

Full Length Research Paper

Epoxidation of *Ximenia americana* seed oil

M. H. Shagal*, J. T. Barminas, B. A. Aliyu and S. A. Osemeahon

Department of Chemistry, Modibbo Adama University of Technology, P. M. B. 2076, Yola, Adamawa State, Nigeria.

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Epoxidized *Ximenia americana* seed oil may be well suited in the partial replacement of petroleum products in synthesis of polyol. However, a process is needed to obtain this material from *X. americana* seed oil at sufficient conversion and scale to assess products. Therefore, *X. americana* seed oil was extracted using hot-water process and finally epoxidized in a solvent-free process in a three neck flask with the use of acetic acid as oxygen carrier, sulphuric acid as a catalyst and hydrogen peroxide. The studied parameters were iodine value conversion and oxirane oxygen content at varying time from 0 to 6 h and different temperatures 40 to 80°C. Epoxidized *X. americana* seed oil with up to 95.95 conversions was produced at a time of 6 h and temperature of 80°C. The result shows that the conversion of iodine value increased with reaction time and temperature. The highest amount of oxirane oxygen content of 3.60% was achieved at 4 h reaction time and temperature of 60°C. Interestingly, the oxirane oxygen content increased with reaction time and temperature then decreased after having achieved the optimal point.

Key words: Oxirane, temperature, epoxidation, oil, *Ximenia americana*, seed.

INTRODUCTION

Polyurethanes were first discovered by Professor Otto Bayer in 1973 and are used in a wide variety of applications (Chian and Gan, 1998). They have been exploited as coating, thermoset and thermoplastic materials, adhesives and rigid or non-rigid foams (Guo et al., 2006; Lligadas et al., 2006; Wang et al., 2009). Hence, the worldwide demand for polyols is projected to increase each year. Polyurethanes are generally produced from the reaction between polyol and diisocyanate (Pechar et al., 2006). Polyols are normally derived from petroleum feedstocks and are known as petroleum-based polyols (Tu et al., 2007). As the demand for polyols is increasing whilst the amount of petroleum is declining, alternative raw material for the production of polyols are needed.

In recent years, the price of crude oil has escalated raising many concerns over the stability and the sustainability of petroleum resources. The rising cost of crude oil also impacts the cost of polyurethane products because majority of the raw materials, such as polyols and isocyanates used in foams are petroleum derivatives (Flora, 2011). Finding an alternative feedstock for polyurethane has become highly desirable for both economic and environmental reasons. Natural oils have been shown to be a potential bio-renewable feedstock for polyurethane (Barret et al., 1993; Heidebreder et al., 1999; Petrovic et al., 2005).

The hope is that using renewable resources as feedstock for chemical processes will reduce the environmental footprint by reducing the demand on

*Corresponding author. E-mail: shagal5787@yahoo.com.

non-renewable fossil fuels currently used in the chemical industry and reduces the overall production of carbon dioxide, the most notable greenhouse gas. There is resurgence of interest in the use of annually renewable feedstock like vegetable oil for fuel and industrial applications. The use of agricultural feedstock allows us to manage our own carbon cycle more efficiently and reduce carbon (IV) oxide (CO₂) emissions (Cheng and Rayson, 1999).

Most of bio-based polyols for polyurethanes are synthesized from vegetable oils (Desroches et al., 2012). A vegetable oil polyols can be used as a replacement for conventional polyols, reacting with isocyanates to produce flexible slabstock polyurethane foam (PUF), elastomer and coating (Narine et al., 2007a, b). Polyol from vegetable oils and lactic, glycolic, or acetic acids, provide bio-based building blocks for further polyurethanes syntheses by reaction with diisocyanates. The obtained polyurethanes are partially bio-based and may be applied as binders and coatings (Boutevin et al., 2012). The use of petrochemical polyols is disadvantageous in terms of production, energy and costs. From both economic and environmental point of view, it is desirable to replace petroleum polyols with renewable resources (Veenendaal, 2007; Petrovic, 2008).

