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Characterization of Crude and Purified Glycerol from Biodiesel Production and Purification Techniques

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Abstract: *Glycerol is the byproduct of biodiesel production and each 10 kg of biodiesel produce 1kg of crude glycerol. Crude glycerol contained lots of impurities such as soap, methanol, ash, moisture, MONG etc. crude glycerol has a high value added uses and it is necessary to characterized crude glycerol on the basis of chemical and physical properties.The characterization of impurities which are present in crude glycerol and were characterized for the density, moisture content present in glycerol, ash content, alkalinity, glycerol content, metal content and color intensity all are identify by suitable instrument. Analysis of purified glycerol by HPLC and gas chromatography.There are several purification steps to produce high purity glycerol. Techniques used for purification of crude glycerol are series of treatment like chemical pretreatment, methanol removal, vacuum distillation, ion exchange, activated carbon. Crude glycerol contains impurities such as alcohol, spent catalyst, ash, water, and fatty acid that barely differ from crude glycerol in their physical properties. Physico-chemical treatment based upon repeated cycles of acidification to the desired pH within the range using acid to allowing phase separation and then harvesting of the glycerol rich followed by neutralization of the harvested glycerol phase with sodium hydroxide and obtain high purity glycerol.*

Keywords: *biodiesel, crude glycerol, purification, transesterification, vacuum distillation, ion-exchange.*

1. INTRODUCTION

Glycerol is derived from natural or petrochemical feedstocks, which is produced as a by-product from saponification and hydrolysis reactions in oleochemical plants as well as transesterification reaction in biodiesel plants[1]. Disposal of crude glycerol is costly, it become useful to undergo purification process to generate income. Demand of biodiesel production is increasing continuously has resulted in a large surplus of glycerol and partially purified glycerol in the environment. To increase the economics of biodiesel production, crude glycerol disposal and its utilization has become serious issue and a financial and environmentally suitable for biodiesel industry[2].For the sustainability of biodiesel industry, economic utilization of crude glycerol for value added products are critically important and the recovery and purification of glycerol is play an important role in biodiesel cost reduction[3].

2. DESCRIPTION OF GLYCEROL

Glycerol also known as Glycerine or propane-1-2-3-triol, is a chemical that consists of three-carbon chain with a hydroxyl group attach to each carbon. It is a clear, colourless, odourless, viscous liquid that is widely used in pharmaceutical and manufacturing industries. It is hygroscopic in nature and highly soluble in water. It is a sweet-testing and non-toxic substance [4]. Crude glycerol is 70–80% pure and is often concentrated and purified prior to commercial sale to 95.5–99% purity.

2.1 IMPURITIES

Crude glycerol contains impurities such as alcohol, spent catalyst, ash, water, and fatty acid that barely differs from crude glycerol in their physical properties. The appropriate composition of a typical crude glycerol derived from transesterification, saponification and hydrolysis reaction of fat and oils.

A crude glycerol extracted from sunflower oil biodiesel had a composition (w/w) of 30% glycerol, 50% methanol, 13% soap, 2% moisture, 2-3% salts (primarily sodium and potassium) and 2–3% other impurities (5). In contrast, Hansen et al. [10] reported glycerol contents of 38 to 96% in a set of 11 crude glycerol samples collected from 7 different Australian biodiesel producers. Some of those samples contained more than 14% methanol and 29% ash. Because most biodiesel production uses low-grade methanol and homogeneous alkaline catalysts (sodium methoxide or potassium hydroxide), the quality of the afforded glycerol is poor[5].

2.2 ANALYSIS OF CRUDE GLYCEROL

The chemical composition of crude glycerin has not been frequently determined by laboratory analysis. This lack of information is limiting the use of crude glycerin as a feedstuff for dairy cattle. The sale of crude glycerin for use in feeds would provide another source of income for

biodiesel producers and could potentially make the production of biodiesel more profitable. Using crude glycerol as a feedstuff may also provide a cheaper feed alternative than corn, noting the demand and price for corn has gone up because of ethanol fuel production. The concentrations of glycerol, total fatty acids, methanol, ethyl alcohol, moisture, and ash were determined using various laboratory procedures.

