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A Novel Method for Refining Crude Glycerol a Byproduct from Biodiesel Industries

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ABSTRACT

Crude glycerol is a by-product obtained during the production of biodiesel by a process called transesteri fication. Around 20% of crude glycerol is obtained as byproduct. Refining of crude glycerol is essential for its application to various value products in pharmaceutical, food, cosmetics and lubrication in industries. Present paper reveals refining of crude glycerol effectively by acidification with acid like H_2SO_4, then it was subjected to neutralization followed by decolorize with activated charcoal. During this refinement process residual organic matter, water, salt, methanol and odors are removed. The method which developed for refining of crude glycerol is cost effective for industries. The refined glycerol was extensively characterized by infrared spectrum (IR spectra) and high-performance liquid chromatography (HPLC).

Highlights:

1. Simple method had developed for refining crude glycerol
2. Method is very useful for biodiesel industries to refine by product
3. Crude glycerol is refined up to pharmaceutical grade.
4. Simple and Low cost for refining process.
5. Refining processes make value addition for byproduct to sustain industrial growth.

Keywords: Crude glycerol, Transesterification, Decolorize, IR and HPLC.

INTRODUCTION

Glycerin is a material of outstanding utility with many areas of application. The key to glycerin's technical versatility is a unique combination of physical and chemical properties, ready compatibility with many other substances, and easy handling. Glycerin is also virtually nontoxic to human health and to the environment. Biodiesel is mainly produced by the Transesterification of animal fat or vegetable oils (triglyceride) with methanol in presence of an alkali or acid catalyst [1,2]. During the Transesterification process in a biodiesel plant, crude glycerol is the primary byproduct accounting for about 10 Wt% of the biodiesel product [3-5]. With the rapid growth of biodiesel industry all over the world, a large surplus of glycerol has been created, this huge amount of glycerol, once it enters into the market, would significantly affect the glycerol price. The current market value is US$ 0.27- 0.41 per pound of pure glycerol [6] and as low as US$ 0.04 – 0.09 per pound of crude glycerol (80% purity) [7]. Thus, crude glycerol disposal and utilization has become a serious issue and a financial and environmental liability for the biodiesel industry. Economic utilizations of glycerol for value-added products arecritically important for the sustainability of biodiesel industry. Crude glycerol however has purity of 15-80% and it contains large amount of contaminants such as unreacted oil, methanol and salts of catalyst. There is common practice of using alkaline catalysts during the transesterification process results a high pH (above 10) of this byproduct. The presence of contaminants in this renewable carbon source creates certain challenges for the refining processes. According to literature survey, the most common processes include using of ion exchange resin [8], nano-cavitation technology [9], membrane separation technology (MST), simple distillation under reduced pressure [10] and acidification followed by neutralization and solvent extraction [11].

Compared with other processes, the processes using acidification demonstrated to be more promising due to higher yields and their relatively low costs. Kangju et. al., reported the purification of crude glycerol (30 wt% glycerol content) from a waste Used oil methyl ester plant using 1.19 M H_2SO_4 followed by neutralization and solvent extraction to get purified glycerol of around 93 Wt% purity. In a similar work, Ooi et. al., demonstrated that crude glycerol was upgraded from purity of 34 Wt% to 52 Wt% by using sulphuric acid. However, the main issue in these processes is the use of sulphuric acid that has corrosive nature of sulphuric acid and the non-biodegradability of the produced sulfate salts [12-15].

In this refining process, crude glycerol is obtained from a biofuel information and demo center at Karnataka.These biofuel centers are working with extraction of biodiesel; from *panama pinnate* seeds, and center had major issue in disposing crude glycerol obtained during production. Currently these biodiesel plants are kept unused. Some of the research activities is going on refining of crude glycerol, but a simple method had to develop for refining crude glycerol, which will be helpful for biodiesel industries.

MATERIALS AND METHODS

Crude glycerol had been collected from biofuel information and demonstration center, Shivamogga, Karnataka, INDIA. All chemicals were purchased from SD fine chemicals.

Physical characteristic of crude glycerol: The crude glycerol which obtained initially found dark brown color, semi-solid with unreacted oil (mono and di glycerides), methanol and salt residue.

Refining process for crude glycerol: Based on the solubility of an organic molecule, Glycerol is completely soluble in water and alcohol. It is slightly soluble in ether, ethyl acetate, dioxane and insoluble in hydrocarbons. Water and alcohol are chosen as a solvent for separation of glycerol. In the beginning of the process, collected 500g of crude glycerol is taken in a clean beaker and heated on a hot plate by maintaining 55°C to melt crude glycerol. Melted crude glycerol is treated with 2.5M 100mL sulphuric acid, mixed for about 20min to settle unreacted oil and crude glycerol layer. Separate crude glycerol layer and it is diluted with 500mL distilled water, later the mixture neutralized and transferred to a separating funnel containing 500mL ethyl alcohol and 100 mL of diethyl ether to separate alcohol and an aqueous layer. Separate aqueous layer and it is concentrated by heating to around 85°C which reduces to half of its original volume. A concentrated solution is decolorized by adding 2g of activated charcoal heated for about 30-40°C to 20 min. Later the solution is filtered and the above method was repeated to form clear transparent solution. The refined sample is characterized accordingly.

