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Synthesis and Characterization of Glycerol from Vegetable Oil

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ABSTRACT

Glycerol, also known as 1, 2, 3-propanetriol is a viscous colorless and odorless liquid that tastes sweet; it is derived from both petrochemical and natural raw materials by esterification. The transesterification reactions of two different vegetable oils (sunflower and palm oil) with methanol, using potassium hydroxide as catalyst, for the production of glycerol, were studied. The preparation of ester involved a two-step transesterification reaction that was accompanied by purification. Nuclear magnetic resonance and FITR were employed to detect the spectra of the glycerol's and oils respectively. There was no much difference in the glycerol yield by the two oils in which 2.6% and 2.5% were obtained by the sunflower and palm oil respectively. The physicochemical properties of the glycerol produced by both oils showed no differences in the free fatty acid contents, density and acid value but saponification value of 256.4 mgKOH/g for sunflower oil and 216.3 mg KOH/g for palm oil; viscosity of 8.5cp for sunflower oil and 4.96cp for palm oil; yellow color for to 5.3 that of sunflower oil and dark brown for that of palm oil. The Fatty acid measured by fatty acid methyl ester (FAME) revealed that sunflower oil had a percentage area ranging from 1.3 to 5.32% with retention time of 5.6 to 10 minutes while palm oil fatty acids had a percentage area of 0.02 to 0.17% with a retention time of 8.1 to 14.5 minutes. This has shown that the oils can be good sources for the production of glycerol and biodiesel.

Keywords: Sunflower, Palm oil, Glycerol, Biodiesel, Saponification.

INTRODUCTION

Glycerol, fatty esters and fatty acid are the 3 distinct vegetable oils derivatives. The crude glycerol is obtained as a secondary product of the production process of biodiesel. It has been estimated that for every 10 kg of produced biodiesel, about 1kg of crude glycerol is generated (Johnson & Taconic, 2007). Contrary to glycerol, crude glycerol has a substantially various composition and has multiple impurities such as water, methanol, fatty acid methyl esters, fatty acids, glycerides (Hu *et al*., 2012).

Also known as propane-1, 2, 3-triol or glycerin, glycerol is a chemical produced from saponification as by-product and also by-product of trans-esterification reaction in biodiesel plants as well as that of hydrolysis reactions in oleochemical plants (Ueoka& Katayama, 2001). Glycerol is a highly versatile chemical that is non-flammable, non-volatile and nontoxic with more than 1,500 different documented uses since 1945 (Adhikari *et al*., 2009).

Glycerol is made a good candidate used as a medium for green reaction in synthetic chemistry as a result of its origin renewability and specially combined physicochemical properties, including high boiling point, low toxicity and flammability, high polarity as well as the ability to dissolve both inorganic and organic compounds (acids, bases, salts and complexes of transition metals)and to form strong hydrogen bonds (Wolfson *et al*., 2007).

It is a biodiesel by-product that is generated from fats of animals and vegetable oils using a source that is sustainable. However, a biodiesel is a fuel generated from the reaction cooking oil (vegetable oil) with other common chemicals. Vegetable oil that is esterified contains oxygen that is able to contribute to reduction in level of particulate matter (Schumacher *et al*., 1995; Schumacher *et al*., 1993). The triglyceride is converted in descending order to diglyceride, then to monoglyceride and finally to glycerol (Schuchardt., *et al*., 1998).

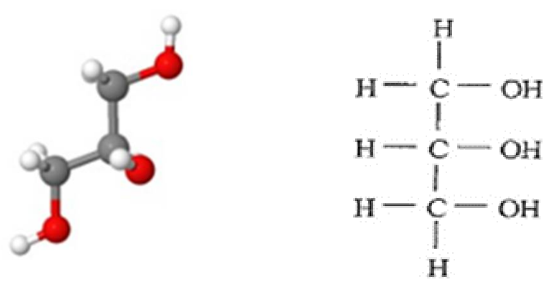

Figure 1: Visualization of molecular and molecular formula of glycerol

Table1: Characteristic of glycerol [6]

Parameter	Value/Characteristic
CAS number	56-81-5
Molecular formula	C3H8O3
Molar mass	92.1 g mol-1
Phase	Fluid
Colour	Colourless

