Vegetable Oils, Animal Fats, Carbohydrates and Polyols

1.1 Introduction

This chapter describes polyols in detail, including diols, the chemical components of which are obtained from sources other than crude oil.

The polyols are used in the manufacture of commercial polymers and polyurethanes, for example.

Among the major natural chemicals from which polyols can be derived are:

- Vegetable oils
- Fish oils
- Animal fats
- Carbohydrates

For industrial purposes vegetable oils and carbohydrates are the most approachable sources of chemicals. Work on polyols derived from animal fats can be found in the patent literature [1].

Those products are, quite rightly, described as green products because they originate from natural sources, the production of which humans can control almost at will. They are renewable because, in contrast to crude oil, they originate from non-depletable sources. Their availability is not the monopoly of some countries which possess vast amounts of oil reserves. Agricultural products require the right weather conditions to grow as well as an area large enough for them to be cultivated on.

The first detailed studies on the use of vegetable oils and animal fats in polyurethane technology date back to the late fifties and early sixties.
Among the reasons given for utilizing polyols from natural sources were:

- Since a favorable price differential exists for castor oil over most polyesters, information concerning the properties of various castor urethane foams should be useful to manufacturers and consumers of expanded foams [2].
- Dimer acids are commercially available and are produced by the polymerization of polyunsaturated fatty acids derived from soybean, cottonseed, and linseed oils. Less expensive polyols should result from the condensation of ethylene oxide with dimer acid [3, 4].
- The properties of the castor oil-based foams (PU) are comparable to those of foams obtained from more costly polyols [5].
- A large potential market exists for polyols from natural sources in the rapidly expanding urethane foam industry [6].

In general, the price of oil (Figure 1.1) used to produce the components of polyether and polyester polyols is determined by speculation largely founded on the production policies of the OPEC cartel.

Unfortunately, the pricing of basic carbohydrates or bean oils generally is not much different from that of crude oil.

Soybean oil futures are traded at the Chicago Futures Market, where the price of soybean oil is still lower than that of petroleum (Figure 1.2).

This means that, triglycerides, even if considered renewable sources of chemicals, are subject to speculative pricing the same way crude oil is. However, the difference is that their production is not restricted to only a

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**Figure 1.1** Crude oil (petroleum) price chart (1 barrel of crude ~ 140 kg) [7].
few countries. Bean oil, or carbohydrate cartels, will be difficult to establish and organize on a global scale. This trading approach does not exclude speculative price hikes similar to those of crude oil.

Polyols based on renewable raw materials, such as fatty acid triglycerides, sugar, sorbitol, glycerol and dimer fatty alcohols, are already used in diverse ways as raw materials in the preparation of polymer chemicals.

It is claimed that soybean-oil-based polyols cost less than the petro-lem polyols they replace, because they require considerably less energy to produce; can be used in a broad range of polyurethane applications; and produce polyurethane products with equivalent or better physical characteristics [8].

In any event, polyols manufactured from petrochemical sources constitute the majority of the polyols, polyesters as well as polyethers used in industry.

Another source of polyols has emerged from the co-polymerization of CO$_2$ and epoxides [9].

### 1.2 Sustainability

During the last few years, the term sustainability has been mentioned repeatedly in published articles, speeches, presentations as well as in company reports, to say the least. This was not the case when fluorocarbons, for example, were widely used as blowing agents in the polyurethanes industry. Many decades have elapsed since their deleterious effect on the ozone layer was discovered.
The negative effect of CO$_2$ on the atmosphere and the migration of bisphenol A from polycarbonate utilized in feeding bottles are additional examples which indicate that the consequences of chemicals are spotted only after a type of specific damage has already been inflicted on the environment, the economy, human health, etc.

According to the *Cambridge Dictionary*, the verb “to sustain” has the following meanings:

- To allow something to continue for a period of time; *(The economy looks set to sustain its growth into next year.)*
- To keep alive; *(Many planets are unable to sustain human or plant life.)*
- To experience; *(The company has sustained heavy losses this year.)*
- To support emotionally.