C. F. Hansen etal. Reported that crude glycerol were donated from different biodiesel factories for subsequent determination of pH, density (ISO 12185), glycerol (ISO 2879-1975), moisture (ISO 12937), ash (ISO 6245), methanol (GC-FID) and matter organic nonglycerol (MONG), defined as 100 – (glycerol content, % + water content, % + ash content, %) (ISO 2464).

The ash was very variable due to the catalyst used in production of biodiesel and the different steps used in purifying the glycerin. Ethyl alcohol concentration was low in all of the samples (< 10 ppm). The concentration of methanol was very variable among the samples, reflective of the methanol added during the biodeisel production for formation of fatty acid esters without separation of the alcohol from the glycerin. Moisture was the next most variable in the samples (average = 6.12%, CV = 72.7%). Concentrations of fatty acids in the samples were negligible. Glycerol concentration in the samples was not very variable (average = 30.5%, CV = 1.7%).

2.3 DETERMINATION OF PHYSICAL PROPERTIES

The density of crude glycerol was determined by measuring the volume and weight of crude glycerol at room temperature (23 ± 0.5 °C). For pH determination, Crude glycerol (1.00 ± 0.1 g) was dissolved in 50 mL of deionized (DI) water. The pH of the solution was measured by a digital pH meter (Oakton pH 11 series, South Burlington, VT) at room temperature (23 ± 0.5 °C). The viscosity of crude glycerol was measured at 25 ± 0.5 °C according to ASTM D 4878-0831 using a Brookfield DV II+Proviscometer equipped with a small sample adapter, a temperature probe, and a temperature control unit [6-7]

2.4 WATER CONTENT

The water content of crude or purified glycerol was measured following the standard method ISO 2098-1972 by using the Karl- Fisher titrator V20[6-7].

2.5 ASH CONTENT

Ash content was analyzed according to standard method ISO 2098-1972 by burning 1 g of glycerol in muffle furnace at 750˚C for 3h [6-7].

2.6 SOAP CONTENT DETERMINATION

The soap content of crude glycerol was determined with reference to AOCS Recommended Practice Cc 17-9532 and ASTM D 4662-08.33 Briefly, the unadjusted soap content of crude glycerol was determined according to AOCS Recommended Practice Cc 17-95. The alkalinity of crude glycerol was determined according to ASTM D 4662-0833 and used to adjust the soap content [6-7]. The adjusted soap content of crude glycerol was calculated as follows:

Soap as sodium oleate, % = $(V_s\text{-}V_a) \times N \times 30.44/W$

where V_S = mL of titrant consumed, soap titration; Va = mL of titrant consumed, alkalinity titration; N = normality, HCl solution; W = mass (g) of crude glycerol weighed.

2.7 INFRARED SPECTROSCOPY

Fourier transform infrared spectra (FT-IR) were obtained using the KBr method on a Nicolet Magna-IR 560 spectrometer operating at 1 cm-1 resolution in the 400-4000 cm-1 region [6-7].

2.8 NMR SPECTROSCOPY

1H NMR and 13C NMR (nuclear magnetic resonance) spectra of resin disolved in d6-DMSO were acquired at 25oC on a Varian Inova 600 NMR spectrometer equipped with a Varian 5 mm triple-resonance indirect-detection HCX probe.

2.9 Three methods, including iodometric–periodic acid method, high performance liquid chromatography (HPLC), and gas chromatography (GC), were shown to be suitable for the determination of glycerol content in crude glycerol.

2.9.1 GLYCEROL CONTENT DETERMINATION BY IODOMETRIC–PERIODICACID METHOD

The determination of the free glycerol content of crude glycerol by iodometric–periodic acid method was conducted with reference to AOCS Official Method Ca 14-56.3 [6-7]

2.9.2 HPLC ANALYSIS OF GLYCEROL AND METHANOL

The free glycerol and methanol contents of crude glycerol were determined by HPLC analysis using aqueous fractions obtained from crude glycerol fractionation without saponification. The total glycerol content of crude glycerol was determined by HPLC analysis using aqueous fractions obtained from crude glycerol fractionation with saponification. Aqueous fraction samples were filtered and analyzed using a LC- 20 AB HPLC system (Shimadzu, Columbia, MD) equipped with a RID-10A refractive index detector and a RFQ-Fast Fruit H+ (8%) column (Phenomenex, Torrance, CA). The mobile phase used was 0.005 N H_2SO_4 at a flow rate of 0.6 mL/min. The column and RID temperatures were maintained at 60 and 55 °C, respectively. The injection volume was 10 µL. An external calibration curve was constructed by analyzing standard glycerol and methanol solutions at different concentration levels [6-7].

