

Review Article

A Review of Processes Used In Polyol Synthesis from Vegetable Oils

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Abstract: Polyol resins are high molecular weight highly crosslink polymer with hydroxyl functionality, they are found useful in polyurethane and surface coating industries. They are basically two methods used in synthesis of polyol from vegetable oils, notably direct hydroxylation (one-step synthesis) and two-step synthesis via epoxidation and alcoholysis, with the two-step method commonly used. The focus of this paper is to review the development in the last decade on the synthesis of polyol from vegetable oils with specific focus on the various syntheses methods that have been adopted in production of polyol from vegetable oils, the review showed that the two-step synthesis method commonly used in the production of polyol from vegetable oil have some drawbacks associated with it when compared with the one-step synthesis method, though the one-step synthesis method is not without some drawbacks, but is more advantageous compare with the former in polyol production. The review also pointed out some of the drawbacks of the two-step synthesis method, the advantage associated in producing polyol using one-step synthesis and the synthesis of higher polyhydric alcohol from vegetable oil using the one-step process that could substitute polyol derivatives used in akyd-resin modification and surface coatings.

Keywords: one-step synthesis, two-step synthesis and polyol yield

INTRODUCTION

Polyol are polymer resins with a high molecular weight and highly cross-linked, with two or more hydroxyl functionality. They find there application in polyurethane industries which exist as a large area that covers multiple applications, polyurethane are polymers that are commonly use as elastomer, coating, adhesive, thermoplastic, thermoset and foams but for the flexible, semi-rigid and rigid[1-4]. Most polyol are commonly produced using petrochemical feedstock, the polyol synthesized from this feedstock are associated with a lot of drawbacks when compare with the polyol produce from bio-source. Some of the drawbacks associated with petroleum base polyol are the negative impact the product have on the environment, the energy and high cost required to produce it, unlike the bio-base polyol this drawbacks are highly minimize. Owing to the advantage bio-base polyol have over petroleum based polyol, research are geared toward developing a suitable synthetic route that will be best use for synthesizing vegetable oil base polyol. Research pointed out that they have been a significant improvements on the methods use in synthesizing vegetable oil polyol[5-7], different methods have earlier been used in polyol synthesis from vegetable oil, the use of transesterification process, a reaction between vegetable oil and polyhydric

compound such as glycerol was reported, although this reaction was noted to require high temperature and long reaction time[8]. They are two common methods of synthesizing polyol which are; two-step process and one-step process, several researcher adopted the two-step process which involve two stages, epoxidation and hydroxylation, in the epoxidation stage per-acid is form by reacting peroxide with acetic acid, which attacks the unsaturated portion of the fatty acid in vegetable oil to form epoxide before hydroxylating with a polyhydric to produce polyol. The one-step process use in polyol production from vegetable oil takes place in the present of osmium tetra-oxide as catalyst and an oxidant.

The objective of this paper is to review the development in the last decade on the methods adopted in synthesizing polyol from vegetable oil.

POLYOL APPLICATION AREA AND TECHNOLOGIES

Application area

The common application of polyol are in polyurethane production and as a copolymer in polyester synthesis[2], it is also a component use for making urethane elastomers. Polyurethane formulated by the composition of the polyol and urethane or isocyanate find its application in the following systems

- Thermoplastic and thermoset
- Foam (flexible, semi rigid, rigid)
- Metal and textile coating/linings
- Adhesives etc

Application technologies

The problem associated with formulating polyurethane from polyol depend on accurately calculating weight in percent of the polyol and other additives such as extender and diisocyanate needed to get a polyurethane elastomer of an expected mechanical properties. The product is synthesized through a formulated calculation using the mole ratio of isocyanate/polyol, this is mixed with other additive like extender and fire retardant in a calculated formulation in other to produce a polyurethane with the desired mechanical properties[9].

Different processes of polyol synthesis

They are basically two common methods of synthesizing polyol from vegetable oil, they are as follow.

- One-step process (direct hydroxylation)
- Two-step process (via epoxidation and hydroxylation)

In both processes, the feedstock (vegetable oil) must be highly unsaturated.

Reaction mechanism

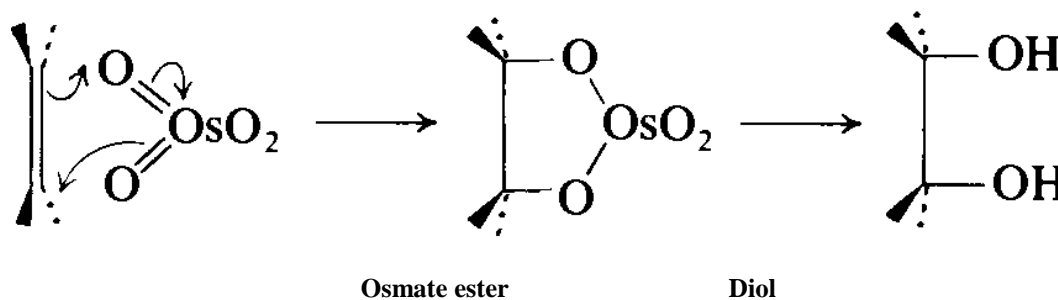


Figure 1: Reaction mechanism

Method2.