A succinct but detailed definition of the name derived from the verb “to sustain,” i.e., sustainability is given in Wikipedia. Accordingly, “Sustainability is the process of maintaining change in a balanced fashion, in which the exploitation of resources, the direction of investments, the orientation of technological development and institutional change are all in harmony and enhance both current and future potential to meet human needs and aspirations.”

Not long ago, the course of the polyurethanes industry was sluggish. Sustainability studies carried out by some multinationals pointed to the closure of old isocyanate plants. A few months later, the state of the economy changed. The polyurethanes market picked up and the same plants, instead of being shut, were upgraded. Ironically, a short time later, the same companies showed poor earnings because the market did not follow the predicted growth trend. But this is not the exception.

The biobased chemicals market has recently seen the collapse of bio-succinic acid producer BioAmber, despite the numerous reorganizations aimed at reviving the sales of the company. A year before the company was shut, BioAmber was planning a seven-fold increase of its production capacity. According to their management, the business plan the company put forward to its creditors was sustainable.

Succinic acid is a dicarboxylic acid widely used in the manufacture of polyester polyols. The manufacturing process from natural sources proves to be expensive, even if the science involved is brilliant. Therefore, the profit margins generated to sustain its production must be high. BioAmber’s capacity was 30 Ktpa, but the returns did not justify the operation of the company.
Whereas the applications of succinic acid in the polymers industry are well known, the production of polyols from natural sources has only recently gained momentum. Their successful inclusion in current technologies will show whether their use is sustainable. There is no need to use a polyol produced from palm or rapeseed oil in a polyurethane formulation if its contribution to the properties of the end product does not offer any economic or qualitative appeal to the consumer.

There is no doubt that the final outlet of all industrial and agricultural products are aimed at the direct or indirect consumption by humans. The higher the production rates, the more energy will be required by the production processes. A simple mathematical model will certainly prove that sustainability as well as cyclic economy will be convincingly achieved and implemented, at least, when the growth of the world population will be controllable. But this is a very difficult target to attain.

1.3 Polyols from Vegetable Oils

Vegetable oils have been known to mankind since prehistoric times. Humans have used fats and oils for food, healing and other ends. Over the years, the extraction of oils from agricultural products has been elaborated.

Nowadays, for some polymerization purposes, many vegetable oil molecules must be chemically transformed in order to include hydroxyl groups in their structure.

For instance, soybean oil does not contain any hydroxyl groups but has an average of 4.6 double bonds per triglyceride molecule. The unsaturation of the vegetable oil molecule can accommodate hydroxyl groups. However, many reactions for preparing polyols from vegetable oils are not very selective.

By-products are created during the transformation. Furthermore, many conventional methods of preparing polyols from vegetable oils do not produce polyols having a significant content of hydroxyl groups, and the available methods do not produce products having a desirable viscosity. Greases or waxes often result as a consequence of such chemical transformations.

1.3.1 Polyols from Triglycerides

Chemically, vegetable oils are defined as triglycerides (also called glyceryl trialkanoates) because they are esters of glycerol and fatty acids (Figure 1.3).

The structures in Figure 1.4 put the glyceride definition in a broader context.
In practice, the carboxylic acid moieties are not all the same, but mixtures of several ones, as shown in Figures 1.3 and 1.4. They are also present in different triglyceride molecules in variable ratios. The acids are called fatty because their structure is similar to the acidic constituents of triglycerides found in fats. Fats are solid triglycerides whereas oils are liquids. The carboxylic acids are monobasic with a long hydrocarbon tail chain. Fatty acids, as shown in Figure 1.5, can be fully saturated but they can also contain unsaturated sites as well as hydroxyl groups (ricinoleic acid for example).

Further down in the text, it will be shown how unsaturated triglycerides are hydroxylated.

