Manufacture Glycerol Byproducts From Waste Cooking Oil Through The Transesterification Process In Various Brands Of Oil In The Indonesian Market

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Abstract.

Waste cooking oil is oil that has been used repeatedly, up to 2-4 times in the frying pan. The large number of Indonesian people who often consume waste cooking oil due to economic factors. The use of oil repeatedly reduces the nutritional value and affects the quality and value of fried food ingredients. However, this waste is very useful, it can be processed into glycerol which is useful in the cosmetic industry. The objective of this research is to prove that the glycerol byproduct of waste cooking oil with various oil brands in the Indonesian market has similar functional groups to commercial glycerol. The research was carried out experimentally by making glycerol using waste cooking oil. Glycerol is made using a transesterification process. Transesterification (alcoholic reaction) is a vegetable fat or oil that is reacted with alcohol to produce an ester and glycerol as a byproduct with the help of an alkaline catalyst. Evaluation of glycerol includes organoleptic, specific gravity, viscosity, glycerol content, ash content, moisture content, and sugar content. The results of the study using FTIR showed that the commercial glycerol wave number was 3291cm-1, brand X at 3291cm-1, and brand Y at 3267cm-1, which indicated the presence of an OH (hydroxyl) group. Commercial glycerol absorption bands at 2931 and 2877 cm-1, brand X at 2933 and 2879 cm-1, and brand Y at 2931 and 2877cm-1, indicating the presence of aliphatic (alkyl) CH groups. Based on the research results, it can be concluded that the glycerol byproduct of waste cooking oil using the Indonesian market brands X and Y has similar functional groups to commercial glycerol. However, glycerol is the byproduct of waste cooking oil brand X which has the most similarities with commercial glycerol.

Keyword: *waste cooking oil, glycerol, transesterification, oil Indonesian market*

I. INTRODUCTION

Cooking oil used in industries and households will turn into waste cooking oil in high amounts and there is a danger of consuming waste cooking oil, so it is necessary to make efforts to make use of the waste cooking oil so that it is not wasted and pollutes the environment. Utilization of waste cooking oil can be done by refining it so that it can be reused and used as raw material for oil-based products such as soap, shampoo and diesel fuel [1].

Waste cooking oil can be processed into anti-aging cosmetic products, given the increasing exposure to free radicals, one of which is caused by food sources, environmental contaminants, etc., which can cause premature aging [2]. Waste cooking oil is oil that has been used repeatedly for up to 2-4 frying times [3]. Waste cooking oil that comes from the leftover cooking oil for foodstuffs has always been considered as waste by some people. It can produce a byproduct in the form of glycerol which is commonly known as crude glycerol. Glycerol is very economical and its use is very wide. Glycerol is used in the manufacture of medicines, cosmetics, toothpaste, urethane foam, synthetic resins and others [4].

Glycerol preparation can be done by transesterification reaction. Transesterification (alcoholic reaction) is a vegetable fat or oil that is reacted with alcohol to produce an ester and glycerol as a byproduct with the help of an alkaline catalyst. Catalysts are used to increase the reaction rate and the amount of the product [5]. This glycerol separation process produces biodiesel and crude glycerol. Glycerol production by transesterification is carried out by reacting waste cooking oil and methanol using a KOH catalyst. The glycerol here is a byproduct [6].

II. METHODS

Waste cooking oil is obtained from the rest of the fish frying process 2 times using cooking oil brands X and Y in the Indonesian market.

Manufacture glycerol from waste cooking oil

Manufacture *crude glyserol*

Waste cooking oil is filtered first and 500 g is taken then heated to a temperature of 110 ° C. 5 g KOH dissolved in 250 ml methanol. Waste cooking oil is heated to a temperature of 60 ° C, KOH methanol mixture is added and stirred for 1 hour, after which it is left to stand for about 8 hours so that the biodiesel and crude glycerol separate completely and crude glycerol is separated from biodiesel [7].

Refining crude glyserol

The crude Glyserol obtained was 112.22 g, then 3 ml of phosphoric acid (H_3PO_4) was added until the desired pH was 6. PH measurements are carried out with a pH meter, after forming three layers. The top layer is free fatty acids, the middle layer is glycerol, and the bottom layer is inorganic salts [8]. The glycerol layer was separated from the other layers, then analyzed for glycerol content. Add 70 ml of water to the crude glyserol and 4% activated carbon. The activated carbon used before is washed first. The mixture was stirred for 30 minutes and left for 24 hours, after which it was filtered, then evaporated with a rotary evaporator to remove the remaining methanol and its water content. The sample was put into a rotary evaporator, where the conditions were previously set at vacuum pressure and a temperature of 60° C. The bottom product which is glycerol was analyzed by Fourier Transform Infrared Spectroscopy (FTIR).

Evaluation of glycerol by product of waste cooking oil

Glycerol organoleptic test

Visual observations of odor, color, shape or consistency, and the presence or absence of phase separation in the manufacture of glycerol [9]. Glycerol was put into the vial, stored at room temperature and stability parameters were measured and evaluated.

Determination of specific gravity of glycerol

Determination of specific gravity is carried out at the beginning after the preparation is made by measuring 1 time. Specific gravity is measured using a pycnometer at room temperature. Clean and dry pycnometer is weighed (A g). Then it was filled with aquadest until it was full and weighed (A1 g). The aquadest is removed from the pycnometer and the pycnometer is cleaned. The preparation is filled in the pycnometer until it is full and weighed (A2 g) [10].

2.3.3 Determination of glycerol viscosity

Viscosity measurements were carried out by inserting glycerol into a 100 ml beaker glass and selecting the appropriate spindle number using an NDG 8-s viscometer [11].

Determination of glycerol content

Crude glycerol as much as 0.1 g dissolved in 10 mL of distilled water then added with 1 drop of bromtimol blue indicator. The solution was then acidified with 0.2 N H_2SO_4 until a yellow-green color was formed. The solution was carefully neutralized with 0.05 N NaOH until a blue color was formed. After that, the solution was added with 10 ml of $NaIO_4$ and then stirred slowly. The solution was then closed and allowed to stand in a dark room at room temperature for 30 minutes. The solution is then added with 2 mL of ethylene glycol and then closed and allowed to stand in a dark room at room temperature for 20 minutes. Dilute the solution with 60 ml of aquadest then add 3 drops of bromtimol blue indicator. The solution resulting from the mixture is slowly aspirated with 0.5 N NaOH until a blue color is formed. This process is also carried out for blanks or addition of reagents without samples [12].

$$\mathbf{KG}\ (\%) = \frac{(\mathbf{T_1} - \mathbf{T_2}) \times \mathbf{N} \times \mathbf{9{,}209}}{\mathbf{W}}$$

Explanation:

KG = Glycerol content (%)

T1 = Volume of NaOH for sample titration (mL)

T2 = Volume of NaOH for blank titration (mL)

N = Normality of NaOH (N)

W = Sample weight (g)

9,209 = Glycerol factor

Determination of sugar glycerol content

The reagent used is Maillard's reagent which is made by means of 4 g urea ($CO(NH_2)_2$) and 0.2 grams of $SnCl_2.2H_2O$ heated with 10 mL H_2SO_4 40%. 4 drops of glycerol were put into the reagent tube. Add 1 mL of Maillard reagent; 1 mL of distilled water, then stirred. Heat the tube in a water bath for 15 minutes at 60 ºC. The brown color that appears indicates the presence of sugar in glycerol [12].

Determination of glycerol ash content

A sample of 5 g was weighed and put into a porcelain dish that had been dried and the weight was known. Then the plates and samples are burned with an electric heating, until the sample does not smoke and is ignited in an ashing furnace at a temperature of 550 ° C until a light gray ash or constant weight is produced. Then again cooled in a desiccator and weighed immediately after reaching room temperature [13].

Ash content (%) = $\frac{W1}{W2} \times 100$ (%)

Explanation :

W1= Mass of Ash (g)

W2= Mass of sample (g)

Determination of glycerol water content

A sample of 5 g was weighed and put in a plate that had been dried and the weight was known. Then the samples and plates were dried in an oven at 105 ° C for 3 hours. The plates were cooled and weighed, then dried again until a fixed weight was obtained [13].

$$\mathbf{KA} = \frac{b-(c-a)}{b} \times \mathbf{100\%}$$

Explanation:

KA = Moisture Content (%)

a = Weight of the cup (grams)

b = sample weight (grams)

c = weight of cup + sample (after drying)

III. RESULT AND DISCUSSION

Evaluation of glycerol by product of waste cooking oil

Glycerol organoleptics

The evaluation of the organoleptic observation data of the preparations was carried out for 12 weeks of storage with observations every 1 week, the glycerol was stored at room temperature and observed changes in color, odor and appearance. Based on research, the color of glycerol as a byproduct of waste cooking oil brands X and Y has a clear white color, with a distinctive smell of glycerol. The results obtained are in accordance with commercial glycerol, which is a clear white liquid with a distinctive smell of glycerol.

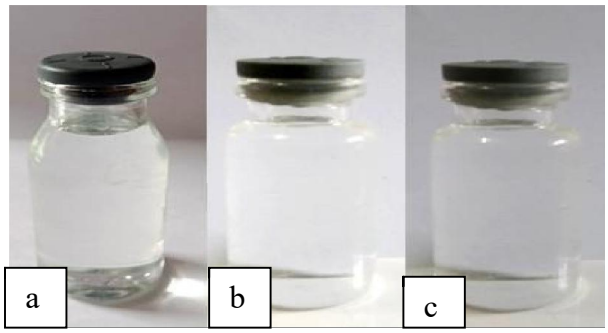

Fig 3.1 a). Commercial glycerol, b). Glycerol byproduct of waste cooking oil brand X, c). Glycerol is a byproduct of waste cooking oil from the Y brand

Specific gravity of glycerol

Determination of the specific gravity of the preparation is carried out at the beginning after the preparation is made by measuring 1 time. Specific gravity is measured using a pycnometer at room temperature. The density of glycerol as a byproduct of waste cooking oil from brand X was 1.25g / ml, while brand Y was 1.19g / ml. So that brand X is closer to the requirements of commercial glycerol with a specific gravity of 1.26g / ml.

Glycerol viscosity

Determination of the viscosity of the preparation was carried out using a viscometer NDG 8-s with spindle number 2 with a speed of 50 rpm and was carried out once. Based on the research, the glycerol byproducts of waste cooking oil showed that the viscosity of the glycerol byproducts of waste cooking oil with the brand X 1407 mPa.s, while the Y brand results were 1405 mPa.s. So that brand X is closer to the requirements of commercial glycerol with a viscosity of 1410 mPa.s

Glycerol content

Based on the research, the glycerol content of the waste cooking oil byproduct of the X brand was 84%, while the Y brand was 72%, so that the X brand met the requirements for the glycerol content of> 80%.

Sugar content of glycerol

In testing the glycerol sugar content qualitatively, if the brown color appears, it indicates the presence of sugar in glycerol. Found a brown color indicates the presence of sugar in glycerol.

3.1.6 Glycerol ash content

Based on the research, it was found that the glycerol ash content from the side product of waste cooking oil brand X was 7.3%, while the Y brand was 8.5%, so that it fulfilled the glycerol ash content requirement of <10%.

3.1.7 Glycerol water content

Based on the research, it was found that the water content of glycerol from the side product of waste cooking oil from brand X was 9.57%, while brand Y got 75%, so that brand X met the requirements for water content of glycerol> 80%

Results of glycerol functional group analysis using FTIR

The results of making crude glycerol obtained crude glycerol of 112.22g, and the results of the purification after the rotary evaporator were 25 ml and the glycerol was FTIR. The results of the analysis of commercial glycerol and glycerol from waste cooking oil products of the X and Y brands using FTIR can be seen in Figure 3.2, Figure 3.3 and Figure 3.4.