The potential for polyols derived from vegetable oils to replace petrochemical-based polyols began garnering attention beginning around 2004, partly due to the rising costs of petrochemical feedstock and partially due to an enhanced public desire for environmentally friendly green products (Niemeyer et al., 2006). Over the last few decades, polyol derived from petroleum oil as feedstock has been used to produce polyurethane to fulfill the world's needs for this polymer. Recently, a number of studies have been conducted to investigate the use of vegetable oils as a renewable and sustainable feedstock to replace the use of petroleum oil. Many researchers have concluded that vegetable oil can be exploited as an alternative raw material to substitute for petroleum oil to produce polyol. Examples include soybean oil, safflower oil, olive oil, canola oil, cottonseed oil, palm oil and rapeseed oil (Petrovic et al., 2003). It has been reported that that High-functionality polyols for application in polyurethanes were prepared by epoxide ring-opening reactions from epoxidized sucrose esters of soybean oil in which secondary hydroxyl groups were generated from epoxides on fatty acid chains (Pan and Webster, 2012). Vegetable oil-based polyol is a sustainable material which can be efficiently produced. *Ximenia americana* seed oil is a potential feedstock source.

X. americana "Wild plum or Plum" in English or locally called "Tsada" in Hausa and "Chabbuli" in Fulani is a medicinal plant that is bushy and spiny shrub, 4 to 5 m high with an open crown. The fruits are green but turn golden yellow or red when ripe. The fruit when eaten is refreshing and has an almond acid taste. The plant is

found from Senegal to Cameroon including Northern parts of Nigeria (Arbonnier, 2004). *X. americana* is widely spread in tropical Africa and tropical America. It is a medium size deciduous tree which is widely cultivated for its yellow, pleasant acid fruits and as a live fence. The tree has large pencils with small white flowers and plum like fruits, which is up to 3.5 cm long. The tree has leaves with common stalk in the range of 30 to 60 cm long. The leaves are 5.8 cm long and are almost paired up in opposite direction. The flowers are green and usually found between March to April and July to August. The fruit are ellipsoid and are usually 2.5 to 3.5 cm long. They are normally found between April to May and July to August and December (Keay, 1989).

The aim of this research work is to assess the potential of *X. americana* seed oil as a chemical feedstock in the polyurethane industry by chemically modifying the *X. americana* seeds oil through epoxidation process.

MATERIALS AND METHODS

Sample collection and preparation

The fruits of *X. americana* were collected locally from the forest around Yola metropolis. The voucher specimen was identified and authenticated by Dr. D. A. Jauro of Forestry Department, School of Agriculture and Agricultural Technology, Modibbo Adama University of Technology, P.M.B. 2076, Yola. The fruits were then washed, air-dried at room temperature and cracked to remove the hard shell in other to obtain the seed. The seeds were washed with distilled water and air-dried at room temperature, after which they were crushed/pounded using mortar and pestle to paste. The pounded materials were stored in a closed container pending use in the extraction processes.

Extraction of *Ximenia americana* seed oil

The crushed seeds were manually/traditionally treated with hot water and continuously stirred in other to get the oil. The seed oil obtained was stored in closed container prior to epoxidation.

Experimental procedure

The epoxidation process was adapted from Goud et al. (2007). Iodine value was determined by applying the Wijs method (Ketaren, 2005; Siggia, 1963; Sudarmaji et al., 1997). The oxirane content was determined by the method adapted from Siggia (1963).

The calculation of chemicals required for the epoxidation reaction using acetic acid as the oxygen carrier is summarized below. Based on the literature, a typical fatty acid composition profile (Eromosele and Eromosele, 2002) for *X. americana* seed oil is presented in Table 1.

Total mole of *X. americana* seed oil (XASO) is expressed as concentration of double bonds (DB) in the oil \longrightarrow (n_1):

Volume of XASO (V) = 200 ml.