The hydroxylated compounds can be made useful, for example, in the formation of urethanes, by reacting the hydroxyl groups with isocyanates. Coatings, adhesives, elastomers, foams and composites can be made from elastomers using such hydroxy functional compounds.

For example, in a first step an excess of a diisocyanate, such as MDI or TDI, the structures of which are shown in Figure 1.6, is reacted with a hydroxyl-containing triglyceride, such as castor oil, so as to form a pre-polymer containing an excess of isocyanate groups [10, 11].

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**Figure 1.3** Products resulting from the hydrolysis of triglycerides.

**Figure 1.4** The definition of glycerides reflects the number of esterified hydroxyl groups of glycerol.

**Figure 1.5** Structures of some saturated and unsaturated fatty acids.
Those free NCO groups originate either from free isocyanates or from the reaction products of castor oil with TDI (or MDI), as shown in the reaction scheme in Figure 1.7.

By reacting the isocyanate mixture with water in the presence of an amine catalyst a foamed product is obtained, because of the evolution of CO$_2$. The reaction is shown in Figure 1.8.

**Figure 1.6** Chemical structures of some commercial aromatic diisocyanates.

**Figure 1.7** Reaction products of castor oil with an excess of 2,4-toluene diisocyanate (TDI).
Polyols obtained from triglycerides are very often propoxylated and/or ethoxylated with propylene oxide or ethylene oxide respectively in order to increase their molecular weight and subsequently their chain flexibility. The structure of each alkylene oxide is shown in Figure 1.9.

An example of such a polyol synthesis is described below [12]:

First, 267.2 g castor oil and 5.73 g KOH are flushed with nitrogen in an autoclave at 110°C with stirring. Then, 747.3 g of propylene oxide are added. After a reaction time of 4 h, 186.8 g ethylene oxide is metered under pressure. After 1 h, the contents of the reactor are cooled to 40°C and neutralized by the addition of 132 g distilled water and 32.4 g, 11.85% sulfuric acid. After addition of 0.65 g Irganox 1076 (antioxidant), dehydration is carried out in vacuo and the mixture is heated thoroughly for 3 h at 110°C and then filtered.

The OH number of the product is 51.7 mg KOH/g, and the viscosity at 25°C is 500 mPas.

The reaction sequences of the above-described experiment are shown in Figure 1.10. It should be noted that propoxylation leads to alcohols with secondary hydroxyl end groups for steric reasons. Ethoxylation, in turn, introduces primary OH groups, which are more reactive towards carboxylic acids and isocyanates.

Therefore, in order to synthesize a completely biobased polyol, chemicals such as propylene oxide and ethylene oxide must also emerge from natural sources. This text will examine if such a process is feasible.

Nevertheless, the final polyurethane cannot be defined as fully biobased as long as the isocyanate component is aromatic. The source of aromatics being, until now, petrochemical.

The same argument is valid for other technologies where polyols originating from natural sources are constituents of thermosets, such as unsaturated polyesters, for example.

![Chemical structures of ethylene and propylene oxide.](image)

**Figure 1.8** Reaction of isocyanate with water.

**Figure 1.9** Chemical structures of ethylene and propylene oxide.
The U.S. Federal Procurement Process has provisions which may favor products which are biobased over those that are petroleum-based. For example, for wall construction, the U.S. Department of Agriculture (USDA) has proposed a minimum biobased content of 8% to be classified as a biobased product for federal procurement purposes. Furthermore, in the United States, again, the Code of Federal Regulations (CFR Title 7 Part 2902) details guidelines for designating biobased products for federal procurement. In this guideline, the preferred procurement product must have a biobased content of at least 7%, based on the amount of qualifying biobased carbon in the product as a percent of the weight (mass) of the total organic carbon in the finished product. The guideline is specifically for spray-in-place plastic foam products designed to provide a sealed thermal barrier for residential or commercial construction applications [13].

