

Production and Physicochemical Analysis of Glycerol Produced from the Transesterification Reaction of Locally Processed Fatty Acids

ABSTRACT

The study uses the transesterification reaction method to extract glycerol from three locally processed fatty acids namely; palm oil, palm kernel and shea butter. The glycerols extracted from the three fatty acids were subjected to physicochemical tests to determine if their properties are in conformity with the reported standard values. Results of the physical properties of the substances tested show that the values were in close agreement with the results of the standard values and the results reported in previous literatures. As such, the investigation concluded that the three fatty acids contain appreciable quantities of crude glycerol and can thus serve as a source for natural glycerol whose properties can be compared with standard glycerin products.

Keyword: Glycerin, transesterification, palm kernel, palm oil, peanut oil.

I. Introduction

Glycerin, also called glycerol is a trihydric alcohol with a molecular formula $C_3H_5(OH)_3$. Its IUPAC name is 1, 2, 3-Propanetriol. It is a colorless, odorless, sweet tasting, very viscous and hygroscopic substance. Glycerin is soluble in different polar liquids but insoluble in higher alcohols, chlorinated solvents and non-polar compounds; such as fatty oils and hydrocarbons [12]. Due to the presence of inter and intramolecular hydrogen bonds, glycerin has a high boiling point of $290^\circ C$ at ambient pressure and high viscosity of 1.412 mpa.s at room temperature. It easily dissolves in water because of the three hydroxyl groups. It combines with three fatty acids to form what is called triglyceride. It is produced by the reaction of oils and fats with water, and is separated and purified to make a high quality product suitable for a wide range of end uses.

Glycerin was accidentally discovered in 1779 by a Swedish chemist K. W. Scheele while heating a mixture of olive oil and lead monoxide and he called it 'sweet principle of fat'. Later in about 1811, a French investigator of fats and oils, M. E. Chevreul, named this 'sweet principle of fat' as Glycerin from Greek word 'glykys' which means 'sweet'. The invention of dynamite in 1866 by Alfred Nobel was what revealed the industrial and economic importance of glycerin [3].

The main sources of triglycerides 'X' is plants formed as a result of photosynthesis. Glycerin as a by product is mainly used in the production of biodiesel, soap, fat splitting, cosmetics, drugs etc. There is also synthetic glycerin and this is obtained from propylene oxide, byproduct of petroleum. It is used mostly by the pharmaceutical sector for manufacturing drugs and other pharmaceutical products [5]. There are three grades of glycerin; crude glycerin that is about 40% to 88% pure with water and other impurities like methanol, sodium chloride, sodium hydroxide, Matter Organic On Glycerin (MONG), etc. This glycerin grade is obtained by recovery process from the waste-stream of the main product. The lower-purity glycerin is generally called crude glycerin [9]

Glycerin has about 2000 applications and it plays an important role and diversity of applications in different fields such as food, cosmetics, pharmaceuticals and polymer industries. In food industry, glycerin is frequently added in food to increase the water-coating ability and act as solvent for various food additives [6]. While in cosmetics industry, glycerin is used as demulcent and anti-inflammatory agent. In pharmaceutical formulations, high purity glycerin is added as lubricant and humectants. It is also useful in production of syrups, creams and balsams [8]

The versatility of glycerin is mainly due to the physical and chemical properties. Due to the presence of polyhydroxyl structure of the glycerin, various valuable compounds can be

produced by several catalytic routes such as lactic acid, acrylic acid, dihydroxyacetone, glycerin carbonate and 1,3-propanediol [4]. In the glycerin derivatives mentioned above, the most desired platform chemicals are lactic acid and its esters. These derivatives are extensively applied in many fields of industries. Recently, glycerin has attained increasing attention due to the expansion of the biodiesel industries since there is an increase in the production of crude glycerin (main byproduct) during the production of biodiesel [11]. In the transesterification process, for instance, for every 100 pounds of biodiesel produced approximately 10 pounds weight of crude glycerin will be generated. A continuous increment in the production of biodiesel will accumulate an excessive amount of glycerin and by the year of 2022, it is predicted that the global production of crude glycerin will be worth USD1,064 billion or around 1.32 million metric tons [10]. Therefore, the development of various innovative uses of crude glycerin by industry and researches is needed in order to open new markets in the near future.

