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Purification of Glycerol Produced as a By-product of Biodiesel Production from Waste Vegetable oil

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Abstract: A combination of physio-chemical methods including electrolysis to purify crude glycerol obtained as a by-product of biodiesel produced by transesterification of blended waste vegetable oil is described. Highlighting the importance of biodiesel, the study focusses on utilization of glycerol in a value-added manner, given its wide-spread application in the food, cosmetic and the drug industry. Following FTIR characterization of crude glycerol and pure glycerol, the crude glycerol is subjected to repeated cycles of acidification with concentrated phosphoric acid, sulfuric acid and hydrochloric acid at pH 1, 2, 3 and 4.5, neutralization with sodium hydroxide, adsorption using activated charcoal and electrolysis. Using titrimetric methods, a purity of 87.54% glycerol is reported for H_3PO_4 at pH 1, 75.55% for H_2SO_4 at pH 3 and 59.16% for HCL at pH 1. Based on the titrimetric analysis, phosphoric acid is reported to give maximum purity.

Index terms: **Transesterification, Fourier Transform InfraRed (FTIR) spectroscopy, Electrolysis, Titrimetric analysis**

Introduction

Glycerol is a colourless, odourless, viscous liquid that is sweet-tasting and non-toxic. The glycerol backbone is found in all lipids known as triglycerides. Glycerol has three hydroxyl groups that are responsible for its solubility in water and its hygroscopic nature. **[Christop *et al.*, 2006]** It weighs 92.094 g/mol. It makes commercial sense to utilize glycerol to produce value-added products to ensure all the surplus crude glycerol is used appropriately. A variety of studies report high purity and cost reduction, which is heavily desired in those industries that use glycerol. Industries also look to inexpensively dispose their crude glycerol when not needed. Thus, glycerol recovery adds on the profitability of process and commercial viability of the process itself. There has been focused research to remove contaminants from glycerol considering how big a role it plays in industries like and not limited to pharma. Freeing contaminants from glycerol could serve the industry essential requirement to produce quality products as well as minimization of waste chemicals in chemical product manufacturing industry. **[Ketkale *et al.*, 2016].**

Glycerol is the one the chief byproduct obtained from biodiesel production by transesterification of waste vegetable oil. About 10% of glycerol is obtained as a byproduct. **[Ketkale *et al.*, 2016]** Biodiesel (fatty acid methyl esters), which is derived from triglycerides by transesterification with methanol, has attracted considerable attention during the past decade as a renewable, biodegradable, and nontoxic fuel. **[Fakuda *et al.*, 2001]** Sustainable economic and industrial growth requires safe, sustainable resources of energy. For the future re-arrangement of a sustainable economy to biological raw materials, completely new approaches in research and development, production, and economy are necessary. **[Naik *et al.*, 2010]** As the need for alternative fuels, cleaner fuels increase, numerous studies have been reported and several are underway to produce a biofuel.

There are four primary ways to produce biodiesel - direct use and blending, micro-emulsions, thermal cracking (pyrolysis) and transesterification. **[Fangrui Ma 1999]** Transesterification remains the most commonly used, primarily due to the cost and ease of obtainability of the raw materials involved. The reaction converts esters from long chain fatty acids into mono alkyl esters. **[Ayhan Demerbas 2008]** Biodiesel consists of fatty acid methyl esters (FAME).

Seeds such as rapseed, soybean, sunflower, palm, jatropha, canola etc. are the sources for biodiesel production. Using blended waste vegetable oil as the source not only serves a good precursor, but also adds value in its utilization in that when repeatedly used, it becomes carcinogenic, deeming harmful to those who consume it. It also protects the environment in that it not disposed directly as a used oil.

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Colour reduction in phosphoric acid at pH 1

Materials and Methodology

Materials

Waste vegetable oil was purchased from vendors. pH buffers, activated charcoal and pure glycerine (Fisher scientific assay 99%) were bought from Vasa Chemicals Pvt Ltd.;
Hydrochloric acid (Fisher scientific, assay 35.0 to 39.0%), sulphuric acid (Fisher scientific Assay 93 to 98 %), phosphoric acid (Fisher scientific, assay 84.5 to 86.0%) and sodium hydroxide pellets (Fisher scientific, assay 95.0 to 100%) were used. Christo Ananth et al.[2] discussed about E-plane and H-plane patterns which forms the basis of Microwave Engineering principles.

Production of Biodiesel

The waste vegetable oil was received from the vendors.
The filtered sample was then heated in the reactor (25 litres) at 105 C for about 30 minutes to remove moisture. The pre-treated sample in the reactor was set to produce biodiesel in a continuous process. The speed of the agitator was adjusted to 350 rpm, temperature of reactor to 55C. Sodium methoxide (3.25 litres) was added in the ratio 1:5 of the moles of oil taken. Agitation was allowed for 50 minutes, after which the product containing both biodiesel and glycerol was recovered.

