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Valorization of Biodiesel Production: Focus on Crude Glycerine Refining/Purification

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Abstract: As the biodiesel industry is rapidly expanding in developed countries and gradually having its feet in developing countries, a glut of the principal by-product; crude glycerine, is being created. Biodiesel emerged as the leading source of glycerol, accounting for over 1.4 million tons of glycerol production in 2013. Therefore, the valorization of glycerol has the potential to improve the profitability of biodiesel in a bio-refinery scenario. This study was carried out using crude glycerine from biodiesel production of neem seed oil and waste cooking vegetable oil (W.C.V.O) and the purified glycerol level achieved was about 97%.

Keywords: Valorization, Biodiesel, Crude glycerine, Purification, Phosphoric acid, isopropyl Alcohol.

1. INTRODUCTION

High purity glycerol is a very important industrial feedstock. Its applications are found in foods, drugs, cosmetics, tobacco industries and a host of others. Glycerol (C₃H₈O₃) is an alcohol with three hydroxyl groups (-OH), which can be produced as a by-product of biodiesel production through transesterification of vegetable oil or animal fat with alcohol, such as methanol [1]. From transesterification reaction, the glycerol obtained contains several impurities, which pose a disposal problem without further purification. The crude glycerol obtained as a by-product from transesterification contains just over one-third glycerol in a mixture of unreacted methanol, most of the homogeneous catalyst (NaOH) and soap. Therefore, a certain purification steps are necessary for the crude glycerol recovery prior to its use as a raw material in many industries and as a potential feedstock for the production of bio lubricants. Presently the conventional refinement of crude glycerol is very expensive and complex causing it to be disqualified for high quality uses. For the purification techniques of crude glycerol, it may comprise steps such as chemical treatments, crystallization, conventional filtration, microfiltration, ultrafiltration using organic polymer membranes, treatment with ion exchange resins, electro dialysis and vacuum distillation. Combination of two or more of these techniques

would lead to producing high purity glycerol. Such treatments required a good understanding of the physical as well as the chemical properties of each of the materials involved, for example, methanol could be separated and recovered by means of vacuum distillation [1].

In the present market, glycerol price is in the range of \$1.28 to \$1.65 per litre. However, crude glycerol derived from biodiesel production possesses very low value, because of impurities. Further refining of the crude glycerol will depend on the economy of production scale and/or the availability of a glycerol purification facility.

2. MATERIALS AND METHODS

Crude glycerol was collected from a biodiesel plant that uses neem seed oil and also from biodiesel production using waste cooking vegetable oil (W.C.V.O), both via alkali catalyzed transesterification.

2.1 FIRST STAGE: NEUTRALIZATION

About 50g of crude glycerol from each source was neutralized using dilute phosphoric acid (H₃PO₄) from its initial pH of about 9 to a pH in the range of pH 3 – 7 in steps of 0.5, with continued stirring, and then left for 2 hours until the solution had phase separated into two or three distinct layers, that is a top layer of free fatty acids, the middle glycerol-rich layer and, the bottom inorganic salt-rich layer (which was absent in the glycerol from waste cooking vegetable oil). The top layer was removed by decantation and the middle glycerol-rich layer was separated from the bottom inorganic salt-rich layer by filtration. The optimal pH for neutralization was then determined by the pH with the highest glycerol content in the extracted glycerol rich layer.

2.2 SECOND STAGE: GLYCEROL LAYER CONCENTRATION AND METHANOL RECOVERY

The glycerol rich layer obtained from stage one was concentrated by distillation to also recover the methanol present in the mixture.

2.3 THIRD STAGE: GLYCEROL EXTRACTION WITH IPA

The concentrated glycerol rich layer was mixed with isopropyl Alcohol in ratio of IPA: Glycerol of 2:1 to extract the glycerol out of the mixture and then allowed to stir on the magnetic stirrer for about 30 minutes. The mixture was then allowed to settle for about 2 hours to enable proper separation of the two layers formed, the glycerol-alcohol phase on the top and the crystallized salt on the bottom. The upper layer was separated by slow decantation to eliminate the crystallized salt and then filtered to remove any traces of salt or solids in it.