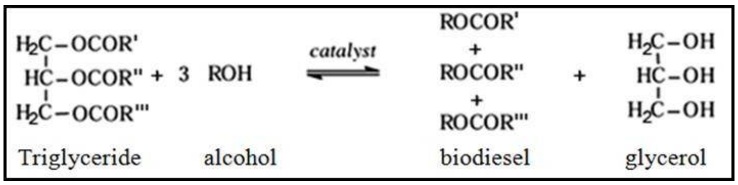

Figure 2: Transesterification process of palm oil to biodiesel and glycerol [8]

Materials

Materials used in this study were the two types of oil included

- palm oil and sun flower.
- The palm oil and sun flower was obtained from commercial grade olive oil was purchased from a local grocery store.
- Reactants for the experiment included methanol (Merk), potassium hydroxide and hydrochloric acid (Merk).
- All chemicals were as used without purification Pluss Polymers Private Limited, Gurgaon and its grade was P 4

METHODOLOGY

Transesterification Procedure: The 400 ml of palm oil and 100 ml of methanol (2:1) were utilized in the test batch production. 400 ml of palm oil was pre-heated to a steady temperature of 55C° using a magnetic heater/stirrer. With the aid of the measuring cylinder, 100 ml of methanol was measured and poured into\the beaker. 4.5 g of KOH pellet was measured using digital balance and added into methanol. The content of the beaker was stirred vigorously using the second magnetic stirrer until the KOH completely dissolved in the methanol. The mixture formed is called sodium methoxide. The methoxide was poured into the conical flask containing the preheated oil (palm oil). The content of the conical flask was stirred with the magnetic stirrer at a steady speed and temperature of 50C°. Then heating and stirring was stopped after hour half and the product was poured into a separating funnel mounted on a clamp stand. The mixture was allowed to settle down from 24 hours. The separating funnel was opened at the bottom allowing the glycerin at the bottom ran off after which the biodiesel was collected in a beaker and poured into a container for storage.

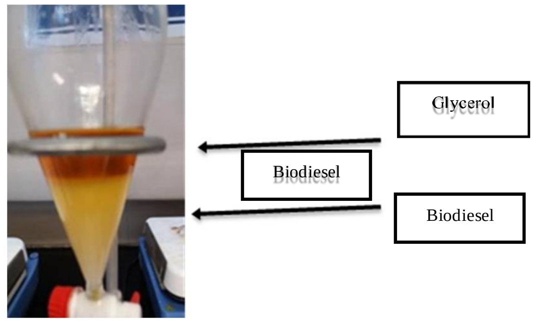

Figure 3: Two layer of product produced from transesterification process of vegetable oil

The bottom layer (glycerin) was poured into the beaker where the colour changed to orange and tested with litmus paper which gives blue colour. Then, 8.5 ml of concentrated hydrochloric acid (HCl) was added to the beaker and then stirred with magnetic stirrer at a constant speed. Thereafter, litmus paper test gave red colour. Stirring was stopped after the product was poured into a separating funnel mounted on a clamp stand.

Figure 4 Three Layers Formed after Adding Hydraulic Acid

Figure 5: Crude glycerol obtained from palm oil biodiesel production.

The separating funnel was opened from the bottom allowing the bottom layer to descend into the beaker and 25 ml KOH was added and diluted with magnetic stirrer at a constant speed and temperature 1000C until it became a thick texture. Then heating and stirring was stopped. Another litmus paper test revealed blue colour. Methanol (4 x crude glycerol volume) was added and also 3g activated charcoal was added and the mixture stirred with magnetic stirrer at a constant speed for 7 minutes.

Finally, filtration was done to remove carbon and heated to remove methanol. The above steps described for palm oil i.e. from the test to the final production were repeated for sun flower.

RESULTS AND DISCUSSION

The yield of production of the two oils used is presented in Table 4.1. There was no difference in the yield of the two oils for both the production of biodiesel and glycerol. However, the glycerol yield of glycerol of sunflower oil (10.3 ml) was slightly higher than that of palm oil (10 ml). It can be observed that biodiesel production of percentage volume by palm oil was 88.25% and that of palm oil as 88.75%. In addition, the glycerol yield was 2.5% and 2.6% for palm oil and sunflower oil respectively. This is in line with the study by (Marbun *et al*., 2013) who found out that refined glycerol had higher quality than the crude one; and this is similar in the case of biodiesel.

