International Journal of Scientific Research in Chemistry (IJSRCH)
© 2019 IJSRCH | Volume 4 | Issue 5 | ISSN : 2456-8457

Epoxidation and Hydroxylation of Sunflower Seed Oil

J. M. Yelwa[1*], S. Abdullahi[2]

[1]Scientific and Industrial Research Department, National Research Institute for Chemical Technology, Zaria.

[2]Chemistry Department, Gombe State University of Science and Technology, Kumo.

ABSTRACT

Sunflower oil is a renewable resource that can be epoxidized and hydroxylated. Epoxidized and hydroxylated sunflower oil has the potential for use as an environmentally friendly, reactive material in polymeric formulations. Epoxidation and hydroxylation were performed using formic and acetic acid to develop epoxidized oil and alcohol to develop polyol. Some preliminary studies on epoxidation and hydroxylation sunflower seed oil have been carried out. The results from the epoxidized oil showed that, yield is 83%, moisture content is 2.81%, oxirane content is 2.6%, iodine value (IV) is 105, Acid value(AV) KOH(g) /100 g is 5.1, saponification value (SV) KOH(mg) /100g is 186 and for hydroxylated oil showed that yield is 89 %, moisture content is 8.34%, Acid value is 5.036 mgKOH/g, Iodine value is 67 (I2 /g) and Hydroxyl content is 78.36 %. The reaction was monitored and confirmed using FTIR.

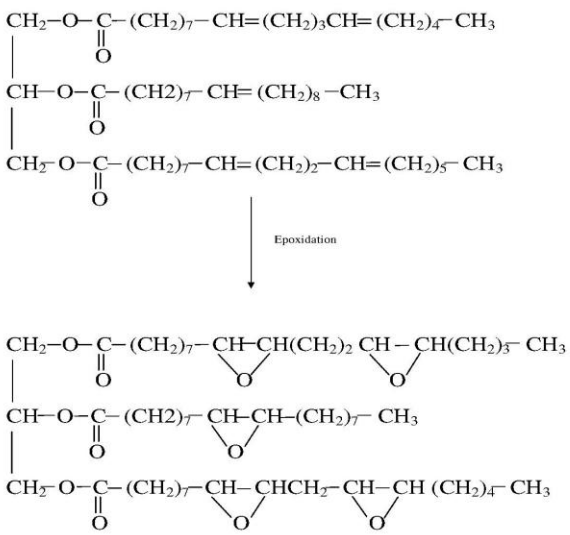
Keywords : Epoxidation, Hydroxylation, Sunflower, Oil.

I. INTRODUCTION

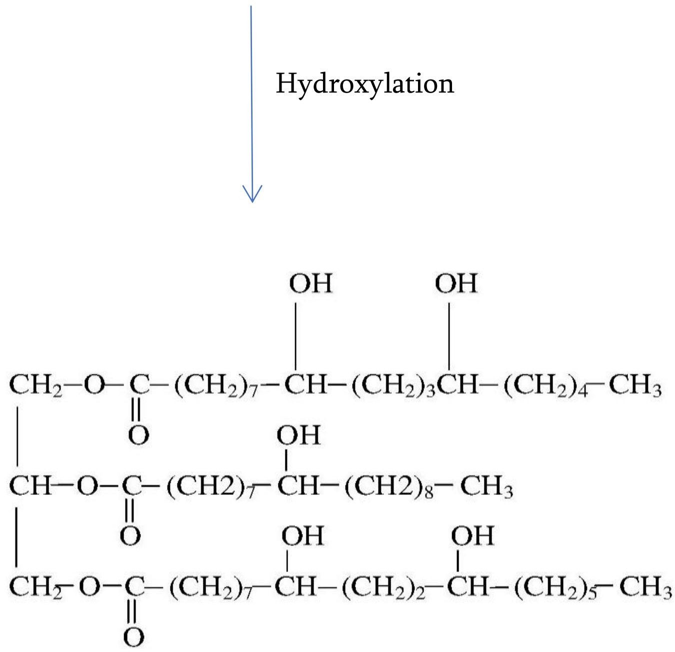
Due to petroleum oil depletion, global warming and other environmental concerns, the transition of petroleum feedstock to renewable resources is crucial to a sustainable development in the future. Green chemistry is defined as "the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances" (Anastas & Warner, 1998). This concept introduced the use of plant-based chemistry in order to help protect the environment. Green chemistry is a concept that will continue to be used widely within the chemistry community, educational facets, as well as in technological development. Under the umbrella of green chemistry principles, chemists will place more focus on developing plant-based chemistry applications, an essential component in the advancement of green chemistry (Anastas & Warner, 1998). The results of green chemistry produce cost effective techniques and processes, improve the safety of the environment and human health, and contribute to the world's sustainable development progress. As a response to the increasing fossil fuel prices, depleting oil reserves, increasing greenhouse gas emission, and other environmental concerns, development of alternative resources to petrochemical-based industry is essential.