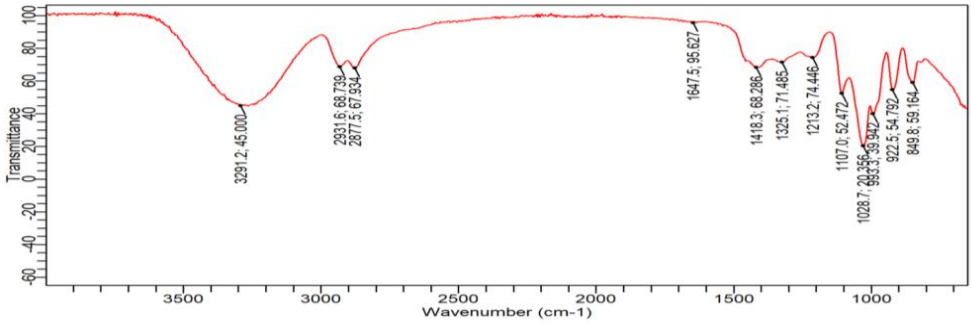

Fig. 3.2 FTIR results of commercial glycerol

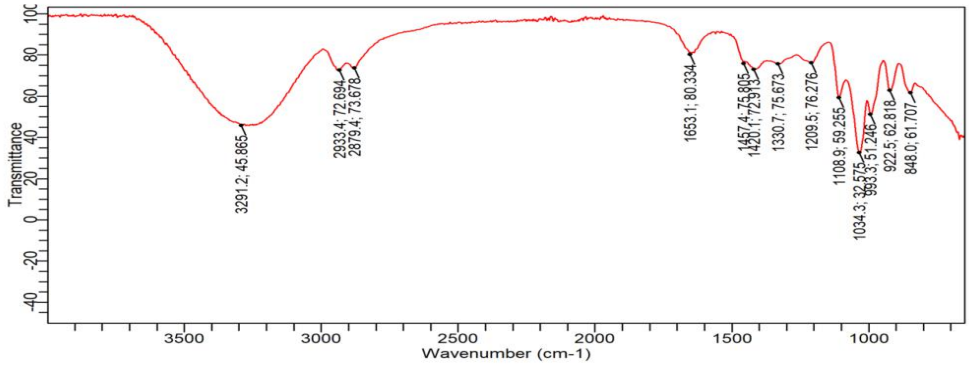

Fig 3.3 FTIR results of waste cooking oil glycerol with the X brand

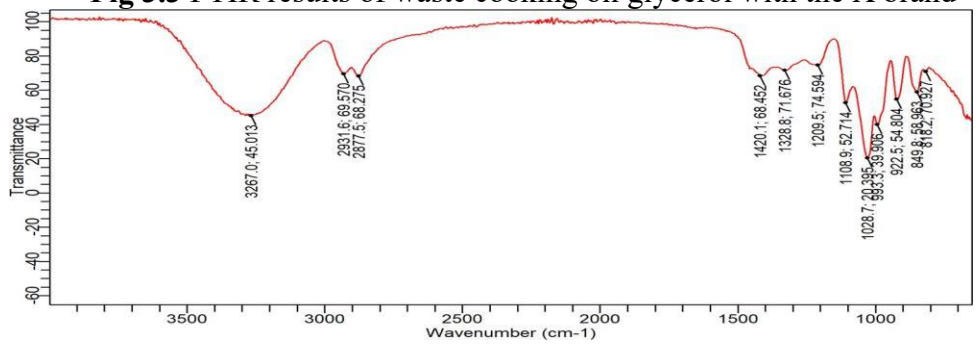

Fig 3.4 FTIR results of waste cooking oil glycerol of the Y brand

Figure 3.3 and Figure 3.4 show that there is a change in waste cooking oil to glycerol. Glycerol has the molecular formula $C_3H_8O_3$ with the chemical name 1,2,3-Propanetriol. The results of the analysis of commercial glycerol samples showed a wide band at a wavelength of 3291cm-1 which indicated the presence of an OH (hydroxyl) group. The results of the analysis of the glycerol sample resulting from the waste cooking oil byproduct brand X showed a wide band at a wavelength of 3291cm-1 which indicated the presence of an OH (hydroxyl) group, while the results of the analysis of the glycerol byproducts of waste cooking oil brand Y showed a wider band at wave 3267cm-1 which indicates the presence of an OH (hydroxyl) group. Commercial glycerol absorption bands at 2931 and 2877 cm-1 indicate the presence of aliphatic (alkyl) CH groups. The results of the analysis of the sample of glycerol as a byproduct of waste cooking oil brand X showed that the absorption band at 2933 and 2879 cm-1 showed the presence of an aliphatic (alkyl) CH group, while the results of the analysis of the glycerol byproduct of waste cooking oil brand Y showed an absorption band at 2931 and 2877cm-1 which indicates the presence of an aliphatic (alkyl) CH group.

IV. CONCLUSION

Based on research on the IR spectrum of glycerol as a byproduct of waste cooking oil brands X and Y compared to commercial glycerol, there are OH hydroxyl groups, aliphatic CH, which indicate the presence of glycerol. However, the glycerol as a byproduct of waste cooking oil brand X is the closest to commercial glycerol both in terms of functional group similarities, in the glycerol evaluation tests that have been carried out include organoleptic, specific gravity, viscosity, glycerol content, ash content, moisture content, and content. sugar. So it can be concluded that the glycerol as a byproduct of waste cooking oil using oil in the Indonesian market, brands X and Y, has similar functional groups to commercial glycerol. It was found that the glycerol as a byproduct of waste cooking oil uses X brand oil which is the most similar to commercial glycerol.

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REFERENCES

[1] Harianja, E. (2010). Pra Rancangan Pabrik Biodiesel dari Minyak Jelantah dengan Kapasitas 15.000 ton/tahun. *Skripsi*. Fakultas Teknik. Universitas Sumatera Utara. Medan.

[2] Winarsi, H. (2007). Antioksidan Alami dan Radikal Bebas. Penerbit Kanisius. Yogyakarta.

[3] Dalimunthe, N. A. (2009). Pemanfaatan Minyak Goreng Bekas Menjadi Sabun Mandi Padat. Tesis. Medan : Universitas Sumatera Utara.

[4] Appleby, D.B, (2005). *Gliserol on The Biodiesel Handbook*. AOCS Press.

[5] Listiadi, A. P., dan Putra. (2013). Intensifikasi Biodiesel dari Minyak Jelantah dengan Metode Transesterifikasi dan Pemurnian Dry Washing. *Skripsi*. Universitas Sultan Agung Tirtayasa. Banten.

[6] Aziz, I., Siti, N., dan Juwita, S. (2013). Pemurnian Gliserol Dari Hasil Samping Pembuatan Biodiesel Menggunakan Bahan Baku Minyak Goreng Bekas. Program Studi Kimia . *Jurnal Valensi*. Fakultas Sains dan Teknologi. UIN Syarif Hidayatullah Jakarta.

[7] Aziz, I. (2008). Kinetika Reaksi Transesterifikasi Minyak Goreng Bekas. Edisi I. ***Jurnal Valensi.*** Prodi Kimia FST UIN Syarif Hidayatullah Jakarta.

[8] Manosak R, Limpattayanate S, and Hunsom M. (2010). Sequential-refining of crude glycerol derived from waste used-oil methyl ester plant via a combined process of chemical and adsorption. Fuel Process Technology. 104: 92-99.

[9] Ditjen POM RI. (1995). *Farmakope Indonesia.* Edisi IV. Jakarta: Departemen Kesehatan Republik Indonesia.

[10] Hakim, N.A., Arianto, A., dan Bangun, H. (2018). Formulasi dan Evaluasi Nanoemulsi dari Extra Virgin Olive Oil sebagai Anti-aging. *TM Conference Series* (2) : 397-403.

[11] Kaplan, A.B. H., Cetin, M., Orgul, D., Hacimufnewlu, A., dan Hekimoglu, S. (2019). Formulation and In Vitro Evaluation of Topical Nanoemulsion based Gels Containing Daidzein. ***Journal of Drug Delivery Science and Technology*** (19) : 30263.

[12] SNI (1995). Standarisasi Nasional Indonesia. SNI 06-1564-1995: Gliserol Kasar. Dewan Standarisasi Nasional. Jakarta.

[13] AOAC. (1995). Meth Official Methods of Analysis of The Association of Analytical Chemists. Washington D.C.