Density of XASO (ρ) = 0.867 g/ml (Eromosele et al., 1993).

Mass of XASO (M) = $\rho \cdot V = (0.867) (200) = 173.4$ g.

Table 1. Fatty acid composition and their molecular weights present in *X. americana* seed oil.

Fatty acids	Molecular formula	Composition (wt %)	Molecular weight (g/mol)
Linoleic	(C ₁₈ H ₃₂ O ₂)	1.34	280.45
Linolenic	(C ₁₈ H ₃₀ O ₂)	10.31	278.43
Arachidonic	(C ₂₀ H ₃₂ O ₂)	0.60	304.47
Eicosatrienoic	(C ₂₀ H ₃₄ O ₂)	3.39	306.48
Erucic	(C ₂₂ H ₄₂ O ₂)	3.46	338.57
Nervonic	(C ₂₄ H ₄₆ O ₂)	1.23	366.62
Oleic	(C ₁₈ H ₃₄ O ₂)	72.09	282.46

$$n \text{ Linoleic acid} = \frac{(0.0134) \times (173.4)}{280.45} = 0.008285$$

$$n \text{ Linolenic acid} = \frac{(0.1031) \times (173.4)}{278.43} = 0.064208$$

$$n \text{ Arachidonic acid} = \frac{(0.006) \times (173.4)}{304.47} = 0.003417$$

$$n \text{ Eicosatrienoic acid} = \frac{(0.0339) \times (173.4)}{306.46} = 0.019180$$

$$n \text{ Erucic acid} = \frac{(0.0346) \times (173.4)}{338.57} = 0.017721$$

$$n \text{ Nervonic acid} = \frac{(0.0123) \times (173.4)}{366.62} = 0.005818$$

$$n \text{ Oleic acid} = \frac{(0.7209) \times (173.4)}{282.46} = 0.442555$$

$$n_{\Sigma} = 0.008285 + 0.064208 + 0.003417 + 0.019180 + 0.017721 + 0.005818 + 0.442555 = 0.56$$

\therefore Total mole of XASO = 0.561 mol.

Acetic acid

Mole ratio of acetic acid to DB = 0.5:1.

Glacial acetic acid (99.5 wt%), molecular weight = 60.05, density = 1.05 g/ml.

Mole of acetic acid (0.5) $n_{\Sigma} = (0.5)(0.561) = 0.281$ mol.

Mass of acetic acid = (0.281)(60.05) = 16.87 gram.

Mass of glacial acetic acid $\left(\frac{100}{99.5}\right) (16.87) = 16.96$ gram

\therefore Volume of glacial acetic acid required = $\frac{16.96}{1.05} = 16.15$ ml

Hydrogen peroxide

Mole of hydrogen peroxide to DB = 1.5:1

Hydrogen peroxide (6 wt%), molecular weight = 34.01, density = 1.10 g/ml.

Mole of hydrogen peroxide = (1.5) (0.561) = 0.842 mol.

Mass of hydrogen peroxide = (0.842)(34.01) = 28.64 gram.

Mass of hydrogen peroxide solution = $\left(\frac{100}{6}\right) (28.64) = 477.33$ g.

\therefore Volume of hydrogen peroxide needed = $\frac{477.33}{1.10} = 434$ ml.

Sulfuric acid catalyst

Mass of sulfuric acid in the mixture is 3% of total mass of hydrogen peroxide and acetic acid.

Sulfuric acid (98 wt. %), molecular weight = 98.08, density = 1.84 g/ml.

Mass of sulfuric acid = $\left(\frac{3}{100}\right) (H_2O_2 + CH_3COOH)$
 $= \left(\frac{3}{100}\right) (28.64 + 16.87) = 1.37$ g.

Mass of sulfuric acid solution = $\frac{1.37}{1.84} = 0.74$ mol.