Vegetables or plant oils represent a renewable resource that can be used as reliable starting material to access new products with a wide array of structural and functional variations. The ample availability and the relatively low cost make plant oils an industrially attractive raw material for the plastics industry (Kale *et al.*, 2017). Epoxides are well known commercially because of the many important reactions they undergo. Fats and oils are renewable resources that can be treated chemically or enzymatically to produce materials which often act as a replacement for petroleum-derived materials. Due to high reactivity of the oxirane ring, epoxides also act as a raw material for a variety of chemicals, such as alcohols, glycols, alkanol amines, carbonyl compounds, olefinic compounds and polymers like polyesters, polyurethanes, and epoxy resins (Kale *et al.*, 2017). Oils derived from plants have a large potential for current petrochemical-based polymer industry because they are biodegradable, sustainable, and can be converted into various industrial polymers (Meyer, 2008). Epoxidized vegetable oils have been applied in many industrial applications as plasticizers (Petrović *et al.* 2003), lubricants (Hwang and Erhan, 2006), polyols (Kiatsimkul *et al.*, 2006), resins, composites (Liu *et al.* 2015), coatings, elastomers and adhesives (Ahn *et al.*, 2011).

Bio-based polyol, a resultant of hydroxylation of plant oil, has typically been studied for polyurethane applications which in the field of elastomers, plasticizers, and coatings. Hydroxylated plant oils are used for cross-linking agents in the polyurethane industry (Lligadas *et al.* 2006). Many researchers have studied hydroxylation of plant oils.



Scheme 1: Proposed chemical structures of the epoxidized sunflower seed oil



Scheme 2 : Proposed chemical structures of the hydroxylated sunflower seed oil

II. MATERIALS AND METHODS

A. Materials

Sunflower seed oil, NaOH, HCl, sodium dihydrogen phosphate, sulphuric acid, acetic acid, formic acid, Hydrogen peroxide, NH_3, Kaolin, Butanol. Petri dishes, Beakers, Conical flasks, Measuring cylinders, three neck flask, hot plate, thermocouple, condenser, stirrer etc. All materials were used as received.

B. Extraction of Sunflower Seed Oil

The crushed seeds were manually/traditionally treated with hot water and continuously stirred in other to get the oil.

C. Syntheses

a. Epoxidation

200 cm^3 of the sunflower seed oil was placed in a 500cm^3 three neck flask equipped with a reflux condenser and a thermocouple (adopted from Goud *et al.,* 2007). The flask was placed on a hot plate with temperature control. Acetic acid and formic acid at a molar ratio of 0.5:1 to the oil and sulphuric acid catalyst 3% weight of hydrogen peroxide as an oxygen carrier was added into the sunflower seed oil. A hydrogen peroxide molar ratio of 1.5:1 to the oil was

added drop-wise into the mixture. This feeding strategy is required in order to avoid over heating the system since the epoxidation reaction is an exothermic reaction. The reaction maintains uniformity by using a magnetic stirrer which runs at about 1600rpm under isothermal condition at 50-6°C. The product was then cooled and decanted in order to separate the organic-soluble compounds (epoxidized oil) from water-soluble compounds. The epoxidized oil has been washed with warm water (in small aliquots) in order to remove residual contaminants. The procedure was repeated 3 times.

b. Hydroxylation

The hydroxylation reaction (adopted from Petrovic *et al.,* 2003) was performed in a 1000cm³ three neck flask equipped with a reflux condenser and a thermocouple. The flask was placed on a hot plate with temperature control. 150 cm³ of the epoxidized sunflower seed oil was hydroxylated using alcohol (methanol and isopropanol) with a molar ratio of 4:1 to the oil and water at a molar ratio of 2:1 was mixed with the epoxidized oil and sulphuric acid catalyst in the reactor. The reaction was performed at a fixed temperature of 60°C for 5 hours. Uniformity was maintained using a magnetic stirrer which runs at about 1600rpm. The product (polyol) was then cooled and decanted in order to separate the organic-soluble compounds from water-soluble ones. The product was washed with warm water (in small aliquots) in order to remove residual contaminants. The procedure was repeated 3 times.

