

# Synthesis of Polyol from Sponge Gourd (*Luffa aegyptiaca*) Seed Oil and Production of Polyurethane Foam

Sanusi Sule<sup>1\*</sup>, Isah Mahmood<sup>2</sup> and F.G. Mohammed<sup>3</sup>

<sup>1</sup>Department of Chemistry, Yobe State University, P.M.B 1144, Damaturu, Yobe, Nigeria.

<sup>2</sup>Department of General Health Science, College of Health Technology, P.M.B 0065, Ningi, Bauchi, Nigeria.

<sup>3</sup>Department of Pure and Industrial Chemistry, Bayero University Kano, P.M.B. 3011, Kano, Nigeria.

\*Corresponding author E-mail: [sulesanusi15@gmail.com](mailto:sulesanusi15@gmail.com)

**Abstract**— The use of modified plant oils as a renewable feedstock in the chemical industry has become more desirable as we move towards a carbon-free society. In particular, epoxidized fatty acid derivatives derived from vegetable sources may be utilized as stabilizers and plasticisers in polymer, as lubricant additives and as constituents of polyurethane foams. *Luffa aegyptiaca* oil is a potentially abundant and inexpensive raw material for such products. The synthesis of a polyol product from *Luffa aegyptiaca* involves two key reaction steps, namely: epoxidation followed by hydroxylation. This study considers the optimization of the reaction conditions for the second step where epoxidized *Luffa aegyptiaca* seed oil is converted into a polyol. The hydroxylation reaction was performed in a batch reactor using a mixture of alcohols (methanol and isopropanol) with sulphuric acid as a catalyst. The conversion reaction of epoxidized *Luffa aegyptiaca* seed oil to product polyol is reaction time and temperature dependent. Optimal condition (maximum polyol yield) was achieved with a reaction time of 3h at a temperature of 50°C.

**Keywords**— Epoxidation; hydroxylation; *Luffa aegyptiaca*; oil reaction conversion; polyol; polyurethanes.

## 1. INTRODUCTION

A Polyurethanes are polymers composed of a chain of organic units joined by carbonates (urethane) links. While most polyurethanes are thermosetting polymers that do not melt when heated, thermoplastic polyurethanes are also available. Polyurethanes were first discovered by professor Otto Bayer and co-workers in 1973 and had some uses such as in coating, rigid and non-rigid foam, thermosetting and thermoplastics materials, adhesives and gum rubber (Guo et al., 2006, Wang et al., 2009). Polyurethanes are generally produced from the reaction between polyols and polyisocyanates (Pechar et al., 2006). Polyols are mostly petroleum based products (Tu et al., 2007). The advantage of using renewable resources as the feedstock of production of polyols here is to reduce the demand on non-renewable fossil fuels which are currently being

used by most chemical industries today. Using such will reduce the overall production and emission of gases. The use of agricultural feedstock allows efficient carbon cycle and drastically reduces carbon (IV) oxide (CO<sub>2</sub>) emissions.

Polyols are compounds with multiple hydroxyl functional groups available for organic reaction. A molecule with three hydroxyl group (OH) is triol, one with four is tetraol and so on. Polymeric polyols are generally used to produce other polymers; they are reacted with isocyanates to make mattresses, insulation for appliances (refrigerators and freezers), home and automotive seats. The use of petrochemical polyols is disadvantageous in terms of production, energy and cost; from both economic and environmental point of view. It is desirable to replace petroleum polyols with renewable resources (Veenendaal, 2007; Petrovic, 2008). In synthesis of polyols, unsaturated fatty acid content is an important factor, as double bond is converted to polyols. Iodine value is the amount of (Iodine) in grams absorbed by 100grams of oil or fat (Ketaren, 2005), thus the amount of iodine absorbed indicates the number of double bonds, hence unsaturated fatty acid concentration in the oil. *Luffa aegyptiaca* seed oil is suitable feedstock that can be used as raw material in synthesis of polyol because its iodine value is within 80 – 240g /100gram oil, 96.52g/100gram oil to be precise (Eromosole, 2002) and it has high content of unsaturated fatty acids, (82.40%), (Oleic and Linoleic acid).

This research aims to access the potential of *Luffa aegyptiaca* seed oil as a chemical feedstock in polyurethane industry.

