Purification of crude glycerol from transesterification reaction of palm oil using direct method and multistep method

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Abstract. Crude glycerol which produced from transesterification reaction has limited usage if it does not undergo purification process. It also contains excess methanol, catalyst and soap. Conventionally, purification method of the crude glycerol involves high cost and complex processes. This study aimed to determine the effects of using different purification methods which are direct method (comprises of ion exchange and methanol removal steps) and multistep method (comprises of neutralization, filtration, ion exchange and methanol removal steps). Two crude glycerol samples were investigated; the self-produced sample through the transesterification process of palm oil and the sample obtained from biodiesel plant. Samples were analysed using Fourier Transform Infrared Spectroscopy, Gas Chromatography and High Performance Liquid Chromatography. The results of this study for both samples after purification have showed that the pure glycerol was successfully produced and fatty acid salts were eliminated. Also, the results indicated the absence of methanol in both samples after purification process. In short, the combination of 4 purification steps has contributed to a higher quality of glycerol. Multistep purification method gave a better result compared to the direct method as neutralization and filtration steps helped in removing most excess salt, fatty acid and catalyst.

1. Introduction

Glycerol is a chemical from the sugar alcohol group. It is a clear liquid oil and stable in normal condition. It consists of three hydroxyl hydrophilic groups for its solubility in water and its hygroscopic nature. Transesterification is a reaction of fat and oil with methanol with a catalyst which produced biodiesel and glycerol [1]. The stoichiometry of the reaction requires three moles of methanol and a mole of triglycerides to produce three moles of biodiesel and a mole of glycerol. Once the reaction ends, glycerol is separated by either precipitation or centrifugation and then pass through several neutralization processes. According to the study conducted by Haas et al. [2] in 2006, the glycerol price is US $ 0.33 per kg. The purified glycerol can be used in pharmaceutical, cosmetics and food industry. It is also used as food additives and labelled as E number which is E422 [3]. Recent developments have shown that glycerol is used in animal foods, carbon feedstock in fermentation, polymers, surfactant and lubricants [4]. Figure 1 shows the market for glycerol and it indicates that glycerol has played a crucial role in bio refineries [5].
Figure 1. The market for glycerol in year 2002 [5].

Crude glycerol produced from the transesterification reaction has limited usage if it is not undergoing any purification process. It contains excess methanol, catalyst and soaps. Therefore, purification of glycerol is needed to remove all impurities and the glycerol purification process has been patterned in US Patent 4990695 [6]. However, conventional method for glycerol purification requires high cost and complex processes. An established method for glycerol purification by vacuum distillation technique has few disadvantages such as the high energy requirement and high maintenance. If purification use activated carbon, the technique is inefficient for elimination of other impurities. Another technique such as using chemical treatment has disadvantages of resulting in low glycerol yield when the repeated acidification process is carried out [7].

Busby and Grosvenor [8] carried out investigations on the purification of glycerol using the ion exchange technique. The result of their experiment showed that a high quality of glycerol (95-99%) can be produced using this technique. Carmona et al. [9] also used the ion exchange technique in the purification of glycerol. In their study, they determined the equilibrium and kinetic data for the purification reaction using ion exchange Amberlite-252. Another study using an ion exchanged method was conducted by Isahak et al. [10, 11] and Javani et al. [12].

In this study, the transesterification of palm oil with methanol have utilized sodium hydroxide as catalyst. The main product was biodiesel and side product was glycerol. The glycerol was considered as crude glycerol as it contains excess methanol, catalyst and soaps, which needs recovery and purification processes to obtain a better quality of the glycerol. Therefore, this study is vital in determining an easy method, hence practical, for purifying crude glycerol for further uses. A pure glycerol can be used in many applications such as moisturizer, plasticizer, emollient, lubricants, antifreeze, drugs, and foods. The objectives of this study are to produce biodiesel and crude glycerol from transesterification of refined, bleach deodorized palm oil and to purify the crude glycerol by two separation techniques; direct and multistep. Then, comparisons of these two techniques are performed for two types of samples; the sample self-produced through the transesterification process of palm oil (CGA) and the sample obtained from a biodiesel plant, Sime Darby Biodiesel Sendirian Berhad (CGB).

