Green Glycols and Polyols

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Report Abstract
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INTRODUCTION

Polyols are compounds containing many hydroxyl groups, while glycol is the term designated for a compound that specifically contains two hydroxyl groups (i.e., a diol). Both glycols and polyols have very important commercial value as they are used as precursors to make important polymers. Ethylene glycol and propylene glycol are two of the most important glycols and the glycol sections of this report will focus on these compounds. The polyols that this report focuses on are those employed in the production of polyurethanes (an incredibly useful polymer with thousands of commercial applications).

Ethylene glycol or monoethylene glycol (MEG) is used in a wide range of commercial applications. Its use in the formulation of coolants (e.g., antifreeze) is well known. However, its largest volume use however is in the production of the large volume polyester, polyethylene terephthalate (PET). PET, of course, is used to make a wide range of products including fibers used in textiles manufacture.

Propylene glycol (PG) also has a broad spectrum of uses including functional fluids (e.g., antifreeze), foods/drugs/cosmetics, liquid detergents, plasticizers, paints and coatings, tobacco humectants, pet foods, etc. The largest market segment however, is in the production of unsaturated polyesters, which are resins used in fiberglass-reinforced structures and surface coatings.

Biodiesel production has given rise to the co-production of vast quantities of crude glycerol. As a consequence, a great deal of research has and is being conducted to try to make value-added molecules from this crude glycerol (typically containing 20 percent water and residual esterification catalyst), as an alternative to disposal by incineration. One of these value-added processes is the production of propylene glycol.

There are two main classes of polyols, polyether polyols and polyester polyols, used in the manufacture of polyurethane.

Polyether polyols represent a range of products produced by the oxyalkylation of discrete polyfunctional initiators or starters. The resulting polyol products vary considerably depending on the initiator system, product molecular weight, and the oxides utilized for the oxyalkylation. Polyether polyols provide unusually high hydrolytic stability and good low-temperature flexibility. Their viscosity is relatively low. They are hampered by susceptibility to degradation by light (ultraviolet radiation) and by oxygen when hot. Both antioxidants and UV stabilizers are used to counteract these forms of degradation. The growth in demand for polyether polyols is largely a function of growth in polyurethane foam usage. Flexible and semi-rigid foams constitute the major portion of the cellular demand for polyethers. In addition to the dominance of the cellular market by the flexible foams, another factor is the higher proportion of polyol (about 69 weight percent) in flexible foam formulations, compared to about 35 percent polyol in rigid foam formulations. Rigid foams have been growing at higher rates than flexible foams, due to increased utilization of rigid urethane in insulation and structural applications.
Polyester polyols provide superior mechanical properties, such as tensile strength, abrasion, and wear resistance, as well as solvent and oil resistance, to the polyurethanes in which they are used.

Making plastics “greener” usually involves replacing some of their petrochemical constituents with alternatives derived from sources other than petroleum. Sometimes the alternative can come from recycled plastics, other times from bio-based chemicals. Polyurethanes are increasingly taking the latter route. For years, some of the urethane formulations used in reaction-injection molding has made use of soy-oil-based polyols. Now, suppliers of urethane foams have likewise developed polyols based on soybeans or other oil seeds (e.g., castor oil, sunflower oil, and rapeseed oil).

**CONVENTIONAL TECHNOLOGY**

Descriptions of the conventional technology for the production of polyols and glycols are given, including:

- Ethylene Oxide and Ethylene Glycol
- Propylene Oxide and Propylene Glycol
- Polypropylene glycols
- Polyether polyols and polyester polyols

Higher Functional Polyols of interest for polyurethane foams generally are based on starters with a functionality of three or higher. Flexible foams usually employ tri-functional polyols, while higher-functional polyols are principally used in the production of rigid foams. Chemistry and process technology for the following are outlined:

- Glycerol-Derived Polyols
- Trimethylolpropane-Started Polyols
- Polyols with Functionality Greater than Three, i.e., Pentaerythritol-Started Polyols; Sorbitol-Started Polyols; Sucrose-Started Polyols
- Polyols Containing Nitrogen or Phosphorous, i.e., Toluenediamine-Started Polyols; Phosphoric Acid-Started Polyols; Acrylonitrile Graft Polyols

**BIOTECHNOLOGY**

The fermentation technologies considered in this report are based on first generation fermentation routes using a variety of raw materials (mainly corn, sugarcane or wheat); these technologies are well established with raw materials used strongly dependant on regional conditions. Second generation bio-technologies from biomass are still in their infancy and are the focus of Research Development, Demonstration and Implementation efforts around the globe.

The following bioproduction technologies are covered in the report:

- Bioethanol
• Bioethylene
• Biopropylene
• Bio-ethylene oxide glycol - employing bio-ethylene produced from bio-ethanol, both bio-ethylene oxide and bio-ethylene glycol can be produced employing conventional EO/MEG technology
• Bio-Propylene Glycol - routes from glycerol
• Biopolyols

Recent Patents and Published Work covering “green” technology to polyols is included in the report.

**ECONOMICS**

Costs of production estimates are presented for bioglycols and biopolyols, and their bio-precursors. Specifically, cost estimates for the following processes have been evaluated:

- Bioethanol production via corn dry milling
- Bioethylene production via Integrated Ethanol Dehydration (fixed-bed)
- Bioethylene oxide production via bioethylene Oxidation
- Bio-ethylene glycol production via bioethylene Oxidation
- Biopropanol production via glycerol hydrogenation
- Bio-Propylene production via biopropanol dehydration
- Bio-propylene oxide production via hydrogen peroxide to propylene oxide (HPPO) technology
- Bio-propylene glycol production via Glycerol hydrogenolysis
- Glycerol-based 3 000 molecