



## **Review of Different Purification Techniques for Crude Glycerol from Biodiesel Production**

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### **Authors' contributions**

*This work was carried out in collaboration between all authors. Authors OOM and EUA did the literature review and also worked on the draft of the paper. Author CSE approved the final manuscript and author GNE supervised the team. All authors read and approved the final manuscript.*

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### **ABSTRACT**

The global glycerol market has experienced a surplus in recent decades due to an increase in biodiesel production and thus created a new form of challenge in terms of purification of the crude glycerol. Various techniques have been developed worldwide on purification of crude glycerol. These processes include chemical pre-treatment, methanol removal, vacuum distillation, ion exchange, adsorption, solvent extraction and membrane separation technology to mention a few. In Nigeria, domesticating these technologies or techniques to suit our peculiar situation and also be cost effective needs a critical evaluation of all the available options. This review, therefore, summarises the progress of crude glycerol purification technologies using various techniques as compared with the process technology developed by researchers at the Federal Institute of Industrial Research, Oshodi, Lagos Nigeria.

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## 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 [1]. Glycerol ( $C_3H_8O_3$ ) 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 [2]. With the rapid growth of the biodiesel industry all over the world, a large surplus of glycerol has been created, leading to the closure of several traditional glycerol production plants. Thus, crude glycerol disposal and utilisation have become a serious issue and a financial and environmental liability for the biodiesel industry [3]. Economic utilisation of glycerol for value-added products is critically important for the sustainability of biodiesel industry.

Crude glycerol, however, has a purity of 15-80% and it contains a large amount of contaminants such as water, methanol, soap/free fatty acids (FFAs), salts, and unused reactants. The common practice of using alkaline catalysts during the transesterification process results in a high pH (above 10) of this by-product. The presence of contaminants in this renewable carbon source creates certain challenges for the conversion processes [4]. Another major challenge for the utilisation of crude glycerol is the inconsistency in its composition since it varies with the feedstock and production procedures. As such, it is of great significance and interest to purify crude glycerol for the aforementioned value-added applications of glycerol [4,5]. High purity glycerol is also an important feedstock for various industrial applications in food, cosmetic and pharmaceutical industries.

Different purification processes have been developed and reported. The choice of which process to adopt largely depends on the economics of scale and the target end grade.

## 2. GRADES OF GLYCEROL

The purpose of purifying the crude glycerol is to enhance its usability by removing the impurities that are present in it according to different sets of standard and usage. Refined glycerol found in the market can be categorised into three main types which are based on their purity level and

end use. These are; Technical grade, United States Pharmacopeia (USP) and Food Chemical Codex (FCC).

Technical grade is mainly used as a chemical product building block and not for food and medicine [6]. United States Pharmacopeia (USP) glycerol which is derived from animal fat or vegetable oil is suitable for both pharmaceutical and food products while the Food Chemicals Codex (FCC) glycerol which is mainly derived from vegetable oil sources is appropriate for use in food [6,7]. The grades of glycerol according to purities are listed in Table 1.0

## 3. GLYCEROL PURIFICATION TECHNIQUES SO FAR

### 3.1 Cai Tianfeng; Li Huipeng; Zhao Hua; Liao Kejian (Orthogonal Test Method)

Purification of the crude glycerol obtained from biodiesel production was conducted by means of a combined chemical and physical treatment method based upon repeated cycles of acidification of liquid phase to the desired pH value by using 5.85%  $H_3PO_4$  solution for pH value adjustment. The mixture was kept at 70°C for 60 min to make phase separation for obtaining a glycerol-rich middle phase. Subsequently, upon reaction of the obtained glycerol phase with 0.03% of sodium oxalate at 80°C for 30 min, the impurity removal rate was equal to 19.8%. The fraction boiling between 164°C and 200°C was collected by vacuum distillation followed by decolourisation with 2% of active carbon at 80°C two times to yield the product glycerol with purity of 98.10% [8].

### 3.2 Martin Hájek, František Skopal

The certain amount of the raw glycerol phase was put into the reactor and diluted by a chosen amount of methanol. The concentrated acid was slowly added to reach pH of 3–4 and the mixture was stirred for 15 min. The acid formed potassium carbonates and bicarbonates to carbon dioxide and soaps to fatty acids. The formed coagulation of salt was filtered off by frit and excess of methanol was distilled off. The distilled methanol can be used again for the dilution of the raw GP. Then, the heterogeneous reaction mixture was cooled to the temperature of 25°C, and an optimum amount of water was

added for better and faster separation. Then, the mixture was poured into the separation funnel where the separation of phases began. After a perfect separation of the reaction mixture to the upper organic phase and the lower pure glycerol phase, both phases were analysed. Many samples of the raw glycerol phase with different composition were tested with different acids. Saponification of esters in the raw GP is another possibility; only higher fatty acids are gained in the OP. The raw GP was put into the batch glass reactor and tempered to 25°C. The potassium hydroxide was solved in methanol and this solution was added to the reactor and the saponification of esters started. After saponification, the reaction mixture was neutralised by concentrated acid. The following process is the same as in neutralisation [9].