Determination of iodine value and conversion

In order to determine conversion of iodine value, the iodine value of *X. americana* seed oil was calculated using the following equation:

$$\text{Iodine value} = \frac{(B - S) \times M \times 12.69}{W}$$

Where: S = Volume of Na₂S₂O₃ solution required for titration of the sample (ml), B = Volume Na₂S₂O₃ solution required for titration of the blank (ml), W = Weight of sample used (g), M = Molarity of the Na₂S₂O₃ (0.1M).

Initial value of *X. americana* seed oil (IV₀) expressed as iodine value at t = 0 (h)

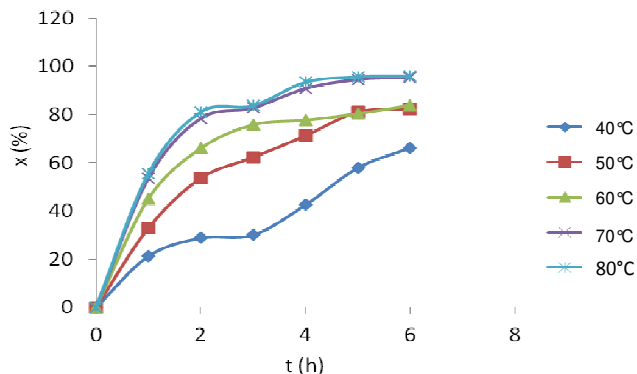


Figure 1. Effects of reaction time (t) on reaction conversion (X) at different temperatures.

$M = 0.10 \text{ M}$, $W = 0.20 \text{ g}$, $B_1 = 19.65 \text{ ml}$, $B_2 = 19.50 \text{ ml}$, $B_3 = 19.65 \text{ ml}$, $B_{AV} = 19.60 \text{ ml}$.

$S_1 = 4.30 \text{ ml}$, $S_2 = 4.35 \text{ ml}$, $S_3 = 4.25 \text{ ml}$, $S_{AV} = 4.30 \text{ ml}$.

$$IV_0 = \frac{(19.60 - 4.30)(0.1)(12.69)}{0.20} = 97.08 \text{ g I/100 goil.}$$

Conversion of iodine value (% x):

$$\% X = (IV_0 - IV / IV_0)(100\%)$$

Where: IV_0 = Initial Iodine Value, IV = Iodine value at certain condition.

1) Calculation at T = 40°C.

a) Reaction time (t) = 1 h

$W = 0.2 \text{ g}$, $S_1 = 7.7 \text{ ml}$, $S_2 = 7.5 \text{ ml}$, $S_3 = 7.6 \text{ ml}$, $S_{AV} = 7.6 \text{ ml}$

$$IV = \frac{(19.60 - 7.6)(0.1)(12.69)}{0.20} = 76.14 \text{ g I}_2/100 \text{ g oil}$$

$$\therefore \% X = \frac{(97.08 - 76.14) \cdot 100\%}{97.08} = 21.57 \%$$

b) Reaction time (t) = 2 h

$W = 0.20 \text{ g}$, $S_1 = 8.7 \text{ ml}$, $S_2 = 8.7 \text{ ml}$, $S_3 = 8.7 \text{ ml}$, $S_{AV} = 8.7 \text{ ml}$.

$$IV = \frac{(19.60 - 8.7)(0.1)(12.69)}{0.20} = 69.16 \text{ gram. I}_2/100 \text{ g oil.}$$

$$\% X = \left(\frac{97.08 - 69.16}{97.08} \right) 100\% = 28.76\%.$$

c) Reaction time (t) 3 h

$W = 0.20 \text{ g}$, $S_1 = 8.90 \text{ ml}$, $S_2 = 8.90 \text{ ml}$, $S_3 = 8.90 \text{ ml}$, $S_{AV} = 8.90 \text{ ml}$.