D. CHARACTERIZATION

a. Fourier Transform Infrared (FT-IR) Spectrometer

The FT-IR spectra were recorded on KBr discs in the wavenumber range of 500 to 4000 cm-1 on Buck scientific infrared spectrophotometer, Model 530.

b. Moisture Content Determination

The moisture content was determined by taking the weight of an empty crucible (Wc). Two drops of oil were put into the crucible and weighed (Wco). It was then put into an oven programmed at 105°C and left for 8 hours; after which it was removed and re-weighed (Wo). The percentage moisture content was computed as follows.

% Moisture content = (Wco-Wo)/ (Wco-Wc) x 100%

The process was repeated two more times and the average moisture content computed.

c. Determination of Iodine Value

Iodine value was determined by cyclohexane-acetic acid method according to AOCS official method Cd 1d-92.

d. Determination of Saponification Value

The method described by Nkafamiya *et al.* (2007) was adopted. Oil sample (2.0g) was added to 0.1M alcoholic KOH. The resulting solution was heated to 60°C with constant stirring for 5 minutes for the oil to saponify. The unreacted KOH was titrated with 0.5M HCl, using phenolphthalein as indicator, until the solution turned pink. The process was repeated two more times and the average titre value was calculated. The saponification value SV was calculated as follows:

SV = [B-S] x M x 56.1 Wt of sample

Where B = blank titre, S = Samples titre volume.

e. Oxirane content

Epoxy content is the most important property of epoxy materials. Samples of ESO were analyzed for their percent (by weight) of epoxy functional groups by an AOCS official method Cd 9-57 (Oxirane oxygen in epoxidized materials).

f. Hydroxyl content

Hydroxylation of the oil was conducted as described for oxidation of the oil, with slight modifications by manipulating the parameter of CH_3COOH, H_2O_2, H_2SO_4, reaction time and temperature (Okieimen *et al.*, 2005).

III. RESULTS AND DISCUSSION

A. Analysis of Sunflower Seed Oil

The oil yield of 78.21 % of the sunflower seed oil (Table 1) is higher than that obtained by Danbature *et al.*,2015; Babakura, *et al.*, 2019; and Abdulhameed *et al*, 2012. The oil yield of sunflower seed is higher than that of mahogany seed oils (58.6%) and (66.3%) (Danbature *et al.*, 2015 and Babakura *et al.,* (2019). The acid value of sunflower seed oil (0.15mgKOH/g) is very much lower than 5.99mgKOH/g reported by Abdulhamid et al., 2012; but highet that reported by Babakura *et al.* 2019 and Danbature *et al.*, (2015). This may be attributed to the modified method of extraction. The low acid value demonstrates the feasibility of alkali – catalyzed reaction. The iodine value of Sunflower seed oil (129I_2/g) is higher than that obtained by Ali et al., (2011) and Danbature *et al.*, (2015) for mahogany seed oils. The differences observed in the iodine values for the oil could be due to differences in plant. The moisture content (2.78%) is much lower than the moisture content of *Khaya senegalinsis* oil (22.297) as reported by Babakura *et al.* (2019). The saponification value is 193mgKOH/g, which is in contrast with 91.6mgKOH/g and 296.8mgKOH/g reported by (Danbature *et al.*, 2015 and Babakura *et al.* (2019).