Glycerin can be produced from the transesterification or hydrolysis of natural oils such as peanut butter and palm kernel oil. Palm kernel oil is the primary raw material from which glycerin is produced as a transesterification by product. In the process, palm oil is treated with methanol and basic homogenous catalyst.

Glycerin can be produced by using different processes and feed stocks. For example, it can be obtained by propylene synthesis via several pathways. Glycerin can also be produced by the hydrolysis of oil or by transesterification of fatty acids/oils. Furthermore, glycerin production can also be carried out by fermentation with yeast; such as *Saccharomyces cerevisiae*, *Candida*, with bacteria such as *Bacillus subtilis* and algae such as *Dunaliellatertiolecta* [14].

In this study, transesterification method will be employed for extraction of glycerin from three locally processed fatty acids/oils. Physicochemical analysis will be carried out to determine the properties of the glycerin extracted. Results of the physicochemical analysis of the extracted glycerol will serve as the basis of comparison to ascertain which of the fatty contains the best glycerin product.

II. Material and Method

II.1 Material

II.1.1 Reagents

The reagents required for the experiments were acquired from chemistry laboratory Federal University Birnin Kebbi, Kebbi State, Nigeria. The materials include dilute sodium hydroxide solution, methanol, activated charcoal, hydrochloric acid, alcoholic potassium hydroxide solution, ethanol, sodium hydroxide, phenolphthalein indicator and potassium hydroxide.

II.2 Method

II.2.1 Sample collection

The oil samples were obtained locally from Birnin Kebbi central market (Peanut oil and Palm oil) and Palm kernel oil from Kano State.

II.3 Extraction of Glycerin from Peanut Oil, Palm oil and Palm Kernel Oil

To an Erlenmeyer flask 200cm³ of Methanol was added. This was followed by the addition of 9g of NaOH and the mixture was stirred until the NaOH dissolves. After several minutes the

NaOH pellets remain, but the solution was still cloudy. In the meantime, while the NaOH is dissolving 800 cm³ of palm kernel oil was heated to around 60°C. When the palm kernel oil reaches 50°C the methanol NaOH solution was added to it. The NaOH acts as a catalyst.

II.3.1 Transesterification Reaction

The methanol was immiscible with the palm kernel oil and it visibly forms a layer and can cause a problem. To get around it, a quite strong stirring was used (If strong stirring is not used, it would simply stay two separate layers and reaction would not work very well). While the temperature was maintained around 50°C, the mixture was stirred for about 30 minutes.

II.3.2 Separation of Crude glycerin from Crude biodiesel

After 30 minutes the stirring stopped and the mixture was allowed to settle. The mixture was left overnight to settle, where it forms two separate layers, with the dark lower layer being mostly glycerin, while the upper layer is biodiesel. The upper layer was decanted by transferring it into another container. This biodiesel was in crude form. In the Erlenmeyer flask there was still a little portion of the biodiesel, but there are also some chunks of mostly gel biodiesel, which tends to be formed at lower temperatures. At the bottom of the Erlenmeyer flask remains a messy mix of gel biodiesel and the glycerin. To separate them, the entire mass was transferred to a beaker. In the beaker, the mixture was stirred and allows the glycerin to settle at the bottom and when the gel biodiesel floats to the top it was simply scooped off using the glass steel rod. At this stage a dark brown crude glycerin mixture was left in the beaker.

II.3.3 Adjustment of pH

Using a pH paper the pH of the glycerin was determined to show a strong basic solution. Next to the crude glycerin a total of 17 cm³ of 31.45% HCl was added. The added HCl reacted with the base to form water and salt, which will precipitate out visibly.

The addition of the acid will also generate fatty acid from the salt formed. The goal of this step is to make it strongly acidic with the pH of around 1. After the solution has been acidified (by adding HCl) the stirring was turned off and allowed to settle, thereby forming two layers. The upper layer is undesired fatty acids and must be removed. The mixture was then transferred into a separating funnel leaving as much salt as possible at the bottom of the beaker. The lower layer is the desired glycerin, which was a little bit cloudy because some of the salts from the beaker poured in. At this point, the pH of the solution is acidic, but the pH of glycerin is required to be neutral. To achieve this, the pH was adjusted using small amount of dilute NaOH solution.