2. Materials and Methods

2.1 Transesterification reaction

RBD palm oil (Seri Murni Brand), methanol and sodium hydroxide were purchased from local groceries, Sigma Aldrich, and R&M Chemical, respectively. Amberlite IRN-78 (SUPELCO brand) and Amberlite 200C ion exchange resins were purchased from Sigma Aldrich. Palm oil and methanol are the main
reactant for transesterification reaction. Palm oil contains 1.128% free fatty acids. Both reactant were mixed at a molar ratio of oil to alcohol 15:1 with the homogeneous base catalyst (sodium hydroxide). The reaction time was set at 2 to 3 hours in a three-neck flask equipped with condenser, thermometer and magnetic stirrer. The mixing speed was set to 500-600 rpm. At the end of the process, the mixture was settled about half an hour. The settling process was required to separate biodiesel from glycerol.

2.2 Purification of glycerol with direct method

After separation of biodiesel and glycerol, the ion exchange process was carried out. The ion exchange process was carried out in a chromatography column. The column was loaded with ion exchange resins (cation and anion) Amberlite IRN-78 and Amberlite 200C type. The purpose of this process being conducted was to neutralize and remove free ions in the glycerol samples. Other than that, silica beads were also loaded on the chromatography column to remove excess moisture which may be existed in the glycerol samples. After the ion exchange process was performed, the methanol removal process was done using a rotary evaporator.

2.3 Purification of glycerol with multistep method

Multistep method was conducted by performing few procedures started with neutralization of crude glycerol, followed by filtration process, ion exchange process and methanol removal process. Neutralization of crude glycerol was conducted using phosphoric acid. The neutralization process has produced salt and therefore the salt need to be filtered using filter paper. After filtration, the samples were put in a chromatography column for ion exchange process and then put into the rotary evaporator for the methanol removal process. The methods in ion exchange and methanol removal process for multistep was identical to the direct method.

2.4 Analysis of purified glycerol samples

The samples were analysed by several types of analysis such as free fatty acids determination, pH value, Fourier Transform Infra-Red (FTIR), High Performance Liquid Chromatography (HPLC) and Gas Chromatography (GC) analysis. Table 1 provides the wavelengths of functional groups [13].

| Wavelength (cm⁻¹) | Group | Classes |
|------------------|-------|---------|
| 3200-3640        | O-H   | Water   |
| 3000-2800        | C-H   | Alkanes |
| 1830-1800        |       |         |
| 1780-1640        | C=O   | Esters  |
| 1650-1580        | C=C   | Alkenes |
| 1475-1350        | C-H   | Alkanes |
| 950-1300         | C-O   | Primer Secondary, Tertiary Alcohol |
| 950-1300         | O-H   | Aromatic compounds |
| 900-650          | O-H   |         |

Table 2 and Table 3 show the operational conditions for HPLC and GC, respectively.
Table 2. Operation condition of HPLC.

| Operation conditions of HPLC | Value |
|------------------------------|-------|
| Mobile phase                 | Acetone/Acetonitrile |
| Permanent phase              | C18 column         |
| Wavelength                   | 254               |
| Mobile phase velocity        | 1 mL/min          |
| Gradient                     | Time (minutes)    | Gradient Ratio (Acetone to Acetonitrile) |
|                              | 0-1               | 60:40          |
|                              | 2-15              | 90:10          |
|                              | 16-26             | 95:5           |
|                              | 27-30             | 60:40          |

Table 3. Operation conditions of GC.

| Operation conditions of GC                  | Value |
|---------------------------------------------|-------|
| Column type                                 | DB-WAX         |
| Length of capillary column                  | 30 m             |
| ID                                          | 0.25 mm         |
| Film thickness of capillary column          | 0.25 µm         |
| GC Injection temperature                    | 200 °C          |
| Column detector temperature                 | 300 °C          |

3. Results and Discussions

In this section, the results of pH values, free fatty acid content, FTIR, GC and HPLC analysis are presented and discussed.

3.1 pH values

The pH value analysis was conducted at room temperature and the results obtained can be compared in Table 4.

Table 4. Results of pH value analysis of samples before and after purification process.

| Samples                                      | pH value |
|----------------------------------------------|----------|
| Pure Glycerol                                | 6.70     |
| CGA-Unpurified Glycerol                      | 9.20     |
| CGA-Purified Glycerol with Direct Method      | 8.50     |
| CGA-Purified Glycerol with Multistep Method   | 7.50     |
| CGB-Unpurified Glycerol                      | 6.0      |
| CGB-Purified Glycerol with Direct Method      | 6.0      |

It is apparent from Table 4 that multistep method was able to purify the pH value of crude glycerol almost the value of the pure glycerol for CGA. It is noted that the purity of the samples obtained from biodiesel plant was 78%. Therefore, in this study, the purification of crude glycerol for CGB sample was conducted using direct method only. The pH value was found slightly acidic (pH 6) which was lower than pure glycerol (pH 6.7). After going through the purification process by the direct method, pH value for sample CGB was unchanged. This might be due to the addition of citric acid during the transesterification process in biodiesel plant. The addition of citric acid during the transesterification was to avoid soap formation, thus producing a high quality of biodiesel.
3.2 Free fatty acids content analysis

In order to access the free fatty acid (FFA) content in the samples, PORIM method was used [14]. Table 5 presents the FFA content of each sample.

| Samples                                   | Free fatty acids content (%) |
|-------------------------------------------|------------------------------|
| Pure Glycerol                             | 0.052                        |
| CGA-Unpurified Glycerol                   | 0.128                        |
| CGA-Purified Glycerol with Direct Method   | 0.077                        |
| CGA-Purified Glycerol with Multistep Method| 0.055                        |
| CGB-Unpurified Glycerol                   | 0.051                        |
| CGB-Purified Glycerol with Direct Method   | 0.025                        |

As shown in Table 5, the results of acid value test indicate that the amount of acids was reduced after purifying of crude glycerol by both methods. The acid value in unpurified CGA samples was 0.128%, but after the purification process with direct and multistep methods, the acid values were reduced to 0.077% and 0.05%, respectively. For unpurified CGB samples, the acid value was found to be 0.051% and then it decreases to 0.025% after purification with direct method. The slight difference in the acid values, while preliminary, suggests that the change of the acid value happened when removing the mineral in ion exchange step. It also suggests that there was acid absorption process happened when glycerol passed through the column.

3.3 FTIR analysis

In order to determine the functional group in the glycerol samples, FTIR tests were used. Figure 2 shows the FTIR results for methanol and pure glycerol. The Figure is used as reference and comparison.

![FTIR results for methanol and pure glycerol](image)

**Figure 2. FTIR of methanol and pure glycerol.**

The results of FTIR analysis for CGA samples using both methods is presented in Figure 3.
Figure 3. FTIR results of crude and purified glycerol for CGA samples.

For discussion of the results of FTIR analysis, Figs. 2, 3 and Table 1 are referred. From Figure 3, it is found that an ester peak (C=O) was detected in unpurified CGA samples at the wavelength of 1741 cm\(^{-1}\). However, none of ester peak was detected in the purified CGA samples using both methods. This result confirms that fatty acid salt was existed in the crude glycerol samples, but then it successfully eliminated from the purification processes by both methods. All peaks for determining the existence of glycerol at each sample were clearly detected which confirms that glycerol was successfully separated from the biodiesel. The peaks are O-H at wavelength of 3200-3600 cm\(^{-1}\), C-H, C-O and O-H at wavelength of 1500-650 cm\(^{-1}\). Similar results were obtained for CGB samples as shown in Figure 4.

Figure 4. FTIR results of crude and purified glycerol for CGB samples.

Ester peak (C=O) was found at wavelength 1738 cm\(^{-1}\) for unpurified CGB samples. However, there was no peak detected for the ester group in CGB samples that purified using the direct method. This finding may be due to fatty acid salt was certainly presented in the unpurified samples and then removed
by purification process. Besides, the main peaks for determining the glycerol samples are found such as O-H peaks at wavelength of 3200-3600 cm\(^{-1}\), C-H, C-O and O-H at wavelength 1500-650 cm\(^{-1}\).

3.4 GC analysis

Sample analysis using gas chromatography was conducted to determine the methanol existence as well as the purity of the glycerol. In this study, Figs. 5 and 6 show the results of GC analysis for both methods of purification. The standard retention time for glycerol and methanol are at minutes 32.75 and 2.57, respectively.

**Figure 5.** Result of GC analysis for CGA samples (a) before purification (b) after purification with direct method and (c) after purification with multistep method.
Figure 6. Result of GC analysis for CGB samples (a) before purification with direct method and (b) after purification with direct method.

When referred to Figs. 5 and 6, it is found that methanol peaks at minute 2.57 were not found in CGA and CGB samples after purification using both methods. This result indicates that methanol was absent in the samples thus it confirms that the methanol has been removed in the purification processes by both direct and multistep methods.

3.5 HPLC analysis

Other than FTIR and GC analysis, HPLC analysis was also conducted in order to quantify the CGA and CGB samples after purified by both methods. Figs. 7 and 8 compare the results of HPLC analysis of CGA and CGB samples.

As Figure 7 shows, there is a significant retention time of glycerol at minute 2.79 with the 100% relative area. The results of CGA sample before purification (Figure 7 (b)) found that the retention time of glycerol at 2.80 min with relative area of 9.06%. Glycerol peak was less tangible as the free fatty acids peak (at retention time of 5.79) has contributed up to 72.82% of relative area. When purified using the direct method, the relative area was reduced to 13.63%. There was significant difference when the relative area of glycerol increase to 100% for CGA samples when purified using the multistep method. Figure 8 shows the comparison of CGB samples when purified with direct and multistep method.

According to Figure 8, the results of HPLC analysis have shown that glycerol peaks were identified at minute 2.84 with relative areas of 96.50% for CGB sample before purification and it increases to 99.58% for CGB sample after purification with direct method. This result indicates that a higher purity of glycerol can be obtained by using the direct method. In summary, the involvement of several separation stages such as neutralization and filtration have contributed to a more quality product if compared with direct method. However, for CGB samples, the purification of crude glycerol using direct method was sufficient to achieve a good purity of glycerol.
Figure 7. Result of HPLC analysis for (a) pure glycerol (b) CGA samples before purification (c) CGA samples after purification with direct method and (d) CGA samples after purification with multistep method.

Figure 8. Result of HPLC analysis (a) pure glycerol (a) CGB samples before purification with direct method and (b) CGB samples after purification with direct method.
4. Conclusion

This study aimed to purify the glycerol from biodiesel production through direct and multistep method. Two samples, CGA and CGB were purified using both methods. This study has found that generally, the absence of glycerol and methanol after purification has been determined through GC analysis, FTIR analysis and HPLC analysis. This study has identified that purification method of CGA samples was best conducted using multistep method. While the direct purification method has found to be an effective way of purifying CGB samples. A further study could assess the effects of converting the pH value of crude glycerol before the purification process is being conducted.

Acknowledgement

The authors acknowledge the financial support from the RAGS grant vot no. R071 of Office for Research, Innovation, Commercialization, and Consultancy Management (ORICC).

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