Table 1 : Oil quality parameters of sunflower seed oil

Parameter	Sunflower seed oil
% oil yield (v/wt)	78.21
% moisture content	2.78
Acid value (mgKOH/g)	0.15
Iodine value (I_2 /g)	129
Saponification value (mgKOH/g)	193

B. Analysis of Synthesized Epoxidized Sunflower Seed Oil

Oxirane content and iodine value are important properties in the characterization of epoxidized vegetable oils. The oxirane content indicates the epoxy groups present in the products while the iodine value indicates the remaining unsaturation after the epoxidation reaction. In the preparation of polymers, epoxy resins with a lower iodine value and higher oxirane oxygen content are desired. The reductions in iodine values indicated the consumption of unsaturation during epoxidation, but they did not represent solely conversion to epoxy groups because the epoxy ring degradation generates side products. Scheme 1 depicted the proposed chemical structures of the epoxidized sunflower seed oil.

Experimentally determined characteristics values of epoxidized sunflower seed oil can be summarized (table 2) as yield is 83%, moisture content is 2.81%, oxirane content is 2.6%, iodine value (IV) is 105, Acid value(AV) measured as mass of KOH(g) /100 g is 5.1, saponification value (SV) calculated as mass of KOH(mg) /100g is 186. The highest epoxy content synthesized epoxidized soy oil (ESO) was 6.13 % and it is almost comparable to the commercial Epoxidized oil (6.3 %). Scheme 1 shows the reaction conversion of Epoxidized sunflower seed oil where the amount of H_2O_2 is varied. Theoretically 1 mole of H_2O_2 will epoxidize one mole of C=C. When the ratio of H_2O_2:C = C is increased the reaction conversion of epoxidized sunflower seed oil increases. The unsaturation and epoxy groups has also been monitored by the Fourier transform infrared (FTIR) spectroscopy. The FTIR spectroscopy is a rapid, non-destructive technique that has been widely applied in the characterization of lipids because lipids have functional groups with characteristic absorption bands in the infrared region of the electromagnetic spectrum. Figure 1 shows the FTIR spectrum of epoxidized sunflower seed oil, spectral analysis of this sample showed that a 95% consumption of the band at 3010cm^{-1} (C-H stretching of non-conjugated unsaturation) characteristic of ethylenic groups. The value (825-840cm-1) of epoxy group confirmed the formation of ethylenic oxide (oxirane) ring and show the appearance of band around 825-840cm^{-1} & 910-925cm^{-1}. The epoxy ring near at the band 839cm-1 & 915cm-1 indicating that all of the C-C double bonds disappeared into oxirane (epoxy) ring peak C–O–C stretching from oxirane vibration appears at 1250 cm^{-1} and 830–850 cm^{-1}. The most representative signal that evidences the oxirane group is the small intensity one sited at 830 cm^{-1}.

Table 2 : Oil quality parameters of epoxidized sunflower seed oil

Parameter	Epoxidized oil
% oil yield (v/wt)	83
% moisture content	2.81
Acid value (mgKOH/g)	5.1
Iodine value (I_2 /g)	105
% Oxirane content	2.6
Saponification value (mgKOH/g)	186

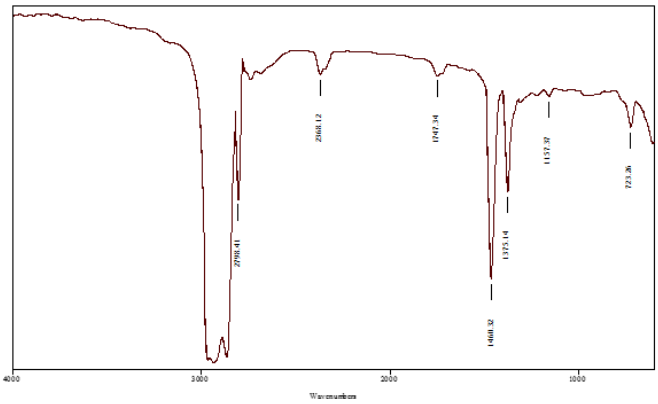


Figure 1: FTIR Spectrum of epoxidized sunflower seed oil

C. Analysis of Synthesized Hydroxylated Sunflower Seed Oil

Scheme 2 shows the proposed reaction for the formation of polyol (Azhar *et al.* 2017). Table 3 gives a brief summary of the parameters that were determined in other to evaluate the physicochemical quality of hydroxylated sunflower oil. Oil yield is 89 %, moisture content is 8.34%, Acid value is 5.036 mgKOH/g, Iodine value is 67 (I_2 /g) and Hydroxyl content is 78.36 %. There a decrease in iodine number of 105mgKOH/g to 67 I_2/g. Azhar *et al.* (2017) reported a hydroxyl number of 78.903 mgKOH/g and iodine number 40.185 gI_2/g for hydroxylated rubber seed oil. Hydroxylation process has improved hydroxyl number.