II.3.4 Evaporation stage

After the pH of has been adjusted to neutral, the next step is to evaporate a lot of the water. The temperature of the solution was increased to about 110°C until the solution reduced to about one-third of its volume. As more water evaporates, the solution becomes darker and salts slowly precipitate out. When it reaches about one-third of its volume the stirring was stopped and the salt was allowed to settle at the bottom. The crude glycerin was then transferred to another beaker and the salt left behind.

II.3.5 Decolourization of glycerin

The next step is to decolorize the glycerin. This was carried out by dissolving the glycerin in four times its volume in methanol (CH₃OH). After it was fully dissolved 6g of activated

charcoal was then added to remove the color as impurities. The crude mixture was still likely to contain a little bit of water. In order to remove the water traces some molecular sieve was used to trap the water out.

II.3.6 Filtration

Filtration was carried out to remove the activated charcoal. The mixture was then stirred for several minutes and the solution left was a colorless solution, with the volume greatly increased because the activated charcoal was washed several times.

II.3.7 Methanol recovery

Finally, the last step was the removal of the methanol, for the solution becomes viscous, it was first transferred to a small beaker and heated to 110°C for 30 minutes to evaporate the final amount of methanol. The resulting solution was a clear glycerin product. At first, it was not viscous because it was just removed from heat.

The same procedure was carried out for the extraction of glycerin from peanut oil and palm oil [15]

II.4 Physiochemical Analysis

II.4.1 Determination of Moisture Content

The crucible with lid was cleaned, dried and weighed as W_1 . The sample (glycerin) was added to the crucible and weighed with lid as W_2 . The crucible was kept in the oven with lid removed. Specimen (glycerin) was dried to a constant weight maintaining the temperature between 105°C to 110°C for 16 hours or overnight. The final constant weight of the crucible with dried sample was recorded as W_3 [7].

Calculation:

$$\text{Moisture (\%)} = \frac{W_2 - W_3}{W_2 - W_1} \times 100$$

II.4.2 Determination of Saponification value

1g of glycerin was weighed in a beaker and dissolved in about 3ml of ethanol. Three times the contents of the beaker were washed with 7 cm³ of the solvent (ethanol) and transferred to a round bottomed flask. 25 cm³ of 0.5N alcoholic potassium hydroxide solution was added and mixed well. The round bottom flask was attached to the reflux condenser. Another reflux condenser was setup as the blank with all reagents present except the sample. Both flasks were placed on a boiling water bath for 30minutes. The resulting solution was allowed to cool and titrated against 0.5N HCl solution adding 1 cm³ of phenolphthalein indicator to each of the flask. The number of cm³ of acid required is noted as 'a'. An exactly identical blank experiment (glycerin) was performed. Number of cm³ of hydrochloric acid required was noted as 'b'[17].

Calculation:

$$\text{Using } \frac{(a - b) \times (N \times 56)}{W}$$

II.4.3 Determination of Ash Content

The crucible was cleaned, dried and weighed as W_1 . 5g of glycerin was weighed accurately into the cleaned, dried crucible and weighed as W_2 . The crucible was placed in the muffle furnace at 550°C for 3 hours. The crucible was cooled in a desiccator and weighed as W_3 [18].

Calculation:

$$\text{Ash Content (\%)} = \frac{(W_3 - W_1)}{W_2} \times 100$$

II.4.4 Measurement of Viscosity

10ml of the sample (glycerin) was weighed in a beaker. The beaker was placed under the viscometer, which was lowered to dip the spindle into the sample up to an immersion mark on the spindle shaft. Length 2 spindle was used, which was suitable for comparative testing of the viscosity of free-flowing fluids. The reading was taken when the viscometer pointer stabilized and the temperature was noted.

II.4.5 Determination of pH

5ml of the sample (glycerin) was weighed into a beaker. A pH electrode was rinsed with distilled water to standardize it to the pH value of 7 and immersed into the sample until a steady reading was reached. The reading was taken.