Recovery of glycerol

Recovered product from the reactor was taken into a separating funnel where the biodiesel and glycerol separated into two layers – the bottom layer being glycerol. The quantity of glycerol recovered was measured.

Characterization of crude glycerol

Density of the crude glycerol sample and its pH was determined. This was followed by Fourier Transform Infrared Spectroscopy (FTIR) analysis.

Purification of Crude Glycerol

The crude glycerol was heated at 65C to remove methanol

Acidification

100ml of the heated glycerol sample was acidified until the desired pH was 1, 2, 3 and 4.5 with each of the following acids – phosphoric acid (), sulphuric acid () and hydrochloric acid (). The acid was added drop-wise with magnetic stirring and pH was continuously monitored on a digital pH meter. After the desired pH was achieved, the amount of acid consumed in doing so was measured for each pH, for each acid.

Acidification for pH 1

Neutralization

The middle layer thus recovered was subjected to neutralization using freshly prepared 25% sodium hydroxide () until the desired pH of 7.5 was achieved. This was carried out on a digital pH meter with magnetic stirring. The amount of sodium hydroxide consumed to achieve the desired pH was noted.

Neutralisation for pH 1

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Adsorption

To de-colorize the glycerol sample, activated charcoal was used as an adsorbent.
Activated charcoal was placed in the hot air over at 90^0 C and 30 minutes to remove the moisture from it. The adsorption column was filled with activated charcoal up to about half its volume and then with the glycerol sample. Adsorption was allowed for 24 hours. The volume of glycerol recovered post adsorption was measured.

Electrolysis

Electrolysis is carried out to separate and remove any ions that may be present in the sample. While literature recommends usage of platinum electrodes, availability constraints has only allowed us to use graphite and aluminum electrodes. Literature also uses high-end hydrothermal setups. Our study comprised a simple electrolysis setup.
Graphite was the anode, aluminum was the cathode used. The cathode was expected to attract sodium ions. Graphite was the inert electrode providing electrons and removing protons.

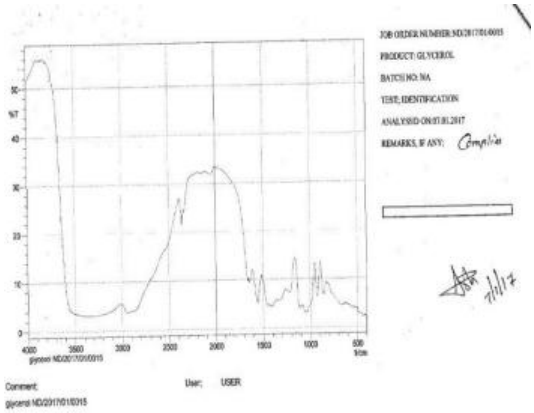
Result and Discussion

Recovery of glycerol

In this study, to 15 liters of blended waste vegetable oil was processed with required quantity of sodium hydroxide based on FFA % and oil to methanol molar ratio 1:5. This gave 3.1 litres of crude glycerol. Glycerol is denser, and hence occupies the bottom layer after separation from biodiesel. Biodiesel is produced as a result of transesterification reaction.

Characterization of glycerol

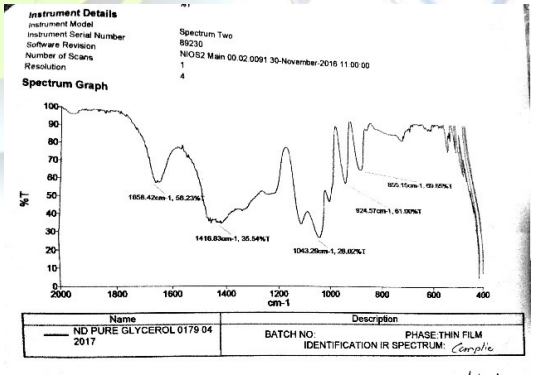
Crude glycerol was dark brown in colour. The density was found to be 1.048 g/cm^3 and pH 10.79. Commercially available pure glycerol (~99% purity) has density and pH of 1.26 g/cm^3 and 7.8 respectively. In order to confirm that the recovered product is indeed glycerol, FTIR analysis was carried out. The FTIR analysis of crude glycerol confirmed the presence of glycerol.



FTIR of crude glycerol

In order to understand the impurities that had to be removed, FTIR was also carried out for pure glycerol.

Comparison between the two peaks resulted in a few key observations. In crude glycerol, the glycerol content was confirmed but it had high matter organic non-glycerol (MONG) and high ash and water contents. Free fatty acids have absorbance at about 1711 cm^{-1}, triglycerides esters at about 1750 cm^{-1} both of whose presence is evident from the rising peaks in crude glycerol. Moisture content gives a peak between 1,640 cm^{-1} to 3,300 cm^{-1} (Manley et al. 2002.) Presence of soap, methanol and methyl esters generated during the biodiesel production causes the formation of MONG. NaOH catalyst during the transesterification process is the origin for the ash content.