$$IV = \frac{(19.60 - 8.90)(0.1)(12.69)}{0.20} = 67.89 \text{ g I}_2/100 \text{ g oil}$$

$$\therefore \% X = \left(\frac{97.08 - 67.89}{97.08} \right) 100\% = 30.07 \%$$

d) Reaction time (t) = 4 h

$W = 0.20 \text{ g}$, $S_1 = 10.8 \text{ ml}$, $S_2 = 10.9 \text{ ml}$, $S_3 = 10.7 \text{ ml}$, $S_{AV} = 10.80 \text{ ml}$.

$$IV = \frac{(19.60 - 10.8)(0.1)(12.69)}{0.20} = 55.84 \text{ g I}_2/100 \text{ g oil}$$

$$\therefore \% X = \left(\frac{97.08 - 55.84}{97.08} \right) 100\% = 42.49 \%$$

e) Reaction time (t) = 5 h

$W = 0.20 \text{ g}$, $S_1 = 13.20 \text{ ml}$, $S_2 = 13.10 \text{ ml}$, $S_3 = 13.20 \text{ ml}$, $S_{AV} = 13.16 \text{ ml}$.

$$IV = \frac{(19.60 - 13.16)(0.1)(12.69)}{0.20} = 40.86 \text{ g I}_2/100 \text{ g oil}$$

$$\therefore \% X = \left(\frac{97.08 - 40.86}{97.08} \right) 100\% = 57.91 \%$$

f) Reaction time (t) = 6 h.

$W = 0.20 \text{ g}$, $S_1 = 14.50 \text{ ml}$, $S_2 = 14.55 \text{ ml}$, $S_3 = 14.50 \text{ ml}$, $S_{AV} = 14.52 \text{ ml}$.

$$IV = \frac{(19.60 - 14.43)(0.1)(12.69)}{0.20} = 32.80 \text{ g I}_2/100 \text{ g oil}$$

$$\therefore \% X = \left(\frac{97.08 - 32.80}{97.08} \right) 100\% = 66.21 \%$$

The reaction conversion at 40°C and other reaction temperatures (50, 60, 70 and 80°C) are summarized in Figure 1.

Determination of oxirane oxygen content

The number of oxirane groups indicated by the percentage of oxirane oxygen content was calculated using the equation below:

$$\text{Oxygen content} = \frac{(B - S) \times M \times 16 \times 100}{W \times 1000}$$

Where: S = Volume of Na_2OH used for sample (ml), B = Volume Na_2OH used for blank (ml), M = Molarity of the $\text{NaOH} = 0.1 \text{ M}$, W = Weight of sample used (g), Volume NaOH used for blank (ml).

$B_1 = 18.7 \text{ ml}$, $B_2 = 19.00 \text{ ml}$, $B_3 = 18.8 \text{ ml}$, $B_{AV} = 18.83 \text{ ml}$.

1) Calculation of T = 40°C.

a) Reaction time (t) = 1 h.

$W = 0.2 \text{ g}$, $S_1 = 17.8 \text{ ml}$, $S_2 = 17.6 \text{ ml}$, $S_3 = 17.8 \text{ ml}$, $S_{AV} = 17.73 \text{ ml}$.

$$\% \text{ Oxirane} = \frac{(18.83 - 17.73)(0.1)(16)(100)}{0.20 \times 1000} = 0.88\%.$$

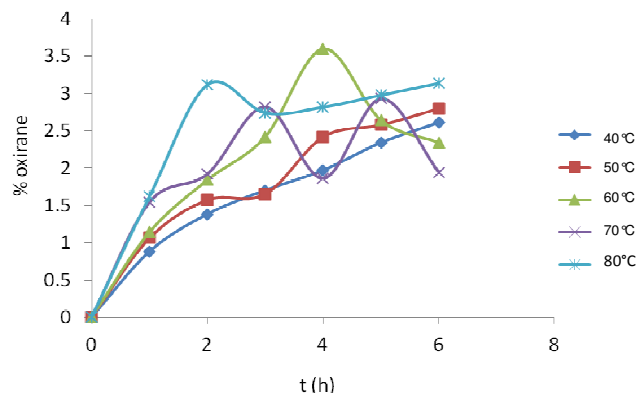


Figure 2. Effects of reaction time (t) on oxirane content (%) at different temperatures.