## 2. MATERIALS AND METHODS

### 2.1 Sample Collection and Preparation

The fruits of *Luffa aegyptiaca* were locally collected in Damaturu, Yobe State. The seeds of the *Luffa aegyptiaca* were removed from the sponge, washed with water and dried by air of ambient temperature (37°C). Small unwanted impurities were removed as well. The seeds were crushed using mortar and pestle, the pounded seed is then stored in a closed container pending for use in the extraction process.

## 2.2 Method of Oil Extraction

### 2.3 Soxhlet Extraction

The lipids of the seeds of cherries were extracted using the soxhlet method. A sample of 20g of seeds flour was extracted using diethyl ether as solvent for six (6) hours. The solvent was removed with a rotary evaporator. The residue was placed in a drier and weighed up to constant value. After extraction, the non-soluble portion of the extracted solid remains in the thimble which is discarded afterwards.

### 2.4 Epoxidation Reaction

The epoxidation reaction is conducted in a 500ml flask batch reactor, equipped with agitator, reflux, condenser and thermocouple. The three neck flask is immersed in a heating mantle whose temperature is controlled at 50°C prior to epoxidation reaction, Luffa aegyptiaca seed oil is analysed to determine its initial iodine value. The Luffa aegyptiaca oil is then used as feedstock for the epoxidation stage. The experimental method for the epoxidation step (adapted from Goud, et al., 2007) is that the Luffa aegyptiaca seed oil in amount of 200ml is placed in 500ml three neck flask equipped with reflux condenser. Acetic acid and sulphuric acid were used as catalysts and were added drop-wise into the mixture. This feeding strategy is required to avoid overheating the system as the epoxidation reaction is highly exothermic. The reaction is well mixed by stirring at a speed of 1600RPM under several temperature and reaction times. The product of the reaction is then cooled and decanted to effect a separation of the organic soluble compounds (epoxidized oil) from water soluble phase. The epoxidized oil is then washed with water (in small aliquots) to remove residual contaminants. The product is then analysed to determine its iodine value and oxirane contents.

### 2.5 Epoxidation Test

Summary of the method used is to evaluate the yield from the epoxidation reaction in terms of two key variables, namely iodine value and oxirane content.

#### 2.5.1 Iodine Value Analysis

Iodine value is determined by applying Wiji's method (Ketaren, 2005) the sequence of the procedure is as follows.

#### Procedure

0.5g of the oil was dissolved in 20cm<sup>3</sup> of carbon tetrachloride in 500cm<sup>3</sup> conical flask, 25cm<sup>3</sup> of Wiji's solution was added to the flask containing the oil, and also to each of the two other flask for blanks (without oil), the three flask were then stored in dark place for an hour at room temperature. After an hour, 20cm<sup>3</sup> of potassium iodide (KI) solution and 100cm<sup>3</sup> of water were added into each flask followed by titration with

Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution to a faint yellow coloration. 2cm<sup>3</sup> of starch indicator solution was then added and the titration continued until the blue colour disappears. The titrimetric value observed was used in calculating the iodine value.

#### Preparation of potassium iodide solution

Potassium iodide solution was prepared by dissolving 150g of KI pellet in distilled water and made up to the mark in a liter volumetric flask. Also in the preparation of sodium thiosulphate pentahydrate, 0.1M of sodium thiosulphate pentahydrate solution was prepared by dissolving 2.5g of sodium thiosulphate pentahydrate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.5H<sub>2</sub>O) in distilled water and diluted for 1 minute in a one litre volumetric flask.

#### 2.5.2 Oxirane Oxygen Analysis

The oxirane content of the epoxidized oil must be quantified to determine the conversion of unsaturated bonds in Luffa aegyptiaca seed oil to oxirane groups. The procedure (adapted from Siggia, 1962) is as follows: 0.2g of epoxidized oil was added into a flask, 5ml of ethyl ether is used to wash the flask side and 10ml of hydro chlorination reagent (0.2M HCl in ethyl ether) was added into the flask, simultaneously a blank solution was prepared using identical procedure. The mixture was then allowed to stand for 3 hours at ambient temperature. The mixture was then titrated with standard 0.1M sodium hydroxide solution. Phenolphthalein was used as indicator.

### 2.6 Hydroxylation Reaction

The hydroxylation reaction was conducted in 1000ml glass reactor, equipped with stirrer, reflux condenser and thermocouple. The reactor was then placed on a heating plate with temperature control. The procedure for hydroxylation reaction (adapted from Petrovic et al., 2003) is as follows: 150ml of epoxidized oil was hydroxylised using a mixture of alcohols (methanol and iso propanol), water mixed with the epoxidized oil and sulphuric acid catalyst in the reactor. The reaction was conducted at several fixed temperature and reaction times. Polyol was produced after the reaction, the product was washed with warm water (in small aliquots) to remove contaminants and then decanted to effect the separation of the organic soluble compounds (polyol) from water soluble ones. The resulting polyols formed from the hydroxylation process was then analysed using two key parameters, the hydroxyl value and the viscosity of the product.