Table2. Production yield using different type of oils

Parameter	glycerol (palm oil)	glycerol (sunflower),
Glycerol volume ml	10 ml	10.3
Biodiesel volume %	88.25	88.75
Glycerol %	2.5	2.6

FTIR analysis

Figure 6 shows the overlaid FTIR spectra of the glycerol from reference, sunflower and palm oil between 4000 – 500 cm-1. From the results, the spectrum of glycerol from sun flower (Figure 6b) and palm oil (c) are very similar to those from commercial glycerol (a). The band at around 2900 cm−1 was corresponded to CH2 functional groups whereas the broad peak between 3600 and 3000 cm-1 were attributed to OH groups. On the other hand, peak at 1000 cm−1 corresponds to the C–O group vibration. These results were supported by the work of Lerma-Garcia *et al*., (2010) & Saifuddin *et al*., (2014) who obtained similar results in their study. Figure 4. Finer mesh size (smaller particles) of wood flour reduces the gap between particles, and improves the compactness and cohesiveness in composites resulting better hardness.

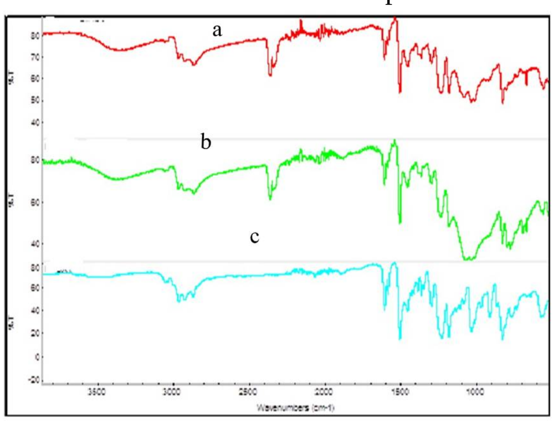

Figure 6: FTIR spectra of a) glycerol b) glycerol sun flower and c)glycerol palm oil.

Nuclear Magnetic Resonance Spectroscopy.

Typical 1H-NMR spectrum of glycerol from sun flower, palm oil and reference are shown in Figure 7a - Figure 6c respectively. The spectrum of glycerol that produced from sun flower oil is very similar to that of pure reference glycerol. Table 3 shows the summary of the peak shift correspond to the proton position in glycerol structure.

Table 3. 1H NMR Spectra interpretation of glycerol

Peak	Position	Shift, δ (ppm)	Assignment
1	d	3.20	HCHOH-
2	c	3.30	HCHOH-
3	b	3.43	-CHOH-
4	a	4.73	-CHOH-