b) Reaction time (t) = 2 h

W = 0.2 g, S₁ = 17.1 ml, S₂ = 17.2 ml, S₃ = 17.0 ml, S_{AV} = 17.1 ml.

$$\% \text{ Oxirane} = \frac{(18.83 - 17.1)(0.1)(16)(100)}{0.20 \times 1000} = 1.38\%.$$

c) Reaction time (t) = 3 h

W = 0.2 g, S₁ = 16.7 ml, S₂ = 16.7 ml, S₃ = 16.7 ml, S_{AV} = 16.7 ml.

$$\% \text{ Oxirane} = \frac{(18.83 - 16.7)(0.1)(16)(100)}{0.20 \times 1000} = 1.70\%.$$

d) Reaction time (t) = 4 h

W = 0.2 g, S₁ = 16.4 ml, S₂ = 16.3 ml, S₃ = 16.4 ml, S_{AV} = 16.37 ml.

$$\% \text{ Oxirane} = \frac{(18.83 - 16.37)(0.1)(16)(100)}{0.20 \times 1000} = 1.97\%.$$

e) Reaction time (t) = 5 h

W = 0.2 g, S₁ = 15.90 ml, S₂ = 16.0 ml, S₃ = 15.8 ml, S_{AV} = 15.9 ml.

$$\% \text{ Oxirane} = \frac{(18.83 - 15.9)(0.1)(16)(100)}{0.20 \times 1000} = 2.34\%.$$

f) Reaction time (t) = 6 h

W = 0.2 g, S₁ = 15.70 ml, S₂ = 15.50 ml, S₃ = 15.65 ml, S_{AV} = 15.62 ml.

$$\% \text{ Oxirane} = \frac{(18.83 - 15.62)(0.1)(16)(100)}{0.20 \times 1000} = 2.57\%.$$

The amount of oxirane oxygen content at 40°C and other reaction temperatures (50, 60, 70 and 80°C) are summarized in Figure 2.

RESULTS AND DISCUSSION

The iodine value and the oxirane oxygen content are the important properties in the characterization of epoxidized vegetable oils. The iodine value indicates the remaining unsaturation after epoxidation reaction, while the oxirane oxygen content indicates the epoxy groups present in the products. In the preparation of polymer, epoxy resins with a lower iodine value and higher oxirane oxygen content are desired. The iodine values of 6 treatments were reduced. The reductions in iodine values indicated the consumption of the unsaturation during epoxidation, but they did not represent solely conversion to epoxy groups because epoxy rings degradation generates side products.

The effects of reaction time and temperature on iodine value and reaction conversion are shown in Figure 1. The result indicated that the conversion of iodine value in the XASO increases linearly with the rise of reaction time and temperature and at a faster rate with temperature than with reaction time. Unsaturated double bonds present in the oil are converted to oxirane rings through the epoxidation reaction as indicated by the decrease in the iodine value. This value in the XASO represents the concentration of double bonds and it decreases with reaction time. Therefore, the reaction conversion increases with reaction time and temperature.

The effect of reaction time and temperature on oxirane content is shown in Figure 2. The result shows that an oxirane content increase with reaction time and temperature and then that value reaches the maximal level. Following this, the oxirane content decreases with reaction time and temperature. This finding supports previous research with the utilization of cottonseed oil as a raw material to produce epoxidized oil (Dinda et al., 2008). The result can be explained by the fact that through epoxidation reaction, double bonds in the oil were converted to epoxidized oil. Maximum oxirane content of 3.60% was achieved at 4 h reaction time and temperature of 60°C. Hence, the results of this study indicate that the optimal operating condition for epoxidation reaction was achieved at a reaction time of 4 h and a temperature of 60°C.