### 2.7 Hydroxylation Test

The summary of the techniques used for evaluation of the hydroxylation step in form of hydroxyl value and viscosity.

### 2.7.1 Hydroxyl Value Analysis

The hydroxyl content of hydroxylated oil (polyol) must be determined as the hydroxyl value of *Luffa aegyptiaca* seed oil based – polyol is a key measure of the quality of the resulting polyols product. The procedure was adapted from the work of (Kataren, 2005). Prior to this, the saponification value of the sample was determined before and after the acetylation process. In the acetylation process, the hydroxyl groups in the oil are converted to ester then analysed in terms of their saponification value before and after the acetylation process to determine the amount of hydroxyl groups. In the acetylation process, 20ml of oil sample was mixed with 20ml of acetic anhydride in a flask. The mixture was then boiled for 2hours. Following this, 50ml of distilled water was added into the mixture and the mixture was subjected to heat and boiled for 15 minutes. The mixture was allowed to cool and then washed with water so as to effect separation from the mixture. Subsequently, 50ml of water was added again to the mixture and boiled for 15 minutes. This procedure was repeated several times until the washing water becomes clear. After the washing water was separated, acetylated oil was then dried over sodium sulphate anhydrous and then filtered.

### Saponification value

The solution of alcoholic potassium hydroxide solution was prepared by dissolving 14g of KOH pellet in 100ml of methanol.

### Procedure

To a 250cm<sup>3</sup> flask, 5.0g of the sample was transferred into 50ml of methanolic potassium hydroxide solution. The mixture was refluxed with occasional shaking until the oil dissolved completely. The heating continued for further one hour. The mixture was then titrated to a phenolphthalein end point with 0.5M Hydrochloric acid. A blank titration was carried out using the same quantity of potassium hydroxide solution at the same time and under the same condition. The titration reading for the saponification of the oil was obtained and the colour change of the end point was pink to colourless.

### 2.7.2 Viscosity

The viscosity of the *Luffa aegyptiaca* seed oil was determined using a simple viscometer.

### Procedure

A tube was connected to the arm of the viscometer, the smaller bulb. The viscometer was then damped to the rector stand; water was then poured into the viscometer as a standard through the arm with the large bulb. The pipe was sucked to draw in water into the small bulb, and the flow rate (time of flow was determined). The same procedure was applied for *Luffa aegyptiaca*

seed oil and the flow rate which is the viscosity was obtained.

## 3. RESULTS AND DISCUSSION

### 3.1 Result of Analysis of *Luffa aegyptiaca* Seed Oil

Under epoxidation reaction, two tests were carried out to confirm the yield of the epoxidized oil. The tests are the iodine value test and oxirane oxygen analysis. The epoxidation reaction was carried out at various temperature and reaction time in order to have optimal operating condition. The results below are the optimal result gotten from the experiment.

#### 3.1.1 Iodine Value of *Luffa aegyptiaca* Seed Oil before Epoxidation Reaction

$$\begin{aligned} \text{Average titre value} &= 30.08\text{cm}^3 \\ \text{Blank average titre value} &= 50.05\text{cm}^3 \end{aligned}$$

$$\text{Iodine value } IV_0 = \frac{Mw \times M (V_2 - V_1)}{W \times 10}$$

$$\begin{aligned} \text{Where } Mw &= \text{Molecular weight of Na}_2\text{S}_2\text{O}_3 \\ M &= \text{Molar concentration of Na}_2\text{S}_2\text{O}_3 \\ V_2 &= \text{Titre value for blank} \\ V_1 &= \text{Titre value for sample titration} \\ W &= \text{Weight of oil used} \end{aligned}$$

$$IV_0 = \frac{248 \times 0.1 (50.5 - 30.8)}{0.5 \times 10}$$

$$IV_0 = \frac{248 \times 0.1 \times 19.7}{5}$$

$$IV_0 = 97.71\%$$

#### 3.1.2 Iodine Value of *Luffa aegyptiaca* Seed Oil After Epoxidation Reaction

$$\text{Average titre value} = 39.00\text{cm}^3$$

$$\text{Blank average titre value} = 50.5\text{cm}^3$$

$$\text{Iodine value } IV = \frac{MW \times M (V_2 - V_1)}{W \times 10}$$

$$IV = \frac{248 \times 0.1 (50.5 - 39.0)}{0.5 \times 10}$$

$$IV = \frac{248 \times 0.1 \times 11.5}{5}$$

$$IV = 57.04\%$$

Conversion of iodine value (%X)