2.4 FOURTH STAGE: ADSORPTION WITH ACTIVATED CARBON

Finally, the color, as well as some fatty acids and other components, of the refined crude glycerol was reduced by adsorption with commercial activated carbon. It had the BET surface area, pore size and micro-pore volume of 146 m²/g, 40.9 nm and 0.174 cm³/g, respectively. Prior to use, the activated carbon was dried at 105 °C for 30 min to eliminate free moisture, sieved and the fraction with a particle size of between 0.1 and 0.3 mm was selected. In the adsorption stage about 10g of activated carbon was mixed with about 300ml of the glycerol-alcohol mixture obtained in stage 3, mixed at 200 rpm for 4 hours and then subjected to filtration to remove the activated carbon.

2.5 FIFTH STAGE: GLYCEROL REFINING AND IPA RECOVERY

The decolorized glycerol-alcohol mixture was then refined by distilling and recovering the IPA at 85°C and the resulting refined glycerol was also heated at about 105°C for 3 hours to remove the moisture content and further concentrate the refined glycerol.

2.6 TEST AND ANALYSIS

The concentration of glycerol was analyzed by Gas Chromatography Mass Spectrometer (GCMS). The water content was measured following the Standard method (ISO 2097-1972) by using the volumetric Karl Fisher titration. Ash content was analyzed according to the Standard method (ISO 2098-1972) by burning 1 g glycerol in a muffle furnace at 750 °C for 3 h. The MONG levels were calculated by the difference from a hundred of the previous three compositions (100 – (% glycerol content+% water content+% ash content)). The pH of the glycerol solution was measured with a pH meter. The color of glycerol was measured by a UV/Vis spectrophotometer at a wavelength of 457 nm.

3. RESULTS AND DISCUSSION

3.1 CHARACTERISTICS OF THE CRUDE GLYCEROL SAMPLES

The crude glycerol obtained from neem oil biodiesel plant was a dark brown liquid and that obtained from the waste

cooking vegetable oil biodiesel process was also brown coloured but lighter with both having a high pH (Table 1.0).

TABLE 1: Physico-chemical properties of the crude glycerol

Parameter	Crude Glycerol (Neem)	Crude Glycerol (W.C.V.O.)
pH	9.82	9.2
Glycerol content (%)	41.33	35.66
Ash (%)	4.31	4.08
Moisture (%)	15.4	12.4
Colour	Dark brown	Brown
MONG (%)	38.96	47.86

As also reported by Rudemas Manosak et al.[4], the crude glycerol has a low content of glycerol and ash, but it had a relatively high water and MONG (Matter Organic Non Glycerol) content (Table 1.0). The ash content was largely composed of inorganic matter, such as sodium salts that originated from the utilized catalyst (NaOH) in the transesterification process, whilst the water content might be attributed to the absorption of moisture from its surroundings during the production process. By far the largest contaminant was MONG, which indeed exceeded the glycerol levels, and was generated by the contamination of soap, methanol and methyl esters in the glycerol residue from the biodiesel production process. During the neutralization stage and phase separation based refining process, some of the fatty acids were released as soluble soap, and some of methyl esters dissolved or suspended in the glycerol solution. These free fatty acids and methyl esters then reacted with the excess NaOH in the subsequent neutralization step to re-form soap which remained in the glycerol residue. Besides glycerol, crude glycerol contains various compounds, including fatty acids and their derivatives, such as methyl oleate, methyl palmitate, palmitic acid, methyl stearate, oleic acid, methyl taurate, methyl myristate, methylpalmitoleate, amongst others, which are the main components of vegetable oil.

3.2 NEUTRALIZATION STEP

For the neutralization stage with dilute phosphoric acid, the optimal pH of was determined by the GCMS analysis of the glycerol rich phase obtained from various pH values obtained from pH 3 – 7. 99.5% analar grade glycerol was used to prepare the calibration curve. The optimal pH was determined to be between 6.0 for the crude glycerol from waste cooking vegetable oil biodiesel process and 6.5 for that from the neem biodiesel process. The addition of phosphoric acid to the crude glycerol automatically caused the glycerol to phase separate into two or three distinct layers comprised of free fatty acid layer on the top, a glycerol-rich layer in the middle and, an inorganic salt layer on the bottom [2]. For the waste cooking vegetable oil biodiesel crude glycerol, the organic salt layer was absent

probably because the phosphate salt produced dissolved in the solution because of the high water content.