FTIR of pure glycerol

The FTIR of purified glycerol gave the following result, confirming that almost all peaks were a function of pure glycerol.

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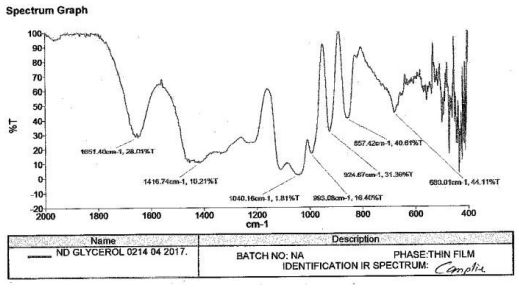
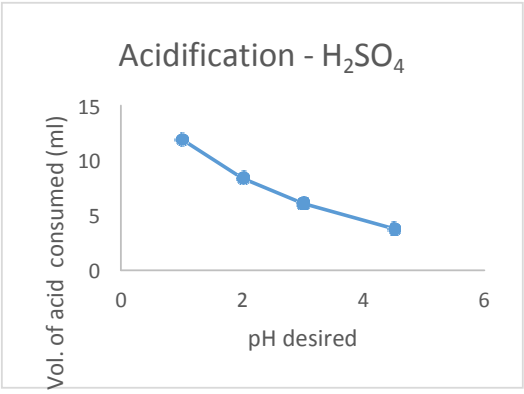


FTIR of purified glycerol

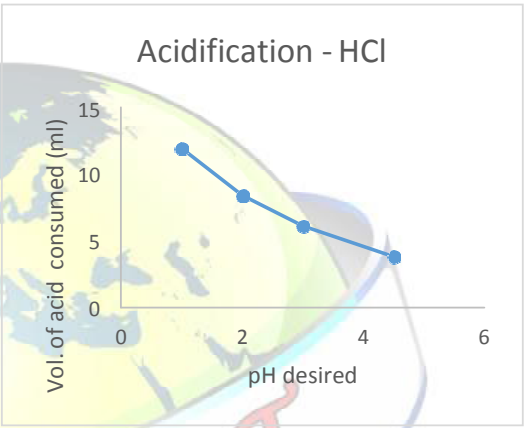


Purification of glycerol

Methanol's boiling point is about 55^0C, hence the heating of crude sample at 65^0C in an open container evaporates the methanol.

Acidification

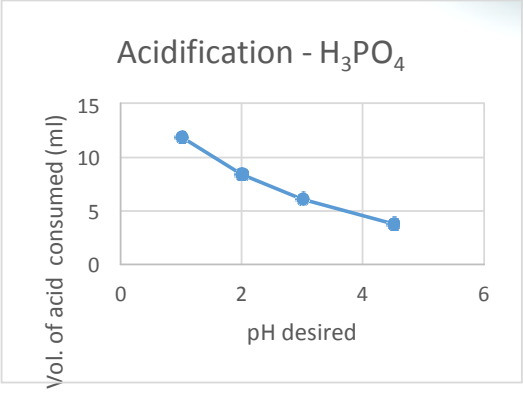
Acidification with a strong acid is done to convert the free acids present in the crude glycerol to esters of fatty acids, soaps which occupy the top layer. This is dark brown in colour. The middle layer contains glycerol which does not react with the acids. This is also dark brown in colour, but a shade lighter than the top layer. The bottom most layer has the salt residues. This layer is yellowish brown in colour.