### **3.3 Nanda M. R., Yuan Z., Qin W., Poirier M.A. and Chunbao X**

The crude glycerol under gentle stirring was acidified with different acids (sulphuric acid, hydrochloric acid, and phosphoric acid, respectively) to the desired pH level and was kept for a sufficiently long time to allow the formation of three separate layers. The top layer is a fatty acid phase, the middle one is a glycerol rich phase and the bottom one is inorganic salt phase. The bottom phase was separated by simple decantation. The fatty acid-rich top phase was separated from the glycerol-rich phase by using a separator funnel. The extracted glycerol phase was neutralised using 12M KOH solution followed by evaporation of water at 110°C for 2h and filtration to remove the precipitated salt. The obtained glycerol was further purified by solvent extraction process using methanol as a solvent to promote the precipitation of dissolved salts. The precipitated salts were separated by filtration and passed through a column of activated charcoal to de-colour and remove odour and some metal ions. The produced purified glycerol is approximately 96 wt% pure [4].

### **3.4 Rudemas Manosak, Siripong Limpattayante, Mali Hunsom**

Initially, the free fatty acid and salt contents were reduced by acidification with the addition of either sulphuric acid, phosphoric acid or acetic acid to the desired pH in the range of pH 1–6, and then left for 12 h 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, if present, the bottom inorganic

salt-rich layer. The top layer was removed by slow decantation and the middle glycerol-rich layer was separated from the bottom inorganic salt-rich layer, if present, by filtration. Prior to removal of the residue salts from glycerol-rich layer, it was neutralised by the addition of 5 M NaOH to pH 7.0, left for a while and then filtered to eliminate the precipitated salt. The glycerol rich layer was then extracted with one of three types of polar solvent; methanol, ethanol and propanol, at a different solvent: Glycerol ratios in the range of 3:1–1:3 (v/v). The obtained solution was mixed by shaking for 0.5 h and left for 1 h to encourage the precipitation of the salts. At this stage, a two-phase solution was obtained, the glycerol-alcohol phase on the top and the crystallised salt on the bottom. The upper layer was separated by slow decantation to eliminate the crystallised salt. The refined crude glycerol was then obtained after evaporation of the polar solvent at 80°C for 20 min. Finally, the colour, as well as some fatty acids and other components, of the refined crude glycerol was reduced by adsorption with commercial activated carbon. The final purity level was found to be 95.74 wt.% [10].

### **3.5 Wan Nor Roslam Wan Isahak, Jamaliah Jahim, Manal Ismail<sup>1</sup>, Nurul Fitriah Nasir, Muneer M. Ba-Abbad, Mohd Ambar Yarmo**

In this study, the first purification stage of the crude glycerol was achieved by employing the neutralisation method, followed by microfiltration using a 0.45µm filter membrane. However, the free ions from salt and catalyst were then eliminated through an ion exchange process using two types of Amberlite resins to produce higher glycerol purity up to 99.4%. The purity of glycerol was confirmed by the other analysis such as the Fourier transform infrared, United States Pharmacopoeia and American society for testing and materials methods [11].

### **3.6 Yong, K. C., Ooi, T. L., Dzulkefly, K., Wan Yunus, W. M. Z. and Hazimah, A. H.**

A known amount of the crude glycerine was placed in a three-neck round bottom flask fitted with a vacuum release apparatus and thermometer and connected to a condenser. A silicone oil bath was used to heat the crude glycerine to the required temperature. The heat generated by the oil bath was conserved in the distillation equipment by covering it with

aluminium foil for insulation. The glycerine distilled over at a top temperature of 120°C - 126°C (the bottom temperature was 165°C - 190°C) and pressure of  $4.0 \times 10^{-1}$  -  $4.0 \times 10^{-2}$  mbar, and was collected in a flask. The condenser was cooled to 8°C in a cooler to condense the glycerol vapour. Some of the water from the crude glycerine was retained in the liquid nitrogen cold trap. The distilled bottom was collected from the three-neck round bottom flask and weighed and kept in containers. The characteristics of the distilled glycerine were: 96.6% glycerol, 0.03% ash, 1% water, 2.4% matter organic non-glycerol (MONG) and pH 3.5 [12].

### 3.7 O. S. Muniru, C. S. Ezeanyanaso, T. K. Fagbemigun, E. U. Akubueze, O. A. Oyewole, O. J. Okunola, G. Asieba, C. C. Igwe, and G. N. Elemo.