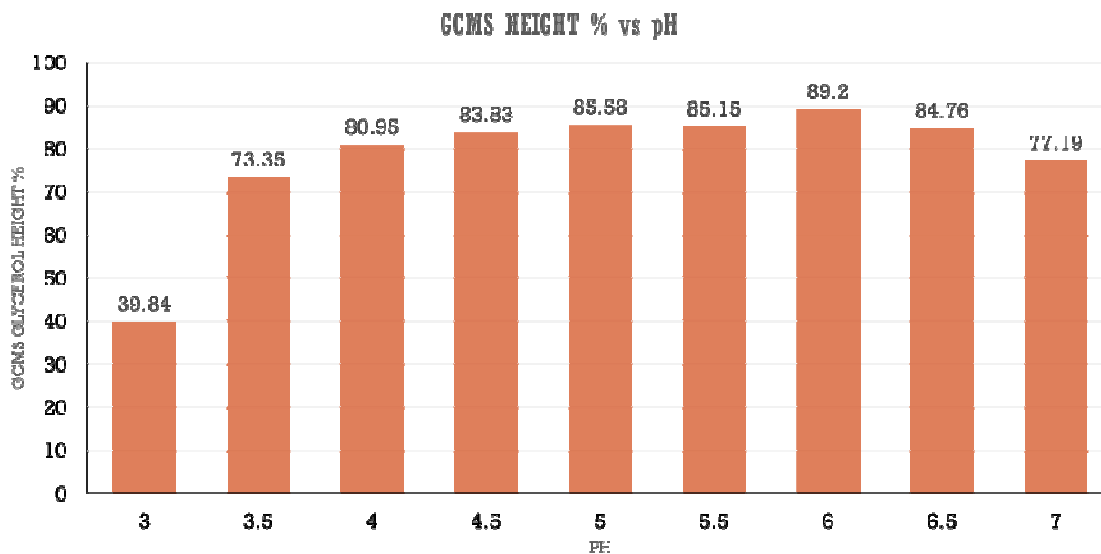


Fig. 1.

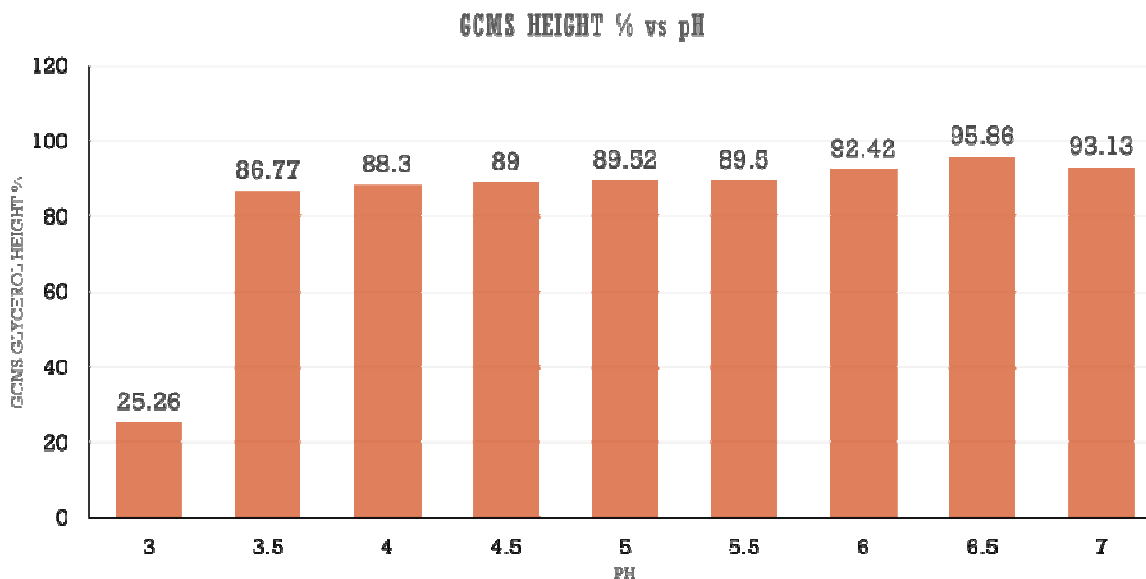


Fig. 2.