III. Result and Discussion

Table 1 below is the result of the quantities of crude glycerin extracted from palm kernel oil, peanut oil and palm oil. The values show that the volumes of glycerin extracted from palm kernel and peanut oils exceed the volume of glycerin extracted from palm kernel oil by a marginal difference of 30%. These results are similar to the values reported in a previous investigation [16]. This goes to show that both the palm kernel and peanut oils contain more glycerol than palm oil. The reason for the high content of the glycerol in palm kernel and peanut oils may be attributable to the fact that both the palm kernel oil and the peanuts oil are obtained from the seeds of the plant, whereas the palm oil is obtained from the fleshy part of the palm fruits. The yields of the glycerin from the three oils show that palm kernel and peanut oils produce 6.25% of the glycerin yield out of the quantities of the oils used and the palm oil produces a glycerin yield of 5.25%. These ratios are very small quantity out of the quantities of oils used. This is an indication that glycerin content in these oils is very small.

Table 1: Quantities of Glycerin and Biodiesel Obtained from the Fatty Acids

OIL TYPE	GLYCERIN EXTRACTED (CM ³)	PERCENTAGE YIELD (%)	BIODIESEL EXTRACTED (CM ³)
Palm kernel Oil	50	6.25	600.5
Peanut Oil	50	6.25	590
Palm Oil	42	5.25	602

Table 2 below contains the results of the physicochemical analysis conducted on the glycerin extracted from the three fatty acids (palm kernel oil, peanut oil and palm oil). The table shows the values of the moisture contents of the glycerin.

Statistically, the results shows that there is significant variation ($p < 0.05$) in the mean of the moisture content between the groups. The moisture contents of the glycerin are also found to be within the values reported in previous investigation.

Figure 1, below is the chart of the ash contents of the extracted glycerin. The chart shows that the glycerin extracted from the palm kernel and palm oil are much higher than the ash content of the peanut oil. Ash content is a major of the mineral composition of a material. The result therefore shows that the mineral composition of palm kernel and palm oil are significantly greater than the mineral composition of peanut oil.

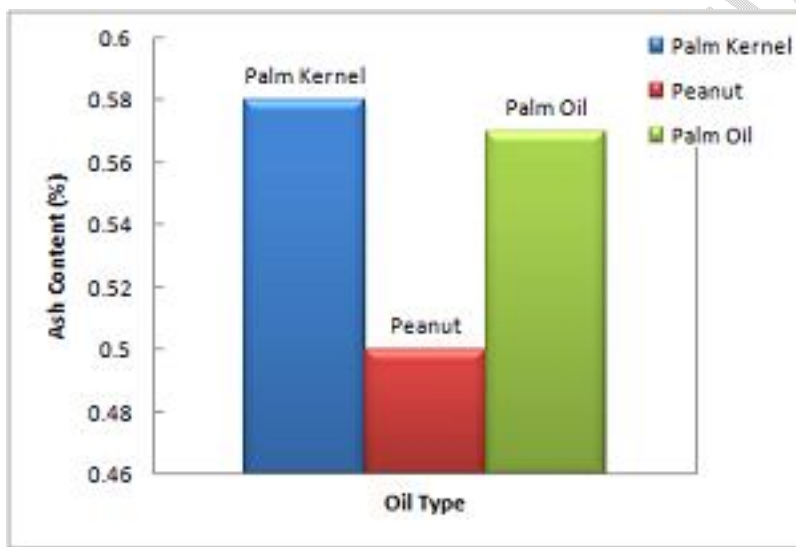


Fig. 1: Graph of the Ash Content Values for the Extracted Glycerin Oils.

Statistical analysis variance within each group shows that there is an insignificant variation in the ash content of the glycerin. Conversely, the result of the statistical analysis shows that there is a significant variation in the mean of the ash content between the groups ($P < 0.05$).

However, the values of the ash contents quoted above may have been exaggerated from the actual values. This is because the activated charcoals such as the one used in this investigation the purification of the glycerin extracts have been reported to have an effect in the ash content of products [4].