Another important finding was that at higher reaction times and temperature than the optimal conditions, it will result lower oxirane content. A possible explanation for this observation might be that higher reaction times and temperature favour a high rate of oxirane ring opening thereby producing epoxidized oil with lower oxirane content (Purwanto et al., 2006). Therefore, side reaction products may be formed as the oxirane ring may be decomposed due to reaction mixture contain materials that are likely to react with the oxirane rings such as sulfuric acid, acetic acid and water (Milchert and Smagowicz, 2009).

Reaction temperature higher than 60°C result in a lower lower oxirane content indicated by a reduced amount of

oxirane content with reaction time. This result may be explained by the fact that epoxidation reaction using peroxy acid in this case peroxyacetic acid is highly exothermic (Millchert and Smagowicz, 2009). Hence, higher temperature during the epoxidation may cause the decomposition rate of epoxy groups to be higher than the formation rate. As a result, lower epoxy groups will be produced.

Conclusion

This research report has considered the possibility to use *X. americana* seed oil as a potential feedstock for polyol production to increase its economic value. The optimal condition for epoxidation reaction using peroxyacetic acid was achieved at a reaction time of 4 h and temperature of 60°C. That means, if we epoxidized *X. americana* seed oil following these conditions then subjected the epoxidized oil to hydroxylation reaction, definitely the polyol to be obtained shall be the one with high hydroxyl value (most important requirement for good polyols).

RECOMMENDATION

It is recommended that further research should be undertaken to perform hydroxylation reaction of the epoxidized oil to produce polyol, to perform the epoxidation reaction using a metal catalyst, and to monitor the unsaturation and epoxy groups in the epoxidized oil by fourier transform infrared (FTIR) spectroscopy.