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

$$\%X = \frac{97.71 - 57.04}{97.71} \times 100\%$$

$$\%X = \frac{40.67}{97.71} \times 100\%$$

$$\%X = 41.62\%$$

### 3.1.3 Oxirane Oxygen Content

$$\text{Blank average titre} = 18.82\text{cm}^3$$

$$\text{Average titre value} = 15.22\text{cm}^3$$

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

B = Volume of NaOH used for blank

S = volume of NaOH used for sample

M = Molarity of NaOH

W = Weight of Sample

$$\% \text{ Oxirane} = \frac{18.820 - 15.22 \times 0.1 \times 16 \times 100}{0.2 \times 100}$$

$$= 2.88\%$$

### 3.2 Hydroxylation Reaction

Two tests were also carried out as well, which were hydroxyl value analysis (which is a key measure of the quality of resulting polyol product) and viscosity value of the *Luffa aegyptiaca* seed oil.

#### 3.2.1 Hydroxyl Value Analysis

$$\text{Average titre value} = 35.7\text{cm}^3$$

$$\text{Blank average titre value} = 86.75\text{cm}^3$$

$$\text{Saponification value } SV_A = \frac{Mw \times m (V_2 - V_1)}{W}$$

Where Mw = Molecular weight of KOH  
 M = Molar concentration of KOH  
 V<sub>2</sub> = Titre value for blank  
 V<sub>1</sub> = Titre value for sample Titration  
 W = Weight of oil used

$$SV_A = \frac{56.11 \times 0.5 (86.75 - 35.7)}{5}$$

$$= 286.442 \text{ mg/g}$$

#### 3.2.2 Saponification Value after Acetylation Process.

$$\text{Average titre value} = 45.7\text{cm}^3$$

$$\text{Blank average titre value} = 86.75\text{cm}^3$$

$$\text{Saponification value } SV_B = \frac{Mw \times m (V_2 - V_1)}{W}$$

$$SV_B = \frac{56.11 \times 0.5 (86.75 - 45.67)}{5}$$

$$SV_B = \frac{56.11 \times 0.5 \times 41.08}{5}$$

$$SV_B = 230.499\text{mg/g}$$

$$\text{Hydroxyl value} = \frac{SV_A - SV_B}{1 - (0.000755 SV_A)}$$

$$= \frac{286.442 - 230.499}{1 - (0.00075 \times 286.422)}$$

$$= \frac{55.943}{0.785}$$

$$= 71.265\%$$

#### 3.2.3 Viscosity of Hydrolysed Oil

Average viscosity value = 224.86 sec

#### 3.2.4 Formation of Polyurethane Foam

The hydroxylised oil (polyol) and poly isocyanates which are liquid at room temperature were reacted. The reaction which produced a solid polymer is rapid and substantially completed within two minutes. The solid product can generally be handled within five minutes from the start of mixing, although rates can be varied enormously by the choice of catalyst and its concentration. The reaction is exothermic – the heat generated may be used to vaporize a liquid ‘blowing agent’ such as fluorocarbon, when the reacting chemicals will polymerized and expand to produce polyurethane foam. Alternatively, some water may be incorporated in the polyol so that it reacts with the poly-isocyanates to release carbon dioxide gas. The reaction which produces polyurethane foam may be summarized as;

[Polyol + water and/or a liquid blowing agent + catalyst (s)] + poly isocyanates = Polyurethane foam.

### 3.3 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 product. In the preparation of polymer, epoxy results with lower iodine value and higher oxirane oxygen content are desired. The iodine value of the treatments was reduced. The reduction in iodine values indicated the consumption of the unsaturation during epoxidation, but they did not represent solely conversion of epoxy groups because epoxy rings degradation generates side products. The effects of reaction time and temperature on iodine value and conversion of *Luffa aegyptiaca* seed oil increases linearly with the increase in reaction time and temperature and at a faster rate with temperature than reaction time.



Therefore, the reaction conversion increases with reaction time and temperature.

The optimal operating condition is 4h reaction time and 60°C. The effect of reaction time and temperature on oxirane content shows that oxirane content increased with reaction time and temperature and then the value reaches the maximum 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 2.88% was achieved at 4h reaction time and temperature of 60°C.