Table 2: Results of Physicochemical Tests of the Glycerin extracted from the Three Fatty Acids used

OIL TYPE	MOISTURE CONTENT (%)	VISCOSITY (mpa.s) at 33.7° C	PH
Palm Kernel	16.42±0.02	1.27±0.01	6.30±0.01
Peanut	15.62±0.01	0.78±0.01	6.66±0.01
Palm Oil	16.46±0.01	1.30±0.01	6.43±0.01

Table 2 above presents the values of the viscosities of the three glycerin extracted in this investigation. From the results it can be seen the palm oil glycerin has the highest viscosity over palm oil and peanut oil glycerin. The palm oil glycerin is the most viscous oil, followed

by the palm kernel oil and lastly the peanut oil. The high viscosity profiles observed are in agreement with the similar work conducted previously [13].

Statistical analysis of variance for the viscosity within each group indicates that no significant variation exists. On the other hand, analysis of variance for the mean of the viscosities shows that there is a significant difference between the groups ($P < 0.05$).

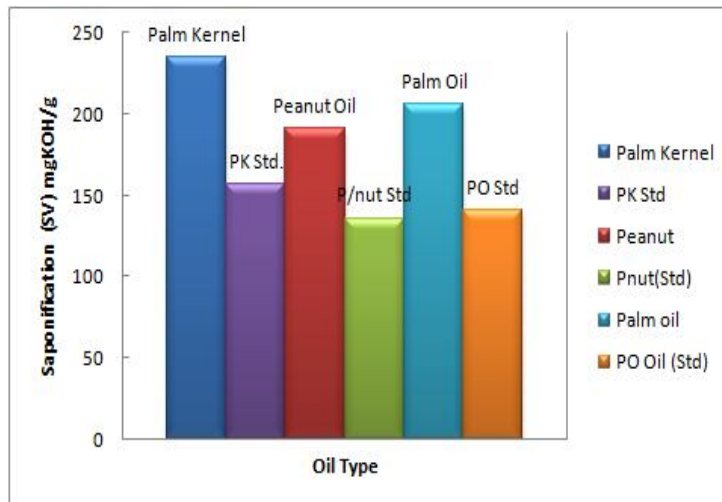


Fig. 2: Plot of the Saponification Values of the Extracted Glycerin Oils.

Figure 2 above represent the graphical plots of the saponification values of the glycerin extracted from palm kernel, peanut oil and palm oil respectively. From the curves it can be seen that palm kernel oil produces the highest saponification value among the three oils. This is followed by the palm oil. It is worthy to mention here that both palm kernel and palm oil are obtained from the same palm tree. As such, it would not be surprising if the saponification values of the two oils are very close. The peanut glycerin has the lowest saponification value among the three oils. The higher values observed indicate lower content of fatty acid. The higher value recorded for crude glycerin from palm kernel oil indicates low fatty acid, this provide evidence that the crude glycerin from palm kernel oil is more industrious as it is more suitable for soap making and cosmetic industries [1].

In addition, figure 2 also shows the comparison of the saponification values determined in this study with the standard saponification values of the fatty acid oils from which the glycerin are extracted. The plots show that the glycerin values obtained from each fatty acid outweigh the standard saponification values of the fatty acids.

Statistical analysis of variance for the saponification value of the glycerin shows that within the groups there is insignificant variation. However, analysis of the means of saponification values show that there is a significant difference between the groups ($P < 0.05$).

The pH of the glycerin can be seen in table 2. The results show the pH values fall within the acidic range. Peanut glycerin has the highest pH of 6.66. This is closer to the neutral value. This was followed by the pH of palm oil glycerin (6.43) and the lowest pH was recorded by palm kernel (6.30). All the values showed that the oils are slightly acidic and acceptable for crude glycerin with pH range of 6.0-7.0 [2]. The pH of the extracted glycerin are also closer to the skin's naturally acidic pH. Hence, they are considered suitable for the industrial production of cosmetics.

Statistical analysis of variance for the mean of the pH of the extracted glycerin shows that there is a significant difference between the groups ($P < 0.05$).

IV. Conclusion

In conclusion, this research has demonstrated that crude glycerin even though in lower quantity can be extracted from locally processed saturated and unsaturated fatty acid oils of palm kernel oil, peanut oil and palm oil using transesterification reaction. The quantity of biodiesel and crude glycerin extracted are evident that the transesterification reaction is a good technique. The oils (P.K.O, P.O and P.N.O) are rich in biodiesel than glycerin. The results obtained for the physicochemical properties are evident that the oil are good for soap making, pharmaceutical and cosmetic industries.