Two-step process

This process takes place step-wise in two-step process namely epoxidation and hydroxylation.

1st step (epoxidation)

In this step, a per-acid reacts with the unsaturated portion of the fatty acid in the vegetable oil at temperature between 40-60°C for 4-5hrs. The mixture is allowed to cool to room temperature and transferred into a separating funnel, this is also allowed to stand for 6-8hr after which a layer of the spent acid is formed at the top which is then decanted leaving the oil.

SYNTHESIS OF POLYOL

Method 1

One-step process (direct hydroxylation)

This process mostly takes place in the presence of osmium tetra-oxide (OsO_4) as a catalyst and hydrogen peroxide as oxidant, however the hydroxylation takes place in the unsaturated functional group of the oil. The process is effected by using a small amount of osmium tetra-oxide together with hydrogen peroxide, this results to a cleavage, forming the first osmate ester and then a diol, the catalyst is regenerated and used in hydroxylating the other unsaturated group in the oil. The synthesis of soybean polyol by direct hydroxylation was carried out using osmium tetra-oxide (OsO_4) as catalyst and 4-Methylmorphine N-oxide (NMO) as oxidant in a one-step hydroxylation process [1], it pointed out that increase in catalyst loading enhance the hydroxyl value and also the effect of the MNO oxidant on the degree of hydroxylation was investigated. In figure 1 below, the osmium tetra-oxide catalyst is first dissolved in an inert solvent such as (ether or dioxane) in the presence of an oxidant before reacting with the unsaturated functionality present in vegetable oil. This process forms a cyclic osmate ester as a reaction intermediate which subsequently undergoes hydrolytic cleavage to give two molecules of hydroxyl per an unsaturated functional group present in the oil.

The epoxidized oil is then neutralized with carbonate and purified with a solution NaCl and carbonate.

2nd step (hydroxylation)

The purified epoxidized oil is reacted with polyhydric alcohol in the presence of a catalyst for 4-5hr at temperature 40-60°C to open up the epoxy-ring and fused the hydroxyl group from the polyhydric compound. This is subsequently neutralized with carbonate and purified with solutions of NaCl and carbonate to have a purified polyol.

Table 1: The disadvantage of two-step over one-step process in polyol synthesis.

s/no	Two- step process	One-step process (direct hydroxylation)
1.	High concentration of lewis acid used as catalyst tend to cause undesired side reactions such as trans-esterification and cross-linkage	Increase in concentration of osmium tetra-oxide (OSO ₄) as catalyst enhances the hydroxylation process with high hydroxyl value
2.	Purification of the epoxidized oil is carried out to remove the undersired side product that will hinder the hydroxylation process	Purification is not carried out as the process of epoxidation is by-passed.
3.	Low product yield	High product yield
4.	Long reaction time	Shorter reaction time
5.	The end polyol product show high viscosity , lower hydroxyl value and low grade product	The synthesized polyol shows low viscosity, high hydroxyl value and generally improved quality product.
6.	The catalyst used are consumed and not regenerated	The catalyst are regenerated and re-used

CONCLUSION

The objective of this paper is to review the development in the last decade on the synthesis of polyol from vegetable oil with emphasis on the various syntheses methods that have been adopted in polyol production. This review shows that they are two methods use in polyol synthesis namely one-step synthesis process (direct hydroxylation) and two- steps synthesis process via epoxidation and alcoholysis (hydroxylation) with the two-step process commonly used. The review pointed out that the two-step process have some drawbacks associated with it when compared with one-step process, some of this drawback are i. long reaction time ii. Low yield iii. High cost of production and low grade polyol. The one-step process reduces some of this shortcomings as this syntheses route tend to avoid any undesired side reaction such as trans-esterification and cross-linkage associated with the two-step process during the epoxidation stage. The problem of undesired side reaction common to the two-step process lead to low product yield, as some of the product are converted to other undesired product, however, after the epoxidation stage, to minimize this side reactions, the product is subjected to purification process in other to remove the spent acid and other impurities, this is not completely eliminated. This paper establish that it is better to use one-step process (direct-hydroxylation) over two-step synthesis process in synthesis of polyol from vegetable oil as it is generally more advantageous.

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