3.3 EXTRACTION OF GLYCEROL WITH IPA

Because the sodium phosphate salt formed during the neutralization step is dissolved in mixture with the glycerol and water system, Isopropyl Alcohol (IPA) was used to solvent extract the glycerol from the mixture. This is because the glycerol is very soluble in IPA while the sodium phosphate (NaH_2PO_4) salt formed is very insoluble in IPA thus precipitating out the salt crystals at the bottom. The Glycerol:IPA ratio of 1:1, 1:2 and 1:3 were used and it was

observed that above ratio of 1:2, there was no difference thus the optimal ratio used was 1:2.

3.4 ADSORPTION WITH ACTIVATED CARBON

The IPA-Glycerol layer decanted after the extraction stage was having a golden yellow colour and was decolourized using commercial activated carbon. the decolorization was carried out in two steps and each step with about 35g/l of carbon to glycerol. At the end of the process, the colour was reduced by about 99% giving a clear solution.

3.5 GLYCEROL REFINING AND IPA RECOVERY

After the decolorization stage, the glycerol was separated/refined by distilling off the IPA at about 85°C and the distilled IPA collected for reuse. The properties of crude

glycerol after purification in comparison with commercial glycerol are listed in Table 2.0, and it can be seen that the performance of purified crude glycerol reached basically the quality level of commercial glycerol.

TABLE 2: Comparison of properties of the glycerol refined in this work with commercial [4]

Parameters	Commercial glycerol	Purified glycerol from this work		Manosak et al. (2011)
		Neem	W.C.V.O.	
pH	6.97	6.30	6.42	7
Ash content (%)	0.000 2	1.30	1.10	2.08±0.06
Density at 20°C (g/cm ³)	1.267 1	1.240	1.234	-
Purity (%)	99.98	97.84	97.37	96.2±0.03
colour	Clear	Clear	Clear	Clear

The heavy metal and elemental analysis, phosphate and chloride tests were also carried out. The results obtained according to table 3.0, shows they are all below 5.0ppm as obtained in commercial grade glycerol

TABLE 3: Elemental analysis of the refined glycerol

Element/Metal	Concentration (ppm)	
	Neem	W.C.V.O.
Zinc (Zn)	0.0463 ± 0.0016	0.0848 ± 0.0034
Iron (Fe)	0.0649 ± 0.0015	0.1759 ± 0.0022
Lead (Pb)	0.0946 ± 0.0002	0.0541 ± 0.0003
Cadmium (Cd)	0.0068 ± 0.0002	0.01606 ± 0.0004
Chromium (Cr)	0.0191 ± 0.0001	0.0343 ± 0.0005
Copper (Cu)	0.0139 ± 0.0003	0.0343 ± 0.0005
Sodium (Na)	0.1298 ± 0.0006	0.1126 ± 0.0004

4. CONCLUSIONS

High purity glycerol is a very important industrial feedstock. Its applications are found in foods, drugs, cosmetics, tobacco industries and a host of others. Refining the crude glycerine by-product of biodiesel production therefore, is of utmost importance in adding value to the overall biodiesel process thus increasing its profitability.

Purification of glycerol from a crude glycerol derived from a neem oil based biodiesel production and from waste cooking vegetable oil was achieved using combined methods of physical and chemical treatment. The acidification conditions used in this work are as follows: a reaction time of 120 min, a reaction temperature of 30 °C, and a pH value of 6 and 6.5 for crude glycerol from waste cooking vegetable oil and neem biodiesel production respectively in the presence of dilute H₃PO₄. After that, the

glycerol-rich layer obtained after neutralization was extracted with Isopropyl Alcohol (IPA) at an IPA:Glycerol ratio of 2:1 (v/v). Then, the samples were decolorized using activated carbon at a dose of about 35g/l of the carbon to glycerol to give a clear solution. The average purity of the refined glycerol was analyzed using the GCMS to give approximately 97% purity.

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