

2 **REVIEW OF DIFFERENT PURIFICATION TECHNIQUES**
3 **FOR CRUDE GLYCEROL FROM BIODIESEL PRODUCTION**

4
5 **ABSTRACT**

6 The global glycerol market has experienced a surplus in recent decades due to an increase in
7 biodiesel production and thus created a new form of challenge in terms of purification of the
8 crude glycerol. Various techniques have been developed worldwide on purification of crude
9 glycerol. These processes include chemical pre-treatment, methanol removal, vacuum
10 distillation, ion exchange, adsorption, solvent extraction and membrane separation
11 technology to mention a few.

12 In Nigeria, domesticating these technologies or techniques to suit our peculiar situation and
13 also be cost effective needs a critical evaluation of all the available options.

14 This review therefore, summarizes the progress of crude glycerol purification technologies
15 using various techniques as compared with the process technology developed by researchers
16 at the Federal Institute of Industrial Research, Oshodi, Lagos Nigeria.

17 **KEYWORDS:** glycerol, refining, technology,

18 **1.0 Introduction**

19 High purity glycerol is a very important industrial feedstock. Its applications are found in
20 foods, drugs, cosmetics, tobacco industries and a host of others. Glycerol (C₃H₈O₃) is an
21 alcohol with three hydroxyl groups (-OH), which can be produced as a by-product of
22 biodiesel production through transesterification of vegetable oil or animal fat with alcohol,
23 such as methanol (Muniru *et. al.*, 2016). With the rapid growth of biodiesel industry all over
24 the world, a large surplus of glycerol has been created, leading to the closure of several
25 traditional glycerol production plants. Thus, crude glycerol disposal and utilization have
26 become a serious issue and a financial and environmental liability for the biodiesel industry.
27 Economic utilizations of glycerol for value-added products are critically important for the
28 sustainability of biodiesel industry.

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

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

41 **2.0 Grades of Glycerol**

42 The purpose of purifying the crude glycerol is to enhance its usability by removing the
43 impurities that are present in it according to different sets of standard and usage. Refined
44 glycerol found in the market can be categorized into three main types which is based on their
45 purity level and end use. These are; Technical grade, United States Pharmacopeia (USP) and
46 Food Chemical Codex (FCC).

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

52 **3.0 Glycerol purification techniques so far**

53 **3.1 Cai Tianfeng; Li Huipeng; Zhao Hua; Liao Kejian (Orthogonal Test** 54 **Method)**

55 Purification of the crude glycerol obtained from biodiesel production was conducted by
56 means of a combined chemical and physical treatment method based upon repeated cycles
57 of acidification of liquid phase to the desired pH value by using 5.85% H_3PO_4 solution for
58 pH value adjustment. **The mixture was kept at 70 °C for 60 min to make phase separation**
59 **for obtaining a glycerol-rich middle phase. Subsequently, upon reaction of the obtained**

60 glycerol phase with 0.03% of sodium oxalate at 80 °C for 30 min the impurity removal
61 rate was equal to 19.8%. The fraction boiling between 164 °C and 200 °C was collected by
62 vacuum distillation followed by decolorization with 2% of active carbon at 80 °C for two
63 times to yield the product glycerol with purity of 98.10%.

64 **3.2 Martin Hájek, František Skopal**

65 The certain amount of the raw glycerol phase was put into the reactor and diluted by
66 chosen amount of methanol. The concentrated acid was slowly added to reach pH of 3–4
67 and the mixture was stirred for 15 min. The acid formed potassium carbonates and
68 bicarbonates to carbon dioxide and soaps to fatty acids. The formed coagulation of salt
69 was filtered off by frit and excess of methanol was distilled off. The distilled methanol can
70 be used again for the dilution of the raw GP. Then, the heterogeneous reaction mixture
71 was cooled to the temperature 25 °C and optimum amount of water was added for better
72 and faster separation. Then, the mixture was poured into the separation funnel where the
73 separation of phases began. After a perfect separation of the reaction mixture to the upper
74 organic phase and the lower pure glycerol phase both phases were analyzed. Many
75 samples of the raw glycerol phase with different composition were tested with different
76 acids. Saponification of esters in the raw GP is another possibility; only higher fatty acids
77 are gained in the OP. The raw GP was put into the batch glass reactor and tempered to 25
78 °C. The potassium hydroxide was solved in methanol and this solution was added to
79 reactor and the saponification of esters started. After saponification, the reaction mixture
80 was neutralized by concentrated acid. Following process is the same as in neutralization.