The biobased content is determined according to ASTM D6866. ASTM D6866-08 includes Standard Test Methods for Determining the Biobased Content of Solid, Liquid, and Gaseous Samples Using Radiocarbon Analysis.
1.3.2 Polyols from Glycerol

Synthetic glycerol is manufactured on an industrial scale mainly from the hydrolysis of epichlorohydrin, as shown in Figure 1.11 [14].

Since glycerol forms the backbone of triglycerides, it is produced upon their saponification or transesterification. This method is a preferred green method, epichlorohydrin being an unsafe product.

Glycerol has been used as such in rigid foam formulations, even if its efficiency as well as its role are very often doubtful. The reactivity of the secondary OH group is low compared to the reactivity of the primary OH groups. The use of glycerol in spray foam formulations contributes to the volume/equivalent weight requirements of the polyol and the isocyanate components. Glycerol is also used in the manufacture of triols through propoxylation and ethoxylation.

Those triols have applications in rigid as well as in flexible polyurethane foams.

For example, Voranol 9815 is a glycerol initiated polyoxypropylene polyoxyethylene (propoxylated and then ethoxylated to introduce primary OH groups) polyol having an average hydroxyl number of 28, which is available from the Dow Chemical Company.

Voranol CP 4702 is a glycerol initiated polyoxypropylene polyoxyethylene polyol having an average hydroxyl number of 32.

Voranol CP 3001 is a glycerol initiated polyoxypropylene polyoxyethylene polyol having an average hydroxyl number of 56.

These polyols are used in flexible foam formulations because of their low OH value or high molecular weight.

On the other hand, Daltolac R 570 is a rigid foam, glycerol initiated polyoxypropylene polyoxyethylene triol produced by Huntsman. Its OH value is 570 mg KOH/g.

![Figure 1.11](image-url) Reactions involved in the synthesis of epichlorohydrin.
Glycerol has become the source of diols, such as 1,3-propane diol, through a fermentation process (Figure 1.12) first developed in the 19th century [15].

DuPont and Genencor have developed an *Escherichia coli* (*E. coli*) strain capable of producing 1,3-propanediol (PDO) from glucose. However, glucose is not the only component of corn.

DuPont and Tate & Lyle have developed a fermentation system that converts corn sugar into propanediol (“BioPDO”). Such a bioprocess is more energy efficient than conventional petrochemical processes (conversion of propylene into propanediol). The bioprocess has smaller environmental impact, lower operating costs, smaller capital investment, and greater sustainability due to the use of renewable corn feedstock [16].

1,3-Propanediol is also a monomer employed in the industrial production of polyester fibers [17] and diols for polyurethanes. It has been used as a chain extender in thermoplastic polyurethanes [18].

1,3-Propane diol can also be condensed with biobased succinic acid to produce polyester diols [19], as shown in Figure 1.13. The diols can be reacted with a chain extender like butane diol to give a thermoplastic polyurethane.

Biobased 1,3-propane diol is used by DuPont to manufacture the more resilient and comfortable Sorona polyester. This polypropylene terephthalate has applications in apparel, upholstery, home fashions, and carpets.

![Figure 1.12 Propane diol obtained from the fermentation of glucose and glycerol.](image)

![Figure 1.13 Synthesis of a thermoplastic polyurethane.](image)
1.4 Polyols from Carbohydrates

Carbohydrates are renewable, which makes them an attractive source of chemicals. The main sources of carbohydrates are:

- Ligno-Cellulosics (Lignin, Cellulose, Hemicellulose)
- Sucrose
- Starch

Carbohydrates bear hydroxyl groups and can therefore be regarded as a viable source of polyols.

1.4.1 Ligno-Cellulosics

Lignocellulose refers to plant biomass that is composed of cellulose, hemicellulose, and lignin. The percentage of each constituent of lignocellulose is shown in Figure 1.14.

Cellulosic biomass can be pretreated with dilute sulfuric acid to recover high yields of sugars directly from hemicellulose and, subsequently, by enzymatic hydrolysis of the residual cellulose.

1.4.2 Cellulose

Cellulose is the most common organic compound on Earth. Its structure is shown in Figure 1.15. About 33% of all plants is cellulose (the cellulose content of cotton is 90% and that of wood is 50%).

![Lignocellulose composition.](image-url)
For industrial use, cellulose is mainly obtained from wood pulp and cotton. It is mainly used to produce cardboard and paper. To a lesser extent, it is converted into derivative products such as cellophane and rayon.

Cellulose is composed of linear chains of covalently linked glucose residues. Chemically, it is very stable. It is extremely insoluble. Cellulose chains form crystalline structures called microfibrils. A microfibril with a diameter of 20–30 nm contains about 2000 glucose molecules. Cellulose undergoes the following basic reactions.

### 1.4.2.1 Hydrolysis

Acids attack the acetal linkages, cleaving the 1-4-glycosidic bonds. Since acetals are quite stable toward alkali, hydrolysis at high pH requires very vigorous conditions. Cellulose is also degraded by cellulase enzymes. Termites and fungi digest cellulose, but the synthetic process of obtaining ethanol from cellulose remains slow. The drawback is the sluggish rate at which the cellulose enzyme complex breaks down tightly bound cellulose into sugars, which are then fermented into ethanol.

### 1.4.2.2 Oxidative Degradation

In general, oxidation of cellulosic hydroxyls forms aldehydes, ketones, and carboxyl groups. Strong oxidizing agents and/or vigorous reaction conditions convert cellulose into CO₂ and H₂O.
1.4.2.3 Thermal Degradation

The applied temperature determines the nature of the degradation products. At low temperatures the degradation products are water, CO, CO$_2$ and a carbonaceous char. At high temperatures, depolymerization of the cellulose chain takes place. Anhydroglucose derivatives, volatile organic materials and tars are formed. At still higher temperatures, more-or-less random bond cleavage of cellulose and intermediate decomposition products results in formation of a variety of low molecular weight compounds.

The conversion of cellulose to glucose is described in several patents [20–23]. For example, a mixture of coniferous wood chips is heated at 200°C in the presence of water, CaCl$_2$ and HCl. The conversion of cellulose to glucose is 80.5%. Other products formed include 5-hydroxymethylfurfural, xylose and furfural. Their structures are shown in Figure 1.16.

1.4.3 Hemicellulose

Hemicellulose consists of shorter chains of 500–3000 sugar units as opposed to 7000–15000 glucose molecules per polymer chain present in cellulose. Its main constituent carbohydrate molecules are shown in Figure 1.17.

![Figure 1.16 Products resulting from the hydrolysis of coniferous chips.](image)

![Figure 1.17 Some monomers of hemicellulose. Xylose is always the sugar present in the largest amount.](image)
In contrast to cellulose that is crystalline and resistant to hydrolysis, hemicellulose has a random, amorphous structure with little strength. It is easily hydrolyzed by dilute acids or bases as well as by hemicellulase enzymes.

1.4.4 Lignin

Lignin is found in the cell walls of plants. Lignin constitutes approximately 30–35 wt% of the dry weight of softwoods, about 20–25% of hardwoods and 15–20% of non-woods. Lignin is a branched phenolic natural biopolymer primarily composed of three phenylpropanoid building units (Figure 1.18).

It is obtained industrially in large quantities especially from kraft pulping processes in the form of “black liquor.” Because of the abundance of OH groups in their structure, certain lignins can function as polyol components in polyurethane systems. They are mainly used in combination with other polyols [24, 25].

**Example [26]:**

In this procedure, 300 parts of a lignin produced from a solvent pulping process and 700 parts of a polyether polyol are mixed. This mixture is heated to 93°C to improve the rate of dissolution. The mixing is continued until a dark solution results. Its viscosity is 1532 centistokes at 38°C.

In addition, depolymerization of lignin is a viable route for the preparation of low molecular weight products such as polyols, for the preparation of polyurethanes, phenol formaldehyde resins and epoxy biomaterials [27–30].

![Figure 1.18 Lignin and its components.](image)
1.4.5 Sucrose

Sucrose (table sugar or saccharose) is a disaccharide of glucose and fructose. The chemical structures of the latter are shown in Figure 1.19.

Sucrose, the chemical structure of which is shown in Figure 1.20, is extracted from sugar cane or sugar beet and then purified and crystallized.

Polyols with a sucrose initiator have eight hydroxyl groups. They are obtained from the propoxylation/ethoxylation of sucrose. Because of their high functionality they are used in rigid polyurethane foam applications.

The preparation of the first alkoxylated sucrose polyols is disclosed in several references [31–33]. A general reaction scheme is shown in Figure 1.21.

In an early patent, the propoxylation of sucrose was carried out as follows:

About 4.76 kg of sucrose is dissolved in 1 liter of water. About 120 g of KOH is added and the mixture is heated close to boiling. Then 4.85 kg of propylene oxide is added under pressure over a period of 3 h. This is followed by the addition of another 4.85 kg of propylene oxide over

![Figure 1.19 Chemical components of sucrose.](image)

![Figure 1.20 Chemical structure of sucrose.](image)
Vegetable Oils, Animal Fats, Carbohydrates and Polyols

17

a period of 1 h and 45 min. The resulting polyol has a hydroxyl value of 455.1 mg KOH/g and a viscosity of 140 000 cP.

Daltolac R 585 (Huntsman) is a sucrose amine-initiated polyol for rigid polyurethane foam. Its OH value is 585 mg KOH/g and its viscosity is 3500 mPa.s at 25°C.

The arguments which have already been mentioned above concerning polyols derived from triglycerides, also hold for sucrose-based polyols.

- First, sugar futures are traded in commodity exchanges. Therefore, the price of sucrose is subject to speculation. Price variations of sugar as well as rapeseed oil, which is also a source of biobased polyol, over a six-month period are shown in Figure 1.22 and Figure 1.23.
- Second, the polyols, which are derived from sucrose, involve ethoxylation and propoxylation.

Therefore, unless ethylene oxide (EO) or/and propylene oxide (PO) originate from green sources, the polyol itself can hardly be defined as entirely biobased.

![Figure 1.21 Propoxylation of sucrose.](image)

![Figure 1.22 Sugar monthly price variations [7].](image)
Initiators, such as sucrose, are not the only chemical component and, consequently, the sole components influencing the price of polyols. Propylene oxide as well as ethylene oxide and eventually their precursors propylene and ethylene respectively contribute to the final price of the polyol. Ethylene oxide (oxirane) is prepared industrially by the direct oxidation of ethylene, as represented in Figure 1.24.

On the other hand, propylene oxide is traditionally produced via the conversion of propylene to chloropropanols as shown in Figure 1.25. The reaction produces a mixture of 1-chloro-2-propanol and 2-chloro-1-propanol, which is then dehydrochlorinated. The reaction is shown in Figure 1.26.

The other general route (PO-SM or Propylene Oxide-Styrene Monomer) to propylene oxide involves the co-oxidation of propylene and ethyl benzene. In the presence of catalyst, air oxidation occurs as follows (Figure 1.27).

In April 2003, Sumitomo Chemical commercialized the first PO-only plant in Japan, which produces propylene oxide from the oxidation of

$$7 \text{CH}_2=\text{CH}_2 + 6 \text{O}_2 \rightarrow 6 (\text{CH}_2\text{CH}_2)\text{O} + 2 \text{CO}_2 + 2 \text{H}_2\text{O}$$

**Figure 1.23** Rapeseed oil monthly price [7].

$$2 \text{H}_3\text{C}-\text{CH}=\text{CH}_2 + \text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{C}-\text{CH}(\text{Cl})\cdot\text{CH}_2\text{OH} + \text{H}_3\text{C}-\text{CH}(\text{OH})\cdot\text{CH}_2\text{Cl}$$

