher temperature than the glycerol standards. It is possible that sample D_{30}, D_{50} and D_{70} have a higher boiling point organic compound mixed with glycerin. At temperatures above 290°C, which is the boiling point of glycerin. The weight of the the glycerins passed electrolysis are continued to decline until temperature of 350 °C, the weights are relatively stable to 900 °C. It is possible that the boiling point of glycerin is raise due to contamination from substances with higher boiling points. The %weight of contaminates in D_{30}, D_{50} and D_{70} are approximately 7.6125%, 6.4510% and 6.0653%. As a result of the TGA may be estimated that the %glycerin of D_{30}, D_{50} and D_{70} are 91.16%, 92.77% and 93.32% respectively.

The curve of the TGA is consistent with the results of titration that the glycerin D_{70} has the highest %Glycerin.

It is possible that the residues is an aluminum compound in the product glycerin passed the electrolysis and this compounds have a boiling point greater than 900°C (Because of this phenomenon does not occur for sample C**).**

The process that gives the best %glycerin was found that the crude glycerin, 400 ml give 190 ml of glycerin D_{70} so yield is 47.5%.

The use of chemicals per 100 ml of purified glycerin, as follows.

1. Activated Char Coal (powder) 5.5 g
2. phosphoric acid 85% 4.5 ml

3. Sodium hydroxide 50% 1.0 ml
4. Activated Char Coal (granulate) 2.0 g

Researchers did not analyze the cost of production because small experiment cannot assess the actual cost. As if made on an industrial scale, Filtering process, Evaporation process can be made much more effective.

4. Conclusion

Purification of glycerin by-product from biodiesel using electrolysis process can be remove some of free fatty acid, MONG and aluminum. The electrolysis process can make purity of glycerin increase and it can cause precipitation of contamination when evaporation. (If glycerin not passed electrolysis, precipitation is very low).

Electrolysis does not affect the amount of aluminum in the glycerin, but causes a residue boiling point above 900 ^{o}C, which may be a compound of aluminum.

The electrolysis process requires that glycerin is a good move, low viscosity and low voltage. In this study found that the proper voltage is about 4 V.DC for a period of 70 minutes and from this condition %glycerin by titration is 96.4%. If voltage higher than 7V found that the glycerin is lost with time of electrolysis.

The results showed that most %yield (volumetric) of this research is only 47.5% that low when compared to distillation process, because of in this experiment using filter paper to filter glycerin, so partially glycerin is absorbed by the filter paper. In this process, the cost of the chemicals per liter of pure glycerin is about 59 Baht.

6. References

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