Another important finding was that at higher reaction times and temperature than optimal conditions, it will result lower oxirane content. A possible explanation for this observation might be that higher reaction times and temperature favours 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 sulphuric acid, acetic acid and water (Mill Chet and Smagowicz, 2009).

The hydroxyl content of hydroxylated oil (polyol) was determined as the hydroxyl value is a key measure of the quality of the resulting polyurethane foam. The result also shows that hydroxyl value increase with reaction time and temperature and then the value reaches a maximal level. The optimal operating condition for hydroxylation is 3h time and 50°C temperature.

The viscosity of the polyol is also useful, as it determines the yield and quality of the resulting polyurethane foam. Generally, high viscosity means better quality product.

Finally, the polyurethane foam can be moulded to various forms by addition of colouring agents for example.

#### 4. CONCLUSION

This research has considered the possibility to use *Luffa aegyptiaca* seed oil as potential feedstock for polyol production to increase its economic value. The optimal operation conditions were ascertained in order to have best possible yield. The optimal condition for epoxidation reaction was at 4h and temperature of 60°C

while the optimal condition for hydroxylation reaction was at 3h and temperature of 50°C. The work determined that the conversion of the epoxidized *Luffa aegyptiaca* seed oil to product polyol (as measured by the hydroxyl value) reaches a maximum and then falls as unwanted by-products are produced.

#### REFERENCES

- [1] Eromosele, C.O. and Eromosele, IC. (2002). Fatty acid composition of seed oils of *Haemotostaphis barteri* and *Ximenia americana*. *Biores. Tech.*, 82(3): 303-304.
- [2] Guo, A., Zhang, W. and Petrovic, Z.S. (2006). Structure-property relationships in polyurethanes derived from soybean oil. *Journal of Materials Science*, 41(15): 4914-4920.
- [3] Goud, V.V., Pateardhan, A.V., Dinda, S. and Pradhan, NC. (2007a).
- [4] Epoxidation of karanja (*Pongamia glabra*) oil catalyzed by acidic ion exchange resin. *European Journal of Lipid Science and Technology*. 109(6): 575-584.
- [5] Hanna, J.G. and Siggia, S. (1962), Primary and secondary hydroxyl group content of polypropylene glycols. *J. Polym. Sci.*, 56: 297-304.
- [6] Ketaren, S. (2005). *Edible oils and fats*, UI-Press, Jakarta.
- [7] Milchert, E & Smagowicz, A 2009, 'The influence of reaction parameters on the epoxidation of rapeseed oil with peracetic acid', *Journal of the American Oil Chemists' Society*, vol. 86, no. 12, pp. 1227-1233.
- [8] Pechar T.W., Sohn, S., Wilkes, G.L, Shosh, S., Frazier, C.E., Fornof, A. and Long T.E. (2006). Characterization and comparison of polyurethane networks prepared using soybean-based polyols with varying hydroxyl content and their blends with petroleum-based polyols. *Journal of Applied Polymer Science*, 101(3): 1432-1443.
- [9] Petrovic, Z.S. (2008). Polyurethanes from vegetable oils. *Polymer Reviews*, 48(1): 109-155.
- [10] Petrovic Z., Guo, A. and 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, pp6, 354, and 573.
- [11] 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.

- [12] Dinda S, Anand V. Patwardhan, Vaibhav V. Goud and Narayan C. Pradhan, Epoxidation of cottonseed oil by aqueous hydrogen peroxide catalysed by liquid inorganic acids , Bioresource Technology, Volume 99, Issue 9, Pages 3737-3744, June 2008.
- [13] Siggia, S 1963, Quantitative organic analysis, 3th edn, John Wiley & Sons, Inc, New York.
- [14] Tu, Y., Kiatsimkul, P., Suppes, C. and Hsieh, F. (2007). Physical properties of water blown rigid polyurethane foams from vegetable oil-based polyols. Journal of Applied Polymer Science, 114(5): 2577-2583.
- [15] Wang, C., Yang, L., Ni, B. and Wang, L. (2009). Thermal and Mechanical Properties of Ast Polyurethane Resin based on soybean oil. Journal of Applied Polymer Science, 112(3): 1122-1127.
- [16] Veenendaal, B. (2007). Renewable content in the manufacture of polyurethane polyols- An opportunity for natural oils, Polyurethanes Magazine international 4(6): 352-359.



**UIJRT**