**Figure 1.24** Synthesis of ethylene oxide.

$$\text{H}_3\text{C}-\text{CH}(\text{OH})\cdot\text{CH}_2\text{Cl} + \text{OH}^- \rightarrow \text{H}_3\text{C}$$

**Figure 1.25** Synthesis of chloropropanols.

$$\text{H}_3\text{C} + \text{Cl}^- + \text{H}_2\text{O}$$

**Figure 1.26** Synthesis of propylene oxide.
Vegetable Oils, Animal Fats, Carbohydrates and Polyols

CH$_3$CH=CH$_2$ + Ph-CH$_2$CH$_3$ + O$_2$ → CH$_3$[(CHCH$_2$)O] + Ph-CH=CH$_2$ + H$_2$O

**Figure 1.27** PO-SM route to propylene oxide.

cumene without significant production of other products. The reaction scheme is shown in Figure 1.28.

In March 2009, BASF and Dow started their new HPPO (Hydrogen Peroxide-PO) plant in Antwerp, Belgium. In this process, propylene is oxidized to propylene oxide. The reaction is shown in Figure 1.29.

1.4.6 Starch

Many crops, such as maize, rice, wheat, potato, etc., are a source of starch.

Starch is made of glucose molecules attached by α-(1,4) bonds, with some branching by means of α-(1,6) bonds, as shown in Figure 1.30. The degree of branching depends on the source of the starch.

1.4.6.1 Glucose

Glucose (dextrose) is produced commercially via the enzymatic hydrolysis of starch. Its propoxylation leads to a pentol. The whole set of reactions is shown in Figure 1.31 and Figure 1.32.
Glucose can be propoxylated in the presence of cationic catalysts (BF3, HBF4).

On the other hand, the α methyl glucoside is propoxylated in the presence of KOH or tertiary amines to yield the corresponding tetrol, as shown in Figure 1.33.

Finally, as shown in Figure 1.34, the steam cracking of glucose leads to several low molecular weight diols which are useful in the manufacture of thermoplastics as well as thermosets.

1.4.6.2 Sorbitol

The structure of sorbitol and its stereoisomer mannitol are shown in Figure 1.35. It is obvious that the presence of hydroxyl groups makes them eligible as initiators for the synthesis of polyols.
Sorbitol is produced through the catalytic hydrogenation of dextrose \((\alpha-D\text{-glucose, }\alpha-D\text{-glucopyranose})\), as exemplified in Figure 1.36.

Polyols for rigid polyurethane foams are obtained from the propoxylation/ethoxylation of sorbitol. For example, Daltolac R 475 (Huntsman) is

\[
\begin{align*}
\text{Sorbitol} & \quad \text{Mannitol is a sorbitol stereoisomer}
\end{align*}
\]

Figure 1.33  Synthesis of a tetrol from the propoxylation of methylated glucose.

Figure 1.34  Flow sheet for glucose cracking [34].

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\]

Figure 1.35  Chemical structures of sorbitol and mannitol.
Biobased Polyols for Industrial Polymers

a sorbitol-initiated polyol. It has an OH value of 475 mg KOH/g. Its viscosity is very high (15000 mPa.s at 25°C).

The average functionality of sorbitol-based polyols can be reduced by using a mixture of sorbitol and glycerol as initiators of the propoxylation reaction.

Daltolac R 440 (Huntsman) is a sorbitol/glycerol-initiated polyol. It has an OH value of 437 mg KOH/g. Its viscosity is 1650 mPa.s (25°C).

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9. W. Hinz, E.M. Dexheimer, E. Bohres, G.H. Grosch, Process for the copolymerization of alkylene oxides and carbon dioxide using suspensions

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**Figure 1.36** Reduction of D-glucose (dextrose) to sorbitol.

10. S.R. Detrick and E. Barthel, Cellular plastic materials which are condensation products of hydroxy containing fatty acid glycerides and arylene diisocyanates, United States Patent US2787601 assigned to DuPont, April 1957.


