

The effect of concentration and acid types on the acidification process for improving the glycerol concentration and its application as a bio additive

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Abstract. The rise of biodiesel production resulted in an increase in the formation of glycerol as a by-product. It takes some effort to purified the crude glycerol and convert it into more valuable product. One of these is by converting glycerol into triacetin which can be used as a bio additive in fuel through the acetylation process. This study aims to determine the effect of concentration and type of acid used in the glycerol purification. The purification were done by acidification, adsorption, filtration, distillation and evaporation. The acidification processes used H_3PO_4 , H_2SO_4 , HCl with percentage of 0.5%, 1%, 2.5%, 5%, 7.5%, 10%. The purified glycerol was analyzed to determine glycerol content, water content, density and viscosity and converted through acetylation reaction using $\text{Ni}/\text{Zeolite}$ as a catalyst. The reaction products were analyzed by NaOH titration to determine the unreacted acetic acid which is converted into conversion of reaction. It can be concluded that the highest glycerol concentration was achieved in the addition 5% of H_3PO_4 with glycerol content of 79.59% and glycerol conversion in acetylation reaction of 82.39%. And its application as a bio additive can increase the Octane Number of commercial gasoline by 6.5%.

1. Introduction

The usage of biodiesel in Indonesian is now being actively promoted by the government. This is supported by the B20 policy where fuel mix consisted of 80% diesel fuel and 20% biodiesel is applied to all diesel fuel users, both subsidized (public service obligation, PSO) and non-PSO [1]. Therefore, biodiesel production capacity must be increased to achieve these targets. Based on BPDP data from 2015 to 2018, the amount of biodiesel distributed related to B20 policy had reached 9.92 million kiloliters (kL) [1]. In the future, the government will also plan to actualize B100 policy where fuel will contain 100% biodiesel so that the future biodiesel production will also be increased.

The increase in biodiesel production could not be separated from crude glycerol as by-product. Crude glycerol contains many impurities, such as fat compounds, soap, KOH , and others, so it needs to be purified first before being used. Purified glycerol is an important chemical compound in many industries. Glycerol can be utilized as sweetener in food industries, encapsulation material for capsules in pharmaceutical industries, and also can be converted into triacetin by acetylation reaction. Triacetin can be used as aromatic compound in candies, solvent in perfume, and can be utilized as additive compounds in fuel to reduce knocking on car engines [2]. Crude glycerol refining process has been carried out by several researches.



According to a research done by Nanda MR, *et al.* by using acidification with a variation of acid (phosphoric acid, hydrochloric acid, and sulfuric acid) followed by bleaching using active carbon can increase glycerol content to 84% for phosphoric acid and for sulfuric acid, the glycerol content can be increased to 82% [3]. Researcher Nanda *et al.* purified crude glycerol using phosphoric acid as much as 5% v/v of glycerol in the acidification process and reacted at 75-80 °C for 4 hours, active carbon used as adsorbent can increase the glycerol content by 10% [3]. Researcher Aziz *et al.* purified crude glycerol by using phosphoric acid in the acidification process until pH 6 was obtained, the adsorption process used 5% of active carbon and 24 hours of adsorption time, the amount of glycerol obtained increased by 44.2% [4]. Crude glycerol research was done by Paramarta by using phosphoric acid in the acidification process which was added until pH 2.5 was obtained [5]. The adsorption process was carried out using 5% of active carbon which could increase the glycerol content by 6%. In this research, glycerol obtained from the purification process was converted by acetylation process with only 70% of glycerol converted. Due to the glycerol content obtained from this purification process is still relatively low (61%).

Based on the description above, it can be seen that most researchers only focus on the refining process, and do not utilize it for the next stage of the process. This research was conducted with variations of the acid type and the percentage of acid volume in the process of acidification of raw glycerol and synthesizing the results of purification through the acetylation process into useful products such as bio-additives for fuel. With this variation, it is expected resulted in a higher purity of glycerol. And if it applied in the acetylation process will result in maximum conversion.

2. Materials and methods

The method used in this research is a laboratory-scale experiment. The crude glycerol purifying process is carried out by distillation, acidification, filtration, evaporation, and adsorption using active carbon. The variable of reaction are the types and percentage of acid added to crude glycerol. The purified product was analyzed using GC to determine the concentration of glycerol, water content analysis, density, and viscosity. The best result from the purification process was used as the raw material in acetylation/esterification reaction using Ni/Zelite catalyst. The products of glycerol esterification were analyzed using alkalimetric titration to determine the acetic acid conversion.

The stages of the experiment consisted of:

- Crude glycerol purification
- Purified glycerol analysis
- Catalyst preparation
- Esterification reaction
- Conversion reaction analysis

2.1. Materials

Materials used in this research included: crude glycerol from PT. Wilmar Gresik, H_3PO_4 , H_2SO_4 , HCl, aquadest, active carbon, filtration paper, Ni/Zelite catalyst, acetic acid, Methyl Orange indicator and solution of 0.1 N NaOH.

2.2. Methods

2.2.1. Crude glycerol purification. Crude glycerol purification process was carried out to remove water, methanol, and acid residues in biodiesel making process. Acid solution H_3PO_4 , H_2SO_4 , and HCl (according to variables) was added into 100 ml crude glycerol as much as 0.5%, 1%, 2.5%, 5%, 7.5%, and 10% v/v. The solution were set for 24 hours until it formed three phases. The bottom layer (glycerol and salt) was separated from the top layer. Then adsorbed using active carbon methanol in a ratio of 2:3 for 30 minutes. Then filtrated using vacuum filter. The glycerol and methanol mixture was distilled at 65 °C to separate methanol and followed by evaporation at 110 °C for 2 hours to remove the moisture.

2.2.2. Acetylation process. Acetylation process aims to convert glycerol into ester compound using acetic acid. Acetylation or esterification process began with weighing 250 ml glycerol in a three neck flask, then heated at 100 °C. Acetic acid was added with the ratio of 1:7 glycerol reactant to acetic acid. Then Ni/Zelite catalyst in an amount of 5% of the acetic acid added was added. A series of esterification equipment was filled with nitrogen for 10 seconds before tightly sealed. Furthermore, it was heated in a water bath at 100 °C for 2 hours while stirred with a motor stirrer. Then, the mixture was put into a separator funnel until two layers were formed (ester and water layer).

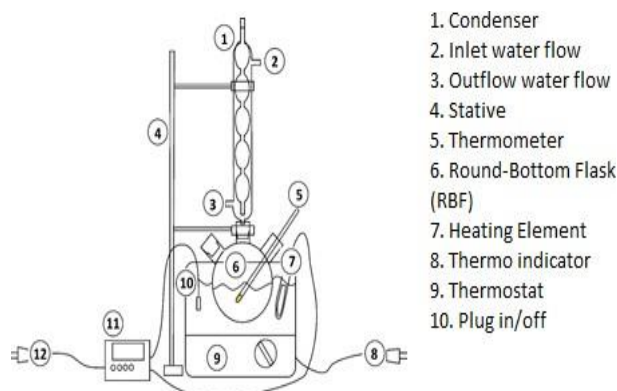


Figure 1. The schema of reaction equipment.

3. Discussion

3.1. Glycerol content

In acidification process, the amount of acid added into the crude glycerol effected to the purification process. The impurities as a soap and catalyst residue in crude glycerol will not be degraded completely into FFA or salt, if the acid concentration added is not suitable compared to the amount of impurities. If the concentration of acid added is too high, the degradation process of soap into FFA would not be effectively [3]. This is due to excessive amount of acid added will increase the solubility of salt catalyst in glycerol, resulted in decreasing glycerol content [2]. The statement is in accordance with the experiment's result which is shown in figure 2.

It can be seen from Figure 2 that the highest purified glycerol content obtained was by adding 5% v/v phosphoric acid (H_3PO_4) with glycerol content of 79.59%. Whereas for H_2SO_4 and HCl , the highest increase in glycerol content was obtained by adding 7.5% v/v with glycerol content of 77.712% for H_2SO_4 and 75.87% for HCl . In acidification process, the type of acid added into crude glycerol will affect the glycerol produced. According to Figure 2, it can be seen that purification will run effectively when acidification process is carried out using phosphoric acid. This is due to the triprotic property of phosphoric acid with higher fat binding ability while sulfuric acid is diprotic and tends to act as a strong dehydrator and monoprotic hydrochloric acid [6,7].

It can be explained that the usage of H_3PO_4 can degrade soap into more fatty acids compared to H_2SO_4 and will produce more precipitate. This is due to H_3PO_4 as a strong acid oxidizing agent where the strength of the acid is weaker compared to H_2SO_4 hence more suitable to degrade soap into fatty acid. Whereas H_2SO_4 , which is also a strong acid oxidizing agent, has a higher acid strength so when it is used only to degrade soap, it will be less suitable because the sulfuric acid will change its function.

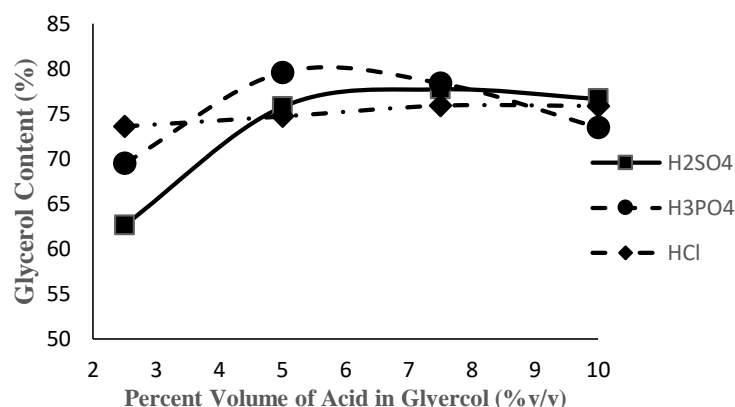
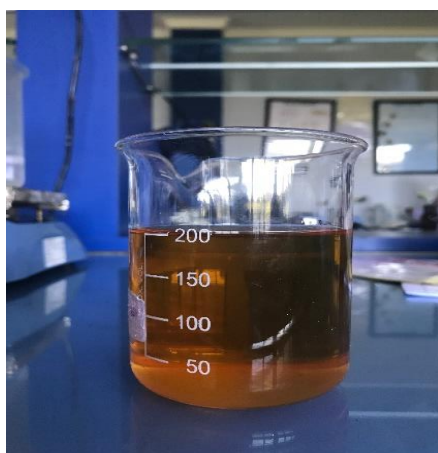
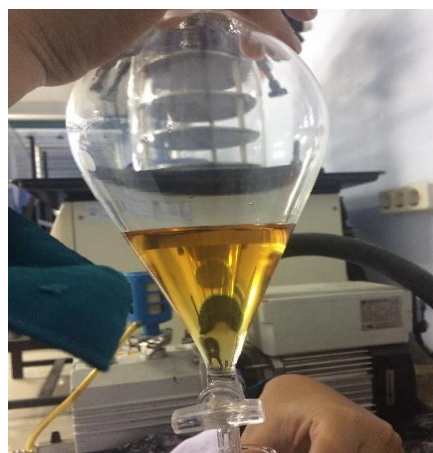


Figure 2. Effect of types and percentage of acid to glycerol content.

Based on the content HSAB (Hard Soft Acid Base), strong acid will prefer strong base and weak acid will prefer weak base [8,9]. Sulfuric acid and phosphoric acid are both strong acids, where sulfuric acid is stronger than phosphoric acid. This can be seen in periodic table where acidic property is stronger on the right and acidic property is weaker downward [10,11].



(a)



(b)

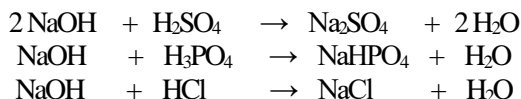
Figure 3. (a) Crude Glycerol (b) Crude Glycerol adding by H₃PO₄.

Sulfuric acid contains S element which is located on the right side of P element from phosphoric acid so sulfuric acid has stronger acidic property than phosphoric acid. Meanwhile in bases, K element from KOH is strong base. K element is located on third period and despite K being a strong base, the level has decreased because in periodic system, basic property decrease downward. K is easier to react with phosphoric acid because it has fulfilled the HSAB concept [9,12].

3.2. Water content

The addition of a variation of acid and volume percentage in crude glycerol affects the water content in the glycerol produced. The more acid added, the water content in glycerol will also increase. As shown in Figure 4, water content increases due to the reaction between the acid added with the remaining catalyst in crude glycerol which produces salt and water. Based on Figure 4 it can be seen that sulfuric acid tends to produce more water content than H₃PO₄. This is due to sulfuric acid has dehydration properties, other than oxidizing properties, hence able to produce a great amount of water [11,13]. The

use of HCl in acidification in large quantity causes a great amount of water, more than those that used H_2SO_4 and H_3PO_4 because the concentration of HCl used is 37% which suggests a greater water content. The reaction is as follows:



Other than neutralization reaction which produces water, the addition of HCl causes glycerol to have more water content [14].

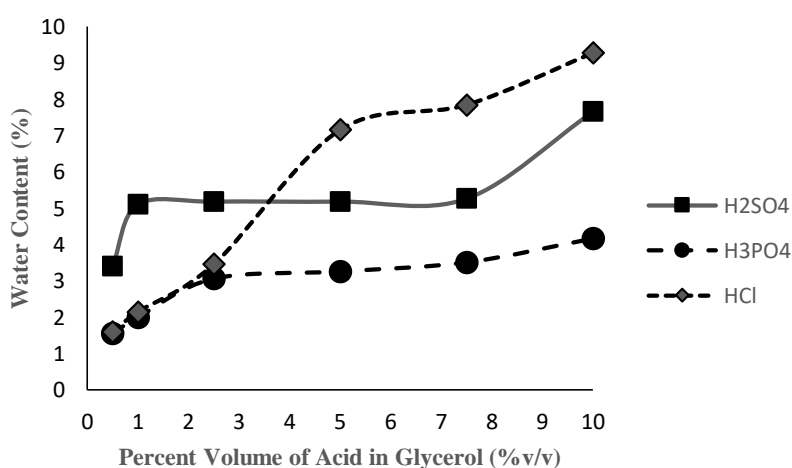


Figure 4. Effect of types and percentage of acid to water content.

From figure 4 shown that glycerol has high water content in average. This can be caused by the lack of evaporation. However, if the evaporation process takes too long with high temperature, it can cause the degradation of the existing glycerol content [15].

3.3. Density

From figure 5, it can be seen that the variation of types and volume percentage of acid added to crude glycerol in acidification affects the density of glycerol. Based on Figure 5, it can be seen that increasing the concentration and percent volume of H_2SO_4 used in the purification process will increase the density of purified glycerol compare to the use of HCl and H_3PO_4 .



(a)



(b)

Figure 5. (a) Distillation process (b) Filtration.

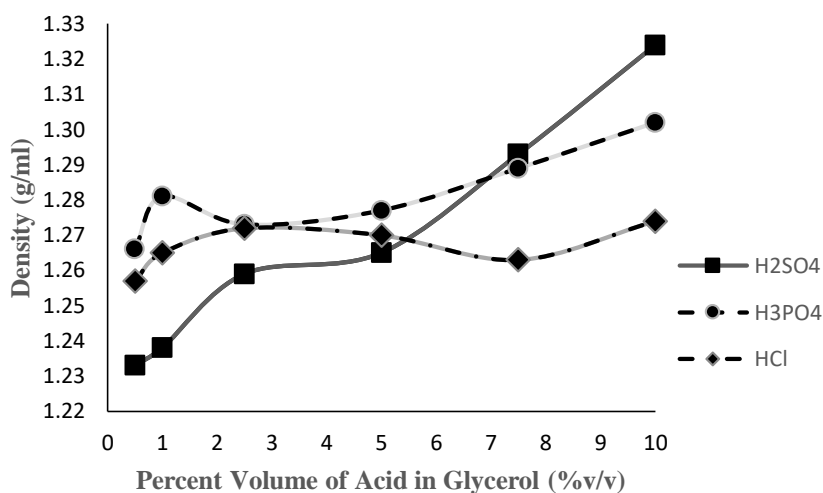


Figure 6. Effect of types and percentage of acid to glycerol density.

This is due to the sulfate salts produced from the neutralization process have a greater density than chloride and phosphate salts [16,17].

3.4. Conversion reaction and octane number analysis

Based on research that has been carried out the conversion of glycerol in the acetylation reaction was 82.39% of the purification results using H₃PO₄ 5% (v/v), 79.5% with H₂SO₄ 7.5% (v/v) and 77.78% with 7.5% (v/v) HCl. From the conversion results it can be seen that the highest glycerol conversion in acetylation reaction produced by glycerol purification using acid type of H₃PO₄ with concentration of 5% (v/v). This is comparable to the level of glycerol which is also the highest among other variables. Based on this data it can be seen that the greater the glycerol content, the greater the glycerol conversion in the acetylation reaction [18-20].

The results of this acetylation reaction when applied as bio-additives by adding into commercial gasoline will increase the octane number from 88 to 93.7 (6.5%).

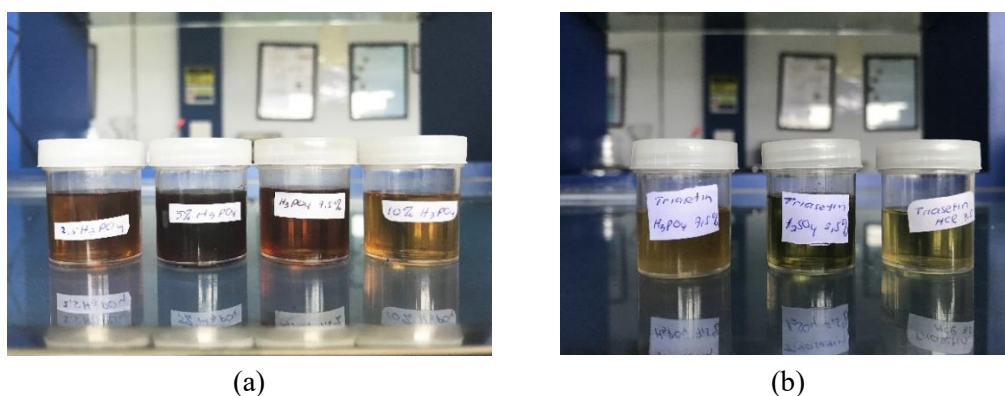


Figure 7. Purified Glycerol (b) Product of acetylation reaction.

4. Conclusion

From the experiments that have been carried out can be concluded that:

- Phosphoric acid (H₃PO₄) is the best type of acid which use in glycerol purification process compared to sulfuric acid (H₂SO₄) and hydrochloride acid (HCl). Glycerol content from the purification process using H₃PO₄ was 79.64%, H₂SO₄ was 77.712%, and HCl was 75.87%.

- The highest glycerol content can be achieved by adding 5% of H_3PO_4 , 7.5% of H_2SO_4 and HCl.
- Glycerol which has highest purity obtained from adding of 5% of H_3PO_4 if converted by acetylation process would resulted in conversion of 82.39% and increase the Octane Number of commercial gasoline from 88 up to 93.7 (6.5%).

Acknowledgments

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References

- [1] BPDP 2018 Peraturan Presiden No.66 Tahun 2018 *Perubahan Kedua atas Perpres Dana Sawit*
- [2] Nuryoto, Sulistyo H, Rahayu S S and Sutijan 2010 Kinetika Reaksi Esterifikasi Gliserol dengan Asam Asetat menggunakan katalisator Indion 225 Na *J.Rek.Pros* **5**(2) 35-39
- [3] Aziz I, Sulistina R C and Adhani L 2018 Purification of Crude Glycerol from Acidification Using Tea Waste *In IOP Conference Series: Earth and Environmental Science* **175**(1) 012010
- [4] Aziz I, Las T and Shabrina A 2014 Pemurnian crude glycerol dengan cara pengasaman dan adsorpsi menggunakan zeolit alam Lampung *CHEMISTRY PROGRESS* **7**(2)
- [5] Paramarta S and Wahyudianto 2018 *Pemanfaatan Gliserol Hasil Samping Pembuatan Biodiesel Menjadi Triacetin Melalui Proses Esterifikasi dengan Katalis Ni/Zeolit* (Politeknik Negeri Malang: Malang)
- [6] Nanda M R, Yuan Z, Qin W, Poirier M A and Chunbo X 2014 Purification of Crude Glycerol using Acidification: Effects of Acid Types and Product Characterization *Autin Chem.Eng.* **1**(1) 1004
- [7] Anzar E, Yusi M S and Bow Y 2018 Purification of Crude Glycerol from Biodiesel By-product by Adsorption using Bentonite *IJFAC (Indonesian Journal of Fundamental and Applied Chemistry)* **3**(3) 83-88
- [8] Kasim R 2012 *Esterifikasi Asam Lemak Bebas Pada Campuran Asam Oleat Dan Minyak Sawit Murni Menggunakan Microwave* (Universitas Negeri Gorontalo: Gorontalo)
- [9] Nasir N F, Mirus M F and Ismail M 2017 Purification of crude glycerol from transesterification reaction of palm oil using direct method and multistep method *In IOP Conference Series: Materials Science and Engineering* **243** (1) 012015
- [10] Rahmi U 2006 Pengaruh Jenis Asam dan pH Pada Pemurnian Residu Gliserol dari Hasil Samping Produksi Biodiesel (Universitas Sumatera Utara)
- [11] Khayoon M S and Hameed B H 2011 Acetylation of glycerol to biofuel additives over sulfated activated carbon catalyst *Bioresource technology* **102**(19) 9229-9235
- [12] Cahyono R, Mufrodi Z, Hidayat A and Budiman A 2016 Acetylation of Glycerol for Triacetin Production Using Zr-natural Zeolite Catalyst *JEAS* **11**(8) 5194-5197
- [13] Rastegari H and Ghaziaskar H S 2015 From glycerol as the by-product of biodiesel production to value-added monoacetin by continuous and selective esterification in acetic acid *Journal of Industrial and Engineering Chemistry* **21** 856-861
- [14] Rizki J, Zuchra H and Hari R 2015 *Pemanfaatan Gliserol dari Produk Samping Biodiesel Menjadi Triacetin Melalui Proses Esterifikasi Menggunakan Katalis Zeolit Alam* JOM FT Universitas Riau **2** 1
- [15] Kadarwati S, Rahmawati F, Rahayu P E and Supardi K I 2013 Kinetics and mechanism of ni/zeolite-catalyzed hydrocracking of palm oil into bio-fuel *Indonesian Journal of Chemistry* **13**(1) 77-85
- [16] Pal P and Chaurasia S P 2016 Characterization of Crude and Purified Glycerol from Biodiesel Production and Purification Techniques *In V International Symposium on “Fusion of Science and Technology* 18-22
- [17] Chang R 2004 *Kimia Dasar 3* (Erlangga Jakarta)

- [18] Levenspiel O 1999 *Chemical Reaction Engineering 3th edition* (Wiley and Sons New York)
- [19] Rao P V and Rao B V A 2011 Effect of adding Triacetin additive with Coconut oil methyl ester (COME) in performance and emission characteristics of DI diesel engine *Int. J. of Thermal Tech* **1** 100-106
- [20] Zhou L, Al-Zaini E, Adesina A and Adesoji 2013 Catalytic Characteristics and Parameters Optimization of the Glycerol Acetylation over Solid Acid Catalysts Fuel **103** 617-625