The crude glycerol was neutralised using dilute phosphoric acid ( $H_3PO_4$ ) 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 the solution left to phase separate 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. 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 neutralisation was then determined using the pH with the highest glycerol content in the extracted glycerol rich layer. The glycerol rich layer obtained was concentrated by simple distillation to remove water and also recover methanol present in the mixture and also, to crystallise some salts out of the solution. The concentrated glycerol rich layer was mixed with Isopropyl Alcohol in the ratio of IPA: Glycerol of 2:1 to extract the glycerol out of the mixture (solvent extraction) 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 upper layer was separated by slow decantation to eliminate the crystallised salt and then filtered to remove any traces of salt or solids in it.

Finally, the colour, as well as some fatty acids and other components, of the refined crude glycerol was reduced by adsorption with commercial powdered activated carbon (PAC). The decolourised 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 moisture and further concentrate the refined glycerol. Purified glycerol level achieved was about 97% [1].

**Table 1. Comparison of the available refining technologies**

	Glycerol		
	Purity (%)	Advantages	Disadvantages
Tianfeng et al.	98.10	<ul style="list-style-type: none"> <li>• High purity</li> <li>• Well established process</li> </ul>	<ul style="list-style-type: none"> <li>• Expensive for small-scale</li> <li>• Energy-intensive</li> <li>• High maintenance cost</li> </ul>
Martin Hájek, František Skopal	86	<ul style="list-style-type: none"> <li>• Simple process</li> <li>• Low maintenance</li> </ul>	<ul style="list-style-type: none"> <li>• low glycerol purity</li> <li>• Low glycerol yield</li> </ul>
Nanda et al.	96	<ul style="list-style-type: none"> <li>• High purity</li> <li>• Simple process</li> </ul>	<ul style="list-style-type: none"> <li>• Too many stages required</li> <li>• Process not optimised</li> </ul>
Manosak et al.	95.74	<ul style="list-style-type: none"> <li>• Good purity level</li> <li>• Simple process</li> </ul>	<ul style="list-style-type: none"> <li>• Too many stages required</li> <li>• Process not optimised</li> </ul>
Wan Isahak et al.	99.4	<ul style="list-style-type: none"> <li>• Simple process</li> <li>• Ease of scale-up</li> <li>• Relatively low cost</li> </ul>	<ul style="list-style-type: none"> <li>• Not good for glycerol with high salt level</li> <li>• Expensive to regenerate resins</li> </ul>
Yong et al.	96.6	<ul style="list-style-type: none"> <li>• Well established process</li> <li>• High purity</li> </ul>	<ul style="list-style-type: none"> <li>• Expensive for small-scale</li> <li>• Energy-intensive</li> <li>• High maintenance cost</li> </ul>
Muniru et al.	97	<ul style="list-style-type: none"> <li>• Simple process</li> <li>• Higher glycerol yield</li> <li>• Ease of scale-up</li> <li>• Relatively low cost</li> </ul>	<ul style="list-style-type: none"> <li>• Many stages required</li> </ul>

#### 4. CHALLENGES OF CRUDE GLYCEROL PURIFICATION

Glycerol purification from biodiesel production is urgently necessary to add value to the biodiesel production process [13]. In developing countries like Nigeria, biodiesel production is quite expensive, in fact, too expensive to compete with fossil-derived diesel. Thus refining the crude glycerol by-product from the transesterification process will definitely go a long way in increasing the returns on investment made.

According to Ardi et al. [7], another form of challenge is derived from the biodiesel production processes itself. A new approach in biodiesel production process is needed as current technology although capable of producing a good quality biodiesel but still has a number of disadvantages. The drawback includes the utilisation of base catalyst that induces soap formation which needs to be removed, the excess amount of alcohol used to shift the equilibrium to more biodiesel produced (more alcohol needs to be separated and recycled), homogeneous catalyst that requires neutralisation which in turn producing a huge amount of salt in the waste stream, high operating cost and expensive separation procedures. Furthermore, vegetable oil and alcohol must be considerably anhydrous and have a low free fatty acid content, because the presence of water or free fatty acid or both promotes soap formation [14,15].

#### 5. CONCLUSION

Glycerol refining and purification techniques available to biodiesel producers are numerous. The choice of a particular technique or combination of techniques depends on the number of unit operations involved, the energy requirement of the process, the cost implications of the required items of equipment and ultimately, the yield and target purity level.

The technologies outlined in this review present ways for the development and sustainability of biodiesel production process in the long run. Though, many of these technologies still require additional research and development to make them economically and operationally feasible. Improvement of the glycerol purification method that is less energy intensive and is capable to yield high glycerol purity will be most likely

incorporated in biodiesel plant as part of a sustainable structure.

#### CONSENT AND ETHICAL APPROVAL

It is not applicable.

#### COMPETING INTERESTS

Authors have declared that no competing interests exist.

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