V. References

- [1] Akbar, E., Zahira, Y., Siti, K.K., Manal, I. and jumiat, S. (2009) Characteristics and composition of jatropha curcas Oil from Malaysia and Its Potential as Biodiesel Feedstock. *European Journal of Scientific Research*, 29: pp396-403.
- [2] Ardi, M.S., Aroua, M.K. and Awanis Hashim (2015), N. Progress, Prospect and Challenges in Glycerol Purification Process: A Review; *Renewable and Sustainable Energy Review* 42: pp1165-1173.
- [3] Ayoub, M. and Abdullah, A. Z., (2012). *Renewable and Sustainable Energy Reviews*, 16(5): pp2671-2686.
- [4] Azita, J., Meisom, H., Kambiz, J. and Meisam, T (2012). High Quality Potassium Phosphate Production through Step-by-Step Glycerol Purification: A Strategy to Economise Biodiesel Production. *Bioresource Technology*, 104: pp 788-790.
- [5] Bogaart, V., (2009). Glycerin Market Brief [Online] http://www.npt.nl/cms/images/stories/Verslagen/Presentatie_Bogaart_Croda_15042010.pdf; [Accessed] 12th August, 2021.
- [6] Ching, N., (2013). Li Urges Pairing State Role to Fuel China Growth. [Online]: <http://www.bloomberg.com/news/2013-03-17/china-s-li-vows-to-keep-7-5-growth-and-spread-wealth-benefits.html> [Accessed] 23rd August, 2021.
- [7] Determination of Water Content (AOAC, 2000), [Online]: https://kb.psu.ac.th/psukb/bitstream/2553/1564/2/279542_app.pdf; [Accessed]: 21st August, 2018.
- [8] Dimitiev, G. S., and Zhanavskina, L. N., (2011). Synthesis of Epichlorohydrin from Glycerin. 24.
- [9] Glycerin Market Analysis. (2012). Retrieved from:[Online] <http://www.biodiesel.ucsd.edu/mediagallery/download.php?mid> [Accessed] 8th September, 2021.
- [10] Global Crude Glycerine Market (2022-2028): [Online]: <https://www.rfdtv.com/story/46755526/Crude-Glycerine-Market-2022-Manufacturing-Size-Share-Business-Insights-Vital-Challenges-and-Forecast-Analysis-By-2028-with-Dominant-Sectors-and-Countries-Data>. [Accessed]: 28th June, 2022
- [11] Habaki, H., Hayashi, T., Sinthupinyo, P. and Egashira, R., (2019). "Purification of Glycerin from Transesterification using Activated Carbon Prepared from Jatropha Shell for Biodiesel Production," *Journal of Environmental Chemical Engineering*, 7(5):103303.
- [12] Jiang, Z., Zhang, Z., Wu, T., Zhang, P., Song, J., Xie, C. and Han, B. (2017). Efficient Generation of Lactic Acid from Glycerin Over a Ru-Zn-Cu/ Hydroxyapatite Catalyst, *Chemistry - An Asian Journal*, 12(13): pp1598-1604.
- [13] KOVÁCS, A. (2011). Aspects of refining biodiesel byproduct glycerin. *Petroleum & Coal*, 53 (1), pp91-97. Retrieved from: <http://www.vurup.sk/volume-53-2011-issue-2>
- [14] Manosak, R., Limpattayanate, S. & Hunsom, M. (2011). Sequential-refining of crude glycerin derived from waste used-oil methyl ester plant via a combined process of chemical and adsorption. *Fuel Processing Technology*, 92 (1): pp92-99.

- [15] NileRed. How to make glycerin (glycerol): {Online} <http://youtube.com/watch?v=yMG0yfGFj00> [Accessed] 15th August, 2018.
- [16] Orua, O.A., Emmanuel J.A. and Aniekan, O. (2011). Production of glycerol from palm Oil, JTD, 8(11): pp40-47.
- [17] Mathur, A. (2016). Extraction and studies on saponification values of some non edible seed oils from arid zone of Rajasthan. International journal of current engineering and scientific research (ijcesr), 3(3): pp 3-8.
- [18] Thiex et al. (2012). Determination of Ash in Animal Feed: AOAC Official Method 942.05.

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