81 **3.3 Nanda M. R., Yuan Z., Qin W., Poirier M.A. and Chunbao X**

82 The crude glycerol under gentle stirring was acidified with different acids (sulphuric acid,
83 hydrochloric acid, and phosphoric acid, respectively) to a desired pH level and was kept
84 for a sufficiently long time to allow the formation of three separate layers. The top layer is
85 fatty acid phase, the middle one is glycerol rich phase and the bottom one is inorganic salt
86 phase. The bottom phase was separated by simple decantation. The fatty acid-rich top
87 phase was separated from the glycerol-rich phase by using a separator funnel. The
88 extracted glycerol phase was neutralized using 12M KOH solution followed by
89 evaporation of water at 110 °C for 2h and filtration to remove the precipitated salt. The
90 obtained glycerol was further purified by solvent extraction process using methanol as
91 solvent to promote the precipitation of dissolved salts. The precipitated salts were separated

92 by filtration and passed through a column of activated charcoal to de-colour and remove
93 odour and some metal ions. The produced purified glycerol is approximately 96wt% pure.

94 **3.4 Rudemas Manosak, Siripong Limpattayanate, Mali Hunsom**

95 Initially, the free fatty acid and salt contents were reduced by acidification with the
96 addition of either sulphuric acid, phosphoric acid or acetic acid to the desired pH in the
97 range of pH 1–6, and then left for 12h until the solution had phase separated into two or
98 three distinct layers, that is a top layer of free fatty acids, the middle glycerol-rich layer
99 and, if present, the bottom inorganic salt-rich layer. The top layer was removed by slow
100 decantation and the middle glycerol-rich layer was separated from the bottom inorganic
101 salt-rich layer, if present, by filtration. Prior to removal of the residue salts from glycerol-
102 rich layer, it was neutralized by the addition of 5 M NaOH to pH 7.0, left for a while and
103 then filtered to eliminate the precipitated salt. The glycerol rich layer was then extracted
104 with one of three types of polar solvent; methanol, ethanol and propanol, at different
105 solvent:glycerol ratios in the range of 3:1–1:3 (v/v). The obtained solution was mixed by
106 shaking for 0.5 h and left for 1 h to encourage the precipitation of the salts. At this stage, a
107 two-phase solution was obtained, the glycerol-alcohol phase on the top and the crystallized
108 salt on the bottom. The upper layer was separated by slow decantation to eliminate the
109 crystallized salt. The refined crude glycerol was then obtained after evaporation of the
110 polar solvent at 80 °C for 20 min. Finally, the colour, as well as some fatty acids and other
111 components, of the refined crude glycerol was reduced by adsorption with commercial
112 activated carbon. The final purity level was found to be 95.74 wt.%.

113 **3.5 Wan Nor Roslam Wan Isahak, Jamaliah Jahim, Manal Ismail, Nurul Fitriah** 114 **Nasir, Muneer M. Ba-Abbad, Mohd Ambar Yarmo**

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

122 **3.6 YONG, K. C., OOI, T. L., DZULKEFLY, K., WAN YUNUS, W. M. Z. and** 123 **HAZIMAH, A. H.**

124 A known amount of the crude glycerine was placed in a three-neck round bottom flask
125 fitted with a vacuum release apparatus and thermometer, and connected to a condenser. A
126 silicone oil bath was used to heat the crude glycerine to the required temperature. The heat
127 generated by the oil bath was conserved in the distillation equipment by covering it with
128 aluminium foil for insulation. The glycerine distilled over at a top temperature of 120°C -
129 126°C (the bottom temperature was 165°C - 190°C) and pressure of 4.0×10^{-1} - 4.0×10^{-2}
130 mbar, and was collected in a flask. The condenser was cooled to 8°C in a cooler to
131 condense the glycerol vapour. Some of the water from the crude glycerine was retained in
132 the liquid nitrogen cold trap. The distilled bottom was collected from the three-neck round
133 bottom flask and weighed and kept in containers. The characteristics of the distilled
134 glycerine were: 96.6% glycerol, 0.03% ash, 1% water, 2.4% matter organic non-glycerol
135 (MONG) and pH 3.5.