RESULTS AND DISCUSSION

Crude glycerol analysis: The crude glycerol obtained from the biodiesel plant initially found dark brown semi solid with a high pH (9.8) and density (1.10 Kg m^3 at 25^0C) as compared to the commercially available pure glycerol (Table 1, pH: 6.97, density: 1.26 Kg m^3 at 25^0C). The glycerol content in crude form was found to be very low in the range of 20 Wt%, but it has high organic matter, unreacted oils and high ash content (Table 1). 500 ml of crude glycerol yielded 100 ml of refined glycerol.

Table 1. Properties of crude glycerol, refined glycerol and commercial glycerol

Properties	Crude glycerol	Refined glycerol	Commercial glycerol
Density (25 °C)	1.10	1.24	1.26
pH	9.8	7.2	6.97
Viscosity at 40 °C cst	---	140	149
Water (Wt%)	10.2	---	---
Ash (Wt%)	6.4	0.1	0.00

Crude glycerol is a byproduct recovered during biodiesel production, it contains 40 to 60% of glycerol and rest of residue which is a mixture of methyl esters, catalyst salts such as sodium or potassium and solvents. Hence, the impurities present in crude glycerol are to be separated and decolorized to obtain a pure form of glycerol. Refined glycerol is characterized by Infrared spectroscopy (IR) and purity of glycerol characterized by high performance liquid chromatography (HPLC).

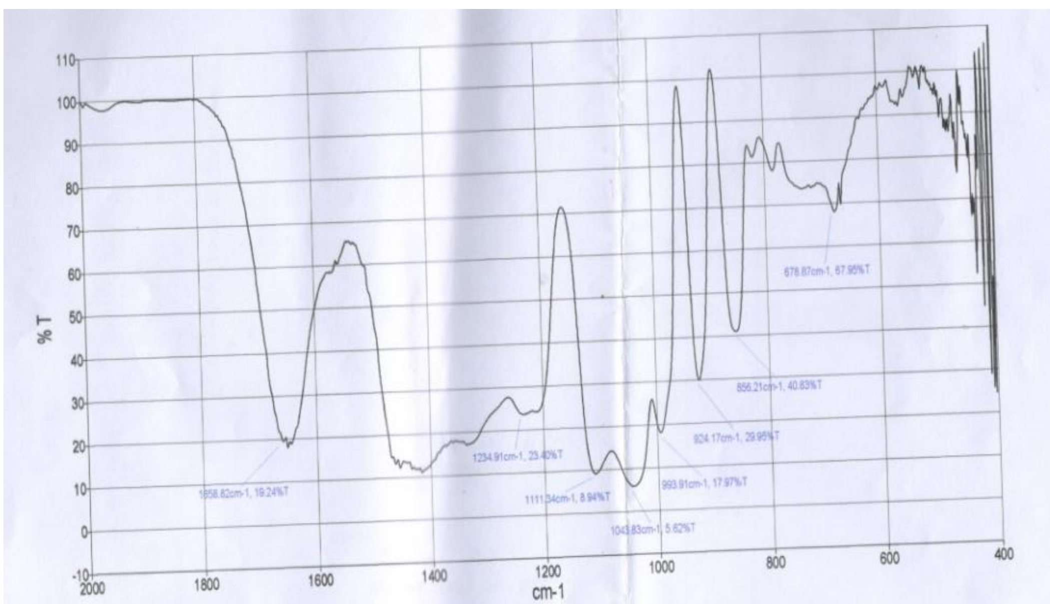
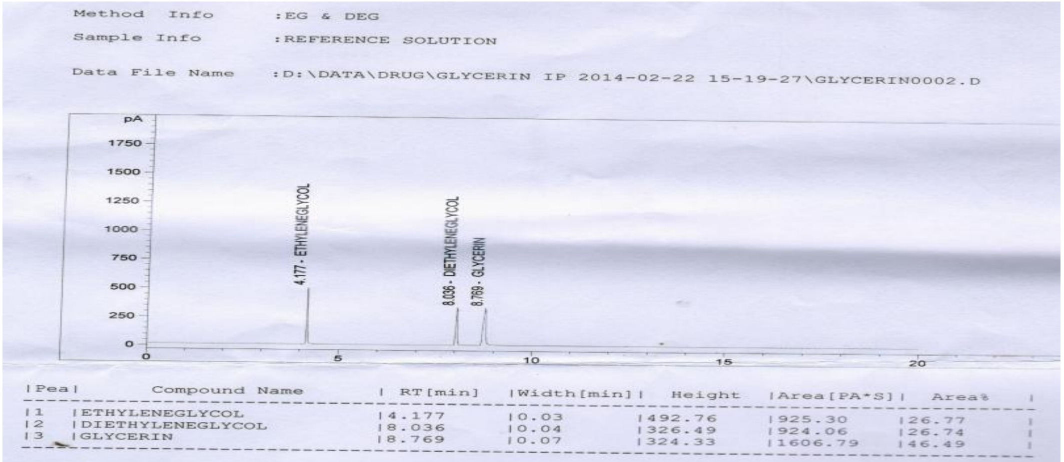
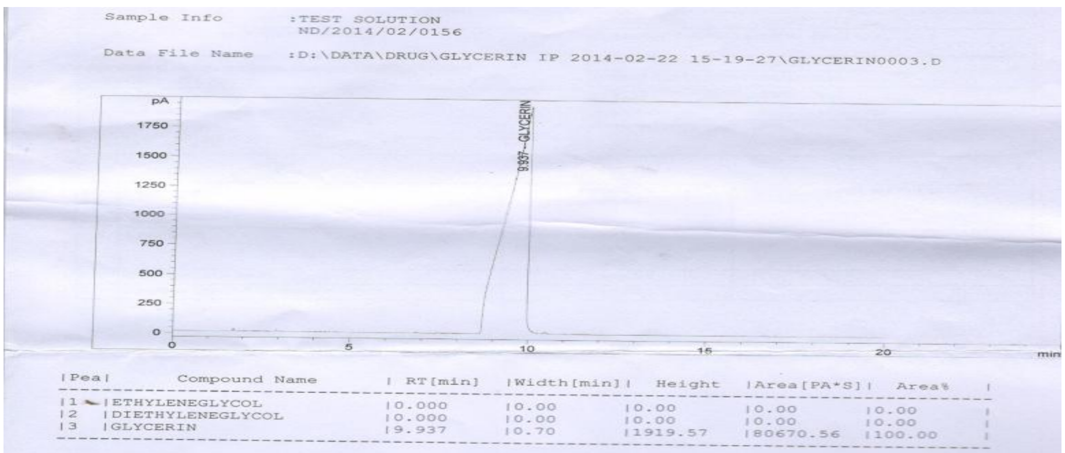


Fig 1. Infrared spectral images of refined glycerol

Above figure represents IR absorption spectra of the sample shows that the IR stretching bands at 1040 cm^{-1} based on the experimental data [13]. This band is reported characteristics of a primary and secondary alcohol, O-H stretching absorption is seen at 1658 cm^{-1} in refined glycerol. The peaks between 1500-700 cm^{-1} are due to C-H bending vibrations and C-O stressing 1200-900 cm-^{1} modes of glycerin, 1234 $cm^{-1}$are due to C-C-C stretch and 993-924 cm^{-1}, peaks represents COH, OC_2H_4 stretching. The spectral data confirm the structure of glycerol which had been refined from by-product crude glycerol.



Peak	Compound Name	RT [min]	Width [min]	Height	Area [PA*S]	Area%
1	ETHYLENEGLYCOL	4.177	0.03	492.76	925.30	26.77
2	DIETHYLENEGLYCOL	8.036	0.04	326.49	924.06	26.74
3	GLYCERIN	8.769	0.07	324.33	1606.79	46.49



Peak	Compound Name	RT [min]	Width [min]	Height	Area [PA*S]	Area%
1	ETHYLENEGLYCOL	0.000	0.00	0.00	0.00	0.00
2	DIETHYLENEGLYCOL	0.000	0.00	0.00	0.00	0.00
3	GLYCERIN	9.937	0.70	1919.57	80670.56	100.00

Fig 3. HPLC chromatogram of test sample

High performance liquid chromatography (HPLC) is a technique for the separation of components of mixture by differential migration through a column containing a micro particulate solid stationary phase. Solutes are transported through the column by a pressurized flow of liquid mobile phase and are detected as they are eluted. Hence the purity of refined glycerol is characterized by HPLC method. From the above Figure 2, chromatogram shows reference standard peak of ethylene glycol, diethylene glycol and glycerol eluted out at retention time4.1, 8.0 and 8.7(RT in min) respectively is compared with figure 3. HPLC chromatogram shows the sample refined glycerol peak at retention time 9.9 (RT in min) only for glycerol. By the above IR spectral and HPLC data derives the refined sample is free from impurities of ethylene glycol, diethylene glycol and other impurities. Hence crude glycerol obtained from biodiesel industry can be easily refined into pure form of glycerol, where glycerol found to be a more valuable product in cosmetics and pharmaceutical industries.

CONCLUSIONS

The following conclusions can be drawn from studies-

1. Simple method had developed for refining crude glycerol
2. Method is very useful for biodiesel industries to refine by product
3. Crude glycerol is refined up to pharmaceutical grade.
4. Simple and Low cost for refining process.
5. Refining processes make value addition for byproduct to sustain industrial growth.

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