2.9.3 GC ANALYSIS OF GLYCERIDES, GLYCEROL, FAMES, AND FFAS

The free glycerol in crude glycerol, the FAMEs and glycerides in organic fractions obtained without saponification, and the fatty acid profiles of the free fatty acids (FFAs) in organic fractions obtained with saponification were determined by gas chromatography (GC) using a Shimadzu GC-2010 plus GC system (Shimadzu, Columbia, MD) equipped with a flame ionization detector (FID). The GC analysis of glycerides was conducted according to ASTM D6584-10a.37 The GC analysis of the free glycerol content of crude glycerol was conducted as follows: weighed crude glycerol (40.0−100.0 mg) was acidified by 100 μL 1:1 HCl (v/v) and then dissolved in 10 mL of pyridine in a 15-mL glass test tube (Pyrex, Corning, NJ). Then, an aliquot of the obtained solution and 100 μL of 1,2,4-butanetriolstandard solution (0.89 mg/mL, internal standard) were mixed and derivatized by MSTFA (100 μL) at 38 °C for 15 min. The sample was then filtered and injected at an injection volume of 1 μL into aMXTBiodiesel TG column (14 m, 0.53 mm, 0.16 μm, Restek, Bellefonte, PA). Helium was used as the carrier gas at a flow rate of 3 mL/min. The injector and column temperatures were ramped from 50 to 110 at 5 °C/min with the detector temperature held constant at 380 °C. A calibration curve was constructed by analyzing pure glycerol at different concentration levels.

For FAME analysis, the organic fraction sample (without saponification) was weighed (20−50 mg) and dissolved in 5 mL of anhydrous hexane in a 15-mL glass test tube (Pyrex, Corning, NJ). An aliquot of the obtained solution and 100 μL of methyl heptadecanoate standard solution (internal standard) were mixed and filtered through a PTFE filter (porosity, 0.22 μm; diameter, 13 mm, Fisher Scientific, Pittsburgh, PA) into a 1.5-mL GC vial. Each sample (1 μL) was injected into a Stabliwax-DA column (30 m, 0.32 mm id, 0.5 μmdf, Restek, Bellefonte, PA) at an injection temperature of 200 °C. The column temperature was ramped from 100 to 250 at 5 °C/min with detector temperature held constant at 250 °C. Helium was used as the carrier gas at a flow rate of 1 mL/min. The calibration curve wasconstructed by analyzing standard FAME solutions at different concentration levels.

The fatty acid profiles of the FFAs in organic fractions (with saponification) were analyzed as follows: sample (60−150 mg) was weighed into a Teflon-capped test tube, followed by the addition of 2 mL of 10% w/w BF3−methanol. The tube was heated in a water bath maintained at 60 °C for 15 min, after which 1 mL of hexane and 1 mL of water were added. The top hexane phase containing methyl estersderivatives of FFAs was analyzed by GC according to the FAME analysis procedure[6-7].

TABLE 1: Characteristics of crude glycerol from different feedstock of biodiesel plants

feedstock	Content of parameter characterized (wt. %)						References
	glycerol	soap	salt	methanol	moisture	MONG	
Vegetable oil	65-75	5	10	0.5	10	5	H.W.Tanetal.
Sunflower oil	30	13	2-3	50	2	2-3	Asad-ur-rehmanetal.
Waste used oil	27-30	-	2-3	-	5-8	50-61	Sangkornkongjaoetal.
Waste cooling oil	50-60	-	-	20-25	-	-	Ampaitepinsinghabhanduetal.
Palm oil	70-85	1-2	5-10	1	5-15	1-2	Tavipolsurrodetal.

TABLE 2: Comparison of purified crude glycerol properties obtained from others works

Author(s)	Source of crude glycerol	Purification procedure	Glycerol (% w/w) (b)		Ash (% w/w) (a)	(b)	MONG (% w/w) (a)	(b)	Water (% w/w) (a)	(b)
Kongjao.S et al.	Transesterification of waste used oil	Chemical and physical treatment	28.5	93.3	2.65	.0004	56.1	5.16	6.7	1.5
Tianfeng.C.et al.	Transesterification of waste cooking oil	Chemical and vacuum distillation treatment	28.5	98.10	2.6	.0002	-	-	-	-

Author(s)	Source of crude glycerol	Purification procedure	Glycerol (% w/w) (b)		Ash (% w/w) (a)	(b)	MONG (% w/w) (a)	(b)	Water (% w/w) (a)	(b)
Xiao.Y.et al.	Model of different oil	Chemical and physical treatment	74.5	94.0	-	-	-	-	-	-
Nanda.M.R. et al.	Transesterification of oil	Acidification	15.0	96-93	6.0	1.4-1.7	70.0	30.0	10	1.3
Manosak.R.et al.	Transesterification of waste used oil	Chemical and adsorption treatment	36.7	96.3	4.31	2.08	44.0	1.50	14.7	0.06
Hazimah et al.	Fatty acid plant	Chemical and vacuum distillation	70	99.3	4	7	-	-	-	-
Schaffner	Synthetic solution	Bipolar-electrodialysis	65	95	2	.054	4	0.56	4	0.45
Asher and simpson	Soap lye solution	Ion exchange	7.5	82.5	13	7	-	-	-	-
Oei et al.	Transesterification of palm kernel oil	Chemical and physical treatment	17.7	51.4	58.7	13.8	17.7	25.9	5.9	8.9

3. METHODS USED TO REMOVE IMPURITIES

Crude glycerol separation and purification activities have expanded considerably, and academic institutions have explored more innovative methods, theories and process designs in these respects.

3.1 SALT SEPARATION

For crude glycerol derived with an alkaline catalyst, treatment begins by neutralization using certain acids. This technique efficiently removes alkaline matter, including excess catalyst and the abundant soaps formed during transesterification processes employing homogeneous catalysts. The neutralization separates the reaction mixture into three phases using a strong- or medium-strength mineral. The three phases consist of the catalyst in the bottom phase, the neutralized glycerol and methanol in the middle phase and the free fatty acids (FFAs) in the top phase .

Acids are used to neutralize excess alkaline catalysts, whereas bases are used to neutralize acidic catalysts. Sometimes, hydrochloric or sulphuric acid is employed in a re-neutralization step and produces sodium chloride or potassium sulphate, respectively. However, using phosphoric acid is more environmentally friendly. Phosphoric acid neutralizations produce a phosphate salt that is widely used as a fertilizer. Sulphuric and hydrochloric acids produce environmental harmful substances during neutralization. The amount and concentration of acids used in neutralization exert major effects on the separation time and the removal of free fatty acids andsalts .

Usually, the crude glycerol is reacted with greater than 1 mole of 85 wt.%sulphuric acid. Afterward, sodium borohydride or sodium hydroxide solution is added to neutralize the excess acid and to remove colored impurities. Hajek and Skopal (93) demonstrated that sequential neutralizations or saponifications could yield 84% purity glycerol. Furthermore, Kongjao et al.asserted that acidifying the crude glycerol with mineral acids (such as sulphuric acid) converted soap impurities into insoluble fatty acids

According to reaction-

$$RCOONa + H_2SO_4 \rightarrow RCOOH + Na+ + SO^{2-}{}_4$$

3.2 CRYSTALLIZATION OR PRECIPITATION

In another separation technique, catalyst salts in solution after acidic treatment are removed by precipitation as hydroxyapatite (HAP). The co-addition of lime ($Ca(OH)_2$) and phosphoric acid to the pre-treated glycerol results in calcium apatite ($Ca_5(PO_4)^3(OH)$) formation. This chemical reaction removes solubilized catalyst from glycerol samples. The reaction and precipitation is driven by calciumion and hydroxide-ion attraction. Separation of the calcium apatite by gravity or centrifugation removes nearly all of the excess catalyst.

3.3 ALCOHOL REMOVAL AND RECYCLING

Excess un-reacted methanol is a major contaminant in crude glycerol. High methanol levels are toxic, particularly in animal feeds and pharmaceuticals. Methanol is inherently toxic but not directly poisonous. Alcohol dehydrogenase enzyme in the liver converts methanol to formic acid and formaldehyde, which causes blindness by the destruction of the optic nerve [5].Where ethanol is less expensive and readily available, it is used in place of methanol.

Occasionally other higher alcohols have been employed for the production of biodiesel [11]. The presence of residual methanol (or other alohols) in biodiesel is undesirable and can lead to a low flashpoint.

The excess methanol must be removed to achieve the level deemed safe by the U.S. Food and Drug Administration (FDA). Brockmann et al. reported excess methanol removal using a flash evaporation. This technique, based on the boiling point of alcohols, removed nearly 100% of the methanol. In summary, a methanol removal step is needed to meet the general usage requirements set by international standards Removal of Solid Contaminants Heterogeneous catalysts are better suited for glycerol production than homogeneous catalysts. Heterogeneous catalysts afford a considerably cleaner crude glycerol, and heterogeneous catalysts can be easily removed by simple filtration. The disadvantages of heterogeneous catalysts include their high cost and difficult syntheses. Homogeneous catalysts are better focussed. However, neutralizing homogeneous catalysts produce more salt. Furthermore, years ago, the Wurster and Sanger singleeffecglycerine evaporator was developed to overcome the salt removal problem . The first of the three apparatuses had a large chamber that functioned to collect salts. After a neutralization, the entire mixture was dropped into a tank with a false bottom comprising a filter bed of wire screen and filter cloth. The crude glycerol was pumped away from below the false bottom. The salt was washed with lye and then with water. The wash liquors were pumped back into the evaporator feed tank. Depending on the crude glycerol content, this procedure decreased the salt content to 0.5 to 2.0 wt.% . This method for removing salt was used only in single-effect evaporations. The second method, which is still extensively used in small and moderately sized plants, has the evaporator bottoms connected to salt filters, salt boxes or salt extractors. For a double-effect evaporator, three salt extractors are typically used. The setup allows for both evaporators to drop salt while one extractor is emptied. Salt is allowed to accumulate in the evaporator during the time required to steam, dry and empty its extractor. Furthermore, this second apparatus allows for the salt to be removed from the evaporators continuously and dyed. The third apparatus utilizes salt drums and centrifuges for complete salt removal.

3.4 REMOVING IONS AND COLORED CONTAMINANTS BY ADSORPTION

During the reaction, some catalysts dissolve into the reaction medium as free ions. To remove these free ions, ion exchange resins have been used. Both column and batch methods have been investigated (129). Synthetic ion exchange resins have been produced commercially since the 1960s. Strong acid cation exchange resins and strong base anion exchange resins, which fully ionise over the entire pH range, are supported on three-dimensional polystyrene cross-linked with an agent such as divinylbenzene. To convert the cross-liked polystyrene to a hydrogel with an ion exchange capability, ionic functional groups are attached to the polymeric network by a variety of chemical means.

4. CONCLUSIONS

In this review, crude glycerol can be produce from biodiesel trans-esterification, saponification, hydrolysis. The production of every 10kg of biodiesel produces 1 kg of glycerol via transesterification process. Recently, the glycerol purification process is expensive and is plagued with handling and separation problems. Method for glycerol purification are neutralization, methanol removal, adsorption by activated carbon, vacuum distillation, ion-exchange. The combination of more than one techniques can give better quality glycerol upto pharmaceutical grade glycerol and this purified glycerol has been converted into many valuable products methanol, hydrogen, glyceroltert butyl ether, 1,3- propanediol. From the economical point of view it appears that physical and vacuum distillation is to be most suitable method to attend the highest purity level of glycerol.

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