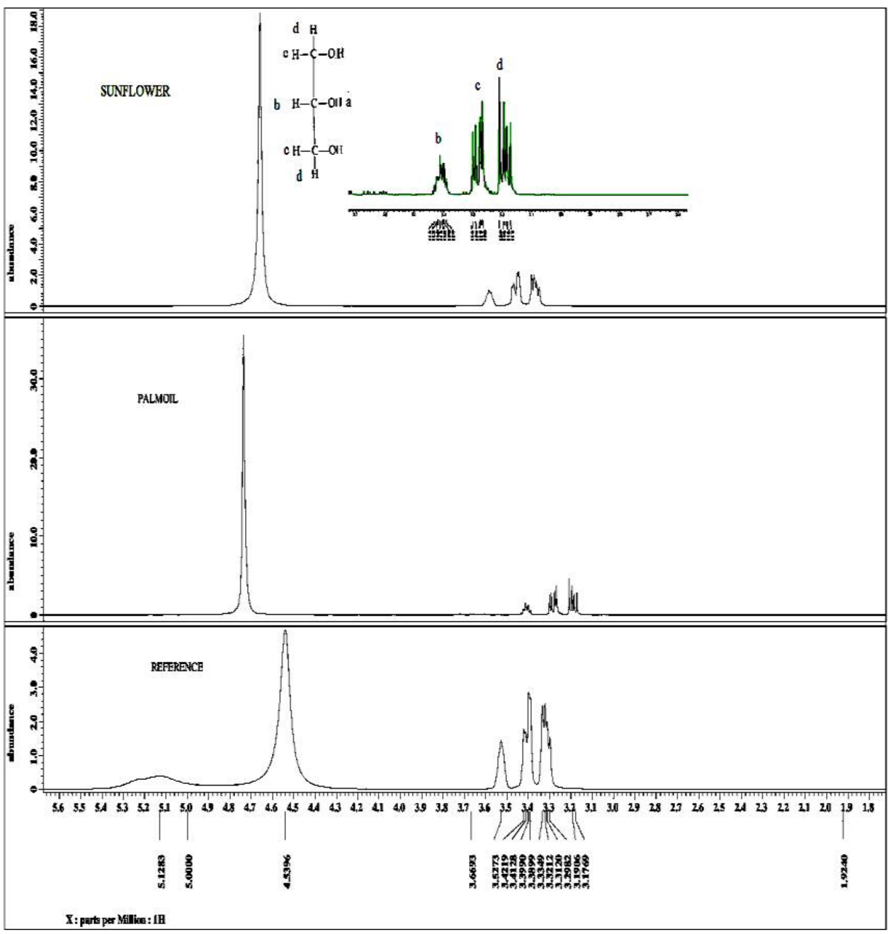

Figure 7: ¹H NMR Spectra interpretation of (a) sunflower, (b) palm oil glycerol

Figures 8a and 8c show the 13CNMR of reference glycerol, palm glycerol and sunflower glycerol respectively. The results show two signals at 62.72 ppm and 72.24 ppm represent the primary and secondary aliphatic carbon atoms, respectively. The peak shift is summarised in Table 4.3

Table 4. ^{13}C NMR Spectra interpretation of glycerol

Type of C	C_1	C_2
Chemical shift(ppm)	72.2	62.7

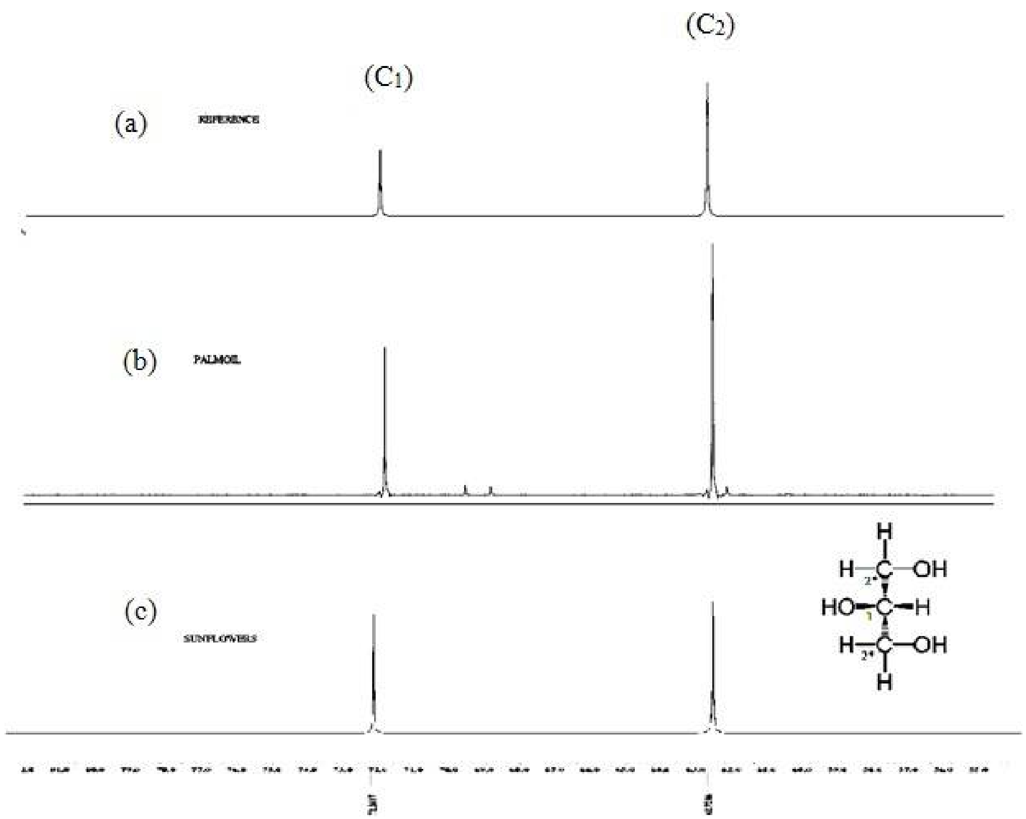

Figure 8: 13C NMR spectra of (a) reference glycerol (b) palm oil (c) sunflower

Figure9 show the 13C DEPT 135° spectra of the glycerol. In DEPT 135°, positive peak means the 13C is from -CH- group whereas negative peak suggest 13C from the - CH2- group. The results concluded that positive peak at 72.2 ppm is C1 carbon from CH or and negative peak at 62.7 ppm is C2 from CH2 groups. This result is an agreement with the glycerol structure. Thus, NMR analysis is confirmed the glycerol product synthesised from sunflower oil and palm oil.