136 **3.7 O. S. Muniru, C. S. Ezeanyanaso, T. K. Fagbemigun, E. U. Akubueze, O.A.**
137 **Oyewole, O.J. Okunola, G. Asieba, C. C. Igwe, and G. N. Elemo.**
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139 The crude glycerol was neutralized using dilute phosphoric acid (H_3PO_4) from its initial pH
140 of about 9 to a pH in the range of pH 3 – 7 in steps of 0.5, with continued stirring, and the
141 solution left to phase separate into two or three distinct layers, that is a top layer of free fatty
142 acids, the middle glycerol-rich layer and, the bottom inorganic salt-rich. The top layer was
143 removed by decantation and the middle glycerol-rich layer was separated from the bottom
144 inorganic salt-rich layer by filtration. The optimal pH for neutralization was then determined
145 using the pH with the highest glycerol content in the extracted glycerol rich layer. The
146 glycerol rich layer obtained was concentrated by simple distillation to remove water and also
147 recover methanol present in the mixture and also, to crystallize some salts out of the solution.
148 The concentrated glycerol rich layer was mixed with isopropyl Alcohol in ratio of
149 IPA:Glycerol of 2:1 to extract the glycerol out of the mixture (solvent extraction) and then
150 allowed to stir on the magnetic stirrer for about 30 minutes. The mixture was then allowed to
151 settle for about 2 hours to enable proper separation of the two layers formed. The upper layer
152 was separated by slow decantation to eliminate the crystallized salt and then filtered to
153 remove any traces of salt or solids in it.
154 Finally, the colour, as well as some fatty acids and other components, of the refined crude
155 glycerol was reduced by adsorption with commercial powdered activated carbon (PAC). The
156 decolorized glycerol-alcohol mixture was then refined by distilling and recovering the IPA at
157 85°C and the resulting refined glycerol was also heated at about 105°C for 3 hours to remove

158 moisture and further concentrate the refined glycerol. Purified glycerol level achieved was
 159 about 97%.

160 **Table 1.0: Comparison of the available refining technologies**

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

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163 **4.0 Challenges of crude glycerol purification**

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165 Glycerol purification from biodiesel production is urgently necessary to add value to the
 166 biodiesel production process. In countries developing countries like Nigeria, biodiesel
 167 production is quite expensive, in fact, too expensive to compete with fossil derived diesel.

168 Thus refining the crude glycerol by-product from the transesterification process will
 169 definitely go a long way in increasing the returns on investment made.

170 According to M.S. Ardi, M.K. Aroua, N. Awanis Hashim (2015), another form of challenge
 171 is derived from the biodiesel production processes itself. New approach in biodiesel
 172 production process is needed as current technology although capable of reducing a good
 173 quality biodiesel but still has a number of disadvantages. The drawback includes the

174 utilization of base catalyst that induces soap formation which needs to be removed, the excess
175 amount of alcohol used to shift the equilibrium to more biodiesel produced (more alcohol
176 needs to be separated and recycled), homogenous catalyst that requires neutralization which
177 in turn producing a huge amount of salt in the waste stream, high operating cost and
178 expensive separation procedures. Furthermore, vegetable oil and alcohol must be
179 considerably anhydrous and have a low free fatty acid content, because the presence of water
180 or free fatty acid or both promotes soap formation.

181 **5.0 CONCLUSION**

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

186 The technologies outlined in this review present ways for the development and sustainability
187 of biodiesel production process in the long run. Though, many of these technologies still
188 require additional research and development to make them economically and operationally
189 feasible. Improvement of the glycerol purification method that is less energy intensive and is
190 capable to yield high glycerol purity will be most likely incorporated in biodiesel plant as part
191 of a sustainable structure.

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