FTIR spectra of hydroxylated sunflower seed oil are shown in Fig 2. The -OH groups of hydroxylated sunflower seed oil at wave number 3441.51 cm^{-1} was observed due to the hydrogen-bonded hydroxyl groups that contribute to the complex vibrational stretches associated with free inter- and intra-molecular bound hydroxyl groups (Yelwa *et al.,* 2017). The bands at 2928.58 cm^{-1} – 2863.21 cm^{-1}, are characteristic of C-H stretches associated with the methane hydrogen atoms, was observed. It shows that the hydroxylation process of sunflower seed oil has reduced the number of double bonds and those results also supported by reduction of iodine number. The band at 1740.00 cm^{-1} was assigned to the C=O stretching of saturated ester. The band at 1460.19 cm^{-1} corresponds to the characteristics of C-H of alkane bending vibration. The band at 1374.92 cm^{-1} was attributed to the C-O bond stretching. The absorption bands from 722.51 cm^{-1} is as a result of C-H of alkene bending vibration.

Table 3 : Oil quality parameters of Hydroxylated sunflower seed oil

Parameter	Hydroxylated oil
% oil yield (v/wt)	89
% moisture content	8.34
Acid value (mgKOH/g)	5.036
Iodine value (I_2 /g)	67
Hydroxyl content (%)	78.36

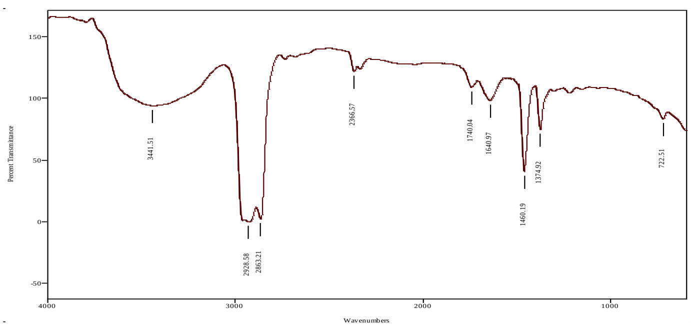


Figure 2: FTIR Spectrum of hydroxylated sunflower seed oil

IV. CONCLUSION

Epoxidized and hydroxylated sunflower oil is receiving more attention in recent days because of its availability, cost and applications. The oxirane 2.6%, iodine value 105 (I2 /g) for the epoxidized sunflower seed oil and hydroxyl number is 78.36% and iodine value 67 (I2 /g) for the hydroxylated sunflower seed oil. The reaction was monitored and confirmed using FTIR.

V. REFERENCES

[1]. Abdulhamid Hamza, Auwal Aliyu, and Elisha Lomshaka (2012). Production of Biodiesel via NaOH Catalyzed transesterification of mahogany seed oil. Advances in Applied Science Research, 3: 615-618.

[2]. Ahn BK, Lee DW, Israelachvili JN, Waite JH. (2014). Surface-initiated self-healing of polymers in aqueous media. Nature materials.13:867-872.

[3]. Anastas, P.T. and Warner, J.C. (1998) Green Chemistry: Theory and Practice. Oxford University Press, New York.

[4]. AOAC (1998). Official Method of Anlysis of the Associaion of Official Anlytical Chemist, Official Methods of Anlysis. Gaithersburg, USA. 16th Edn.

[5]. AOAC. (1990). Associaion of official Analytical Chemist, Arlington. Official Methods of Analysis, 14th edition Vol. 67.

[6]. Azhar, N.H.A., RASID, H.M.D., and YUSOFF, S.F.M., (2017). Epoxidation and Hydroxylation of Liquid Natural Rubber (Pengepoksidaan dan Penghidroksilan Getah Asli Cecair). Sains Malaysiana 46(3): 485-491.