REFERENCES

- Arbonnier M (2004). Trees, shrubs and lianas of West African dry zones. Cirad Margraf Publishers, The Netherlands. pp. 189-426.
- Boutevin B, Caillol S, Desroches M, Boutevin G, Loubat C, Auvergne R (2012). Synthesis of new polyester polyols from epoxidized vegetable oils and biobased acids. Eur. J. Lipid Sci. Technol. 114(12):1447-1459.
- Barret LW, Sperling LH, Murphy CJ (1993). Naturally functionalized triglyceride oils in interpenetrating polymer networks. J. Am. Oil Chem. Soc. 70(5):523-534.
- Cheng OT, Rayson Y (1999). Degredation kinetic of biofluids. Int. J. Lubri. 5:45-50.
- Chian KS, Gan LH (1998). Development of rigid polyurethane foam from palm oil. J. Appl. Polym. Sci. 68(3):509-515.
- Desroches M, Escouvois M, Auvergne R, Caillol S, Boutevin B (2012). From vegetable oils to polyurethanes: synthetic routes to polyols and main industrial products. Polym. Rev. 52:38-79.
- Dinda S, Patwardhan AV, Goud VV, Pradhan NC (2008). Epoxidation of cottonseed oil by aqueous hydrogen peroxide catalysed by liquid inorganic acids. Bioresour. Technol. 99(9):3737-3744.
- Eromosele CO, Eromosele IC (2002). Fatty acid compositions of seed oils of *Haemotostaphisbarteri* and *Ximenia americana*. Bioresour. Technol. 82(3):303-304.
- Eromosele IC, Eromosele CO, Innazo P, Njerim P (1993). Studies on some seeds and seed oils. Bioresour. Technol. 64:245-247.
- Flora EF (2011). Property of polyurethane: from Soy-derived Phosphate Ester. World Academy of science. Eng. Technol. 76:235-238.
- Goud VV, Patwardhan AV, Dinda S, Pradhan N (2007). Kinetics of epoxidation of Jatropha oil with peroxyacetic acid and peroxyformic acid catalysed by acidic ion exchange resin. Chem. Eng. Sci. 62(15):4065-4076.
- Guo A, Zhang W, Petrovic ZS (2006). Structure-property relationships in polyurethanes derived from soybean oil. J. Mater. Sci. 41(15):4914-4920.
- Heidbreder A, Hofer R, Grutzmacher R, Westfechtel A, Blewitt CW (1999). Oleochemical products as building blocks for polymers. Fett/Lipid 101(11):418-424.
- Keay RWJ (1989). Trees of Nigeria. Clarendon Press, Oxford. P. 367.
- Ketaren S (2005). Edible oils and fats, UI-Press, Jakarta. P. 145.
- Lligadas G, Ronda IC, Galia M, Cadiz V (2006). Novel silicon-containing polyurethanes from vegetable oils as renewable resources. Synthesis and properties. Biomacromolecules 7(8):2420-2426.
- Milchert E, Smagowicz A (2009). The influence of reaction parameters on the epoxidation of rapeseed oil with paracetic acid. J. Am. oil Chem. Soc. 86(12):1227-1233.
- Narine SS, Kong X, Bouzidi L, Sporns P (2007a). Physical properties of polyurethanes produced from polyols from seed oils. I. Elastomers. J. Am. Oil Chem. Soc. 84:55-63.
- Narine SS, Kong X, Bouzidi L, Sporns P (2007b). Physical properties of polyurethanes produced from polyols from seed oils: II. Foam. J. Am. Oil Chem. Soc. 84:65-72.
- Niemeyer T, Patel M, Geiger E (2006). "A Further Examination of Soy-Based Polyols in Polyurethane Systems". Salt Lake City, UT: Alliance for the Polyurethane Industry Technical Conference. P. 2-4.
- Pan X, Webster DC (2012). New Biobased High Functionality Polyols and Their Use in Polyurethane Coatings. Chemsuschem. 5(2):419-429.
- Pechar TW, Sohn S, Wilkes GL, Ghosh S, Frazier CE, Fornof A, Long TE (2006). Characterization and comparison of polyurethane networks prepared using soybean-based polyols with varying hydroxyl content and their blends with petroleum-based polyols. J. Appl. Polym. Sci. 101(3):1432-1443.
- Petrovic Z, Guo A, Javni I (2003). Process for the preparation of vegetable oil based polyols and electroinsulating casting compounds created from vegetable oil-based polyols, United States Patent, 6:354-573.
- Petrovic ZS (2008). Polyurethanes from vegetable oils. Polym. Rev. 48(1):109-155.
- Petrovic ZS, Zhang W, Javni I (2005). Structure and properties of polyurethane prepared from triglyceride polyols by ozonolysis. Biomacromolecules, 6(2):713-719.
- Purwanto E, Fatmawati A, Setyoprato P, Junedi, Rosmiati M (2006). Influence of epoxidation reaction period and temperature on the quality of polyol synthesized from soybean oil, in Proceedings of the 13th Regional Symposium on Chemical Engineering 2006 — Advanced in Chemical Engineering and Biomolecular Engineering. Nanyang Technological University, Singapore. pp. 277-279.
- Siggia S (1963). Quantitative organic analysis, 3rd edn, John Wiley & Sons, Inc, New York. P. 103.
- Sudarmaji S, Haryono B, Suhardi D (1997). Analysis procedure for food and agricultural materials, 4th edn, Liberty, Yogyakarta. P. 234.
- Tu Y, Kiatsimkul P, Suppes G, Hsieh F (2007). Physical properties of water-blown rigid polyurethane foams from vegetable oil-based polyols. J. Appl. Polym. Sci. 114(5):2577-2583.
- Veenendaal B (2007). Renewable content in the manufacture of polyurethane polyols-An opportunity for natural oils. Polyurethanes Mag. Int. 4(6):352-359.
- Wang C, Yang L, Ni B, Wang L (2009). Thermal and mechanical properties of cast polyurethane resin based on soybean oil. J. Appl. Polym. Sci. 112(3):1122-1127.