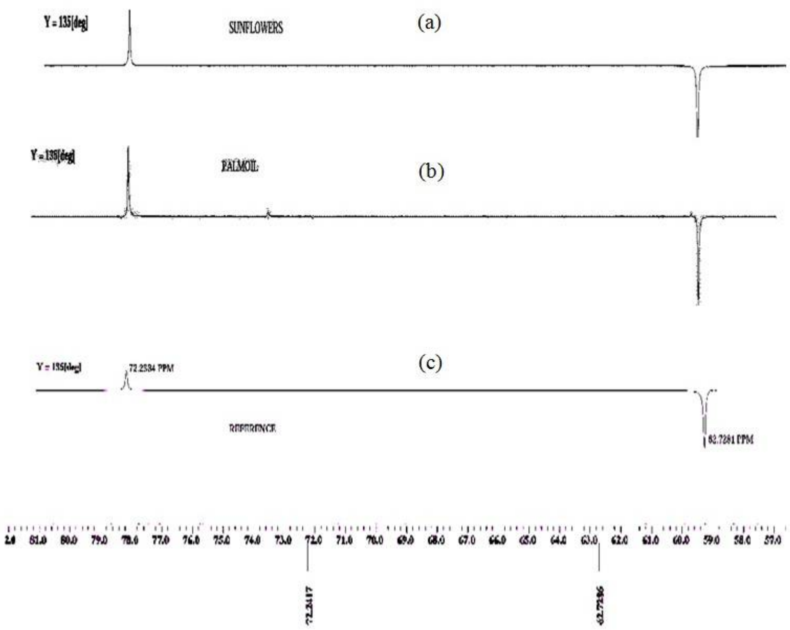

Figure 9: ^{13}C DEPT 135^{o} NMR spectra of (a) sunflower (b) palm oil (c) reference glycerol

Physicochemical properties.

Table 5. Properties of palm oil and sunflower of glycerol

	Property	Palm oil	sunflower
1	Free Fatty Acid (mgKOH/g)	0.188	0.196
2	Saponification value (mgKOH/g)	216.3	256.4
3	Acid value (mgKOH/g)	0.337	0.393
4	Viscosity (rpm/Pa) at 37°C	4.936 cp	8.50 cp
5	Colour	Dark Brown	yellow
6	Density (g/cm3) at 280°C.	1.256	1.280
7	Odor	pleasant	pleasant

Fatty acid methyl esters Analysis (FAME)

Table 6. Different fatty acids crude glycerol from palm oil.

No	Fatty acid	Retention time	A/H	Area %
1	Glycerol	8.155	33.72	98.91
2	Myristic acid	12.934	1.42	0.17
3	Palmiticacid,methyl ester	13.475	1.40	0.04
4	Palmitic acid, isopropyl ester	13.951	1.62	0.03
5	Stearic acid	14.459	1.60	0.02
6	Lauric acid	14.459	1.60	0.02
7	Pentadecanoic acid	14.459	1.60	0.02

Table 7. Fatty acid of the cured glycerol from sun flower

No	Fatty acid	retention time	A/H	Area%
1	Glycerol	8.309	35.87	98.26
2	Myristic acid	6.107	3.07	1.77
3	Palmitic acid, methyl ester	6.107	3.07	1.77
4	Palmitic acid, isopropyl ester	6.602	1.88	1.88
5	Stearic acid	5.583	7.81	1.95
6	Lauric acid	10.002	2.19	1.30
7	Pentadecanoic acid	9.005	2.89	5.32

CONCLUSION

From the results of the study, palm oil and sunflower can be used for production of glycerol by transesterification process. The optimum reaction conditions for transesterification of both the sunflower and palm oils were found to be 50oC reaction temperature, 2:1 molar ratio of methanol to oil, 4.5g KOH pellets as catalyst at 24 hrs reaction time. These conditions gave yielded of 88.75% and 88.25% by weight of biodiesel volume from sunflower and palm oils respectively, and the glycerol viscosity of found to be 8.5 cp and 4.9 cp respectively for sunflower and palm oils at 37 °C.

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