[7]. Babakura, M., Yelwa, J M., Abubakar, I., Aliyu, B.M., Yahaya, J.Y., Umar, J.B., Auwal, M.M. and Ogabidu, A.O. (2019). Synthesis and Characterization of Biodiesel from Khaya senegalensis Seed Oil using Heterogeneous Catalyst. International Journal of Science and Management Studies (IJSMS). 2(4). 101 - 107.

[8]. Danbature, W. L., Aliyu, J. and Adamu, H.M. (2015). Production of Methyl Ester from Mahogany (Khaya senegalensis) Seed Oil. Journal of Chemistry and Chemical Sciences, Vol.5 (9), 489-499

[9]. Goud, V. V., Patwardhan, A. V., Dinda, S. and Pradhan, N. C. (2007): Epoxidation of karanja (pongamia glabra) oil catalysed by acidic ion exchange Resin. European journal of lipid science and Technology, 109: 575-584.

[10]. Hwang, H. and Erhan, S.Z. (2006) Synthetic Lubricant Basestocks from Epoxidized Soybean Oil and Guerbet Alcohols. Industrial Crops and Products, 23, 311-317.

[11]. Kale, A.E., Goswami, D.G., and Zade, P. S.M. B. (2017). Recent advances in epoxidation of vegetable oils. Mandake. Journal of Emerging Technologies and Innovative Research (JETIR), Volume 4, Issue 04. Pp 171-175.

[12]. Kiatsimkul P, Sutterlin WR, Suppes GJ. (2006). Selective hydrolysis of epoxidized soybean oil by commercially available lipases: Effects of epoxy group on the enzymatic hydrolysis. J. Mol. Catal. B-Enzym. 41:55-60.

[13]. Liu K, Madbouly SA, Schrader JA, Kessler MR, Grewell D, Graves WR (2015). Biorenewable polymer composites from tall oil-based polyamide and lignin-cellulose fiber. J Appl Polym Sci 132:42592

[14]. Lligadas G, Ronda JC, Galià M, Cádiz V (2006). Bionanocomposites from renewable resources: epoxidized linseed oil-polyhedral oligomeric silsesquioxanes hybrid materials. Biomacromol 7:3521-3526

[15]. Nkafamiya, I.I., Oseheahon, S.A., Dahiru, D.and UmaruH.A. (2007): Studies on the chemical compression and Physicochemical properties of the Seeds of baobab (Adansonia digitata) African Journal of Biotechnology, 6(6)756-759

[16]. Meyer P.P., Techaphattana. N., Manundawee S., Sangkeaw. S., Junlakan, W., Tongurai. C. (2008).

Epoxidation of soybean oil and jatropha oil. Thammasat Int.J.Sc.Tech., 13, 1-5.

[17]. Muhammad Rizwan, Sobia Naseem (2018). Characterization of Epoxidized High Contents of Linoleic & Oleic Fatty Acids of Citrullus Lanatus Seeds Oil. American Journal of Chemistry and Applications. Vol. 5, No. 1, pp. 1-9.

[18]. Okieimen, F.E., Pavithran, C. & Bakare, I.O. (2005). Epoxidation and hydroxylation of rubber seed oil: One-pot multi-step reactions. European Journal of Lipid Science and Technology 107(5): 330-336.

[19]. Petrovic, Z.S., Zlatanic, A., Lava, C.C. and SinadinovicFiser, S. (2003): Epoxidation of soybean oil in t oluene with peroxy acetic and peroxy formic acids-kinetics and Side reactions, European journal of lipid science and Technology, vol 104, no.5, Pp. 293-299.

[20]. Yelwa, J.M., Osemeahon, S.A., Nkafamiya, I.I and Abdullahi S. (2017). Synthesis and Characterization of Hydroxylated Sunflower Seed Oil/ Poly Vinyl Acetate Copolymer Binder for Possible Application in the Coating Industry. International Journal of Innovative Research and Advanced Studies (IJIRAS) Volume 4 Issue. Pp 417-418.

Cite this article as :

J. M. Yelwa, S. Abdullahi, "Epoxidation and Hydroxylation of Sunflower Seed Oil", International Journal of Scientific Research in Chemistry (IJSRCH), ISSN : 2456-8457, Volume 4 Issue 5, pp. 01-07, September-October 2019.

URL : http://ijsrch.com/IJSRCH19459