Reactions of acidification

RCOONa + H3PO4 → RCOOH + NaH2PO4
RCOONa + H2S04 → RCOOH + NaHSO4
RCOONa + HCl → RCOOH + NaCl

Amount of acid consumed for Acidification



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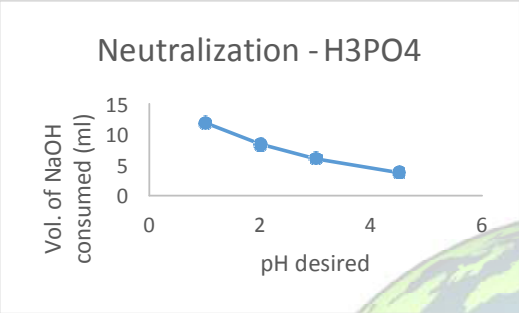
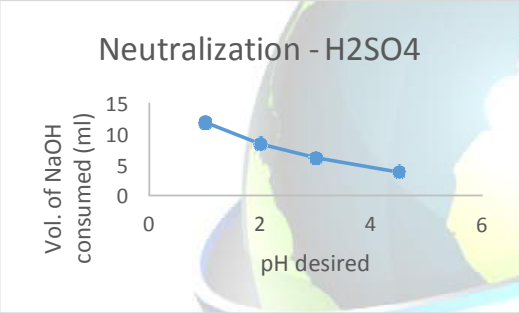
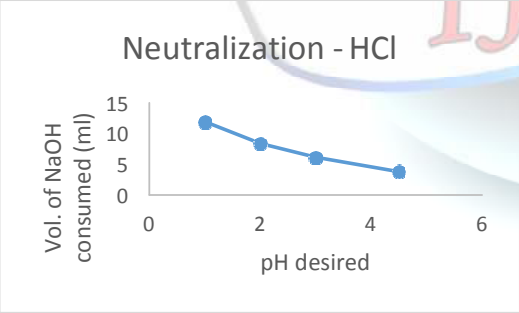
Neutralization

Neutralization is carried out to neutralize any acid that may be present in the glycerol sample.







The general trend observed was a decreasing one of the amount of NaOH consumed for glycerol acidified at pH 1, 2, 3 and 4.5. Purity is not a function of the same.
The three acids have consumed between 5 and 3 ml of NaOH. While phosphoric acid and hydrochloric acid glycerol samples have consumed more of NaOH, sulfuric acid has consumed much lesser.

Adsorption

Adsorption is carried out to decolourize glycerol. Pure glycerol is colourless. Coloured impurities are removed using adsorption. To achieve the same, activated charcoal in granular form was used as the adsorbent. Heating of activated charcoal further removes any moisture that may be present in it.

Amount of glycerol adsorbed

Adsorption yielded minimal loss of glycerol. An average of about 1-2 ml was lost, overall for all three acids. This is due to glycerol being stuck on the walls of the adsorption column.
However, it was observed that powdered activated charcoal did not yield good results. Glycerol formed white foamy substance with the powdered form. Granular form yielded the best results. The maximum colour loss was observed for the sample acidified with phosphoric acid at pH 1.

Glycerol Sample	Density (g/cm^3)
Pure glycerol Sample	1.261
Purified glycerol using H_3PO_4 pH 1	1.195
Purified glycerol using H_3PO_4 pH 2	1.13
Purified glycerol using H_3PO_4 pH 3	1.121
Purified glycerol using H_3PO_4 pH 4.5	1.093
Purified glycerol using H_2SO_4 pH 1	1.175
Purified glycerol using H_2SO_4 pH 2	1.171
Purified glycerol using H_2SO_4 pH 3	1.182
Purified glycerol using H_2SO_4 pH 4.5	1.165
Purified glycerol using HCl pH 1	1.23
Purified glycerol using HCl pH 2	1.239
Purified glycerol using HCl pH 3	1.13
Purified glycerol using HCl pH 4.5	1.149

Glycerol samples chosen for electrolysis

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Graphite was the anode, aluminum was the cathode used. The cathode was expected to attract sodium ions. Graphite was the inert electrode providing electrons and removing protons.

Electrolysis setup

Titrimetric Analysis

The following results were obtained for the three glycerol samples: The maximum percentage purity was obtained for the glycerol sample acidified with phosphoric acid at pH 1. The results were given by IP standards.

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Glycerol Sample	**Percentage purity**
Purified glycerol using H_3PO_4 **pH 1**	87.54%
Purified glycerol using H_2SO_4 **pH 3**	75.55%
Purified glycerol using HCl	59.16%

Conclusion

In times of dire need for alternative, green, non-toxic fuels, this study highlights the importance of biodiesel and focuses on purifying glycerol which is obtained as a by-product of biodiesel produced from transesterification of waste vegetable oil.
Based on the contaminants reflected in FTIR analysis, repeated cycles of acidification with concentrated phosphoric acid, sulphuric acid and hydrochloric acid, neutralization with sodium hydroxide, adsorption and electrolysis were carried out and their effects were studied on pH 1, 2, 3 and 4.5.
Acids consumed ranged from 12 to 4 ml, and neutralization between 5 and 3 ml. The trends of amount of consumption of acids and base were in agreement with the results obtained in literature.
While the yield of glycerol obtained at pH 4.5 was generally high after neutralization, pH 1 and 3 conformed to the properties of pure glycerol better. Yield did not appear to be a function of purity.
Titrimetric analysis of thus purified glycerol yielded purity percentages of 87.54, 75.55 and 59.61 for phosphoric acid at pH 1, sulphuric acid at pH 3 and hydrochloric acid at pH 1. It was concluded that phosphoric acid gives the highest purity over sulphuric and hydrochloric acid for the glycerol sample we intended to purify.
Several literature studies have reported purity of over 90% when the source of oil used is unused vegetable oil.
87% remains one of the higher purities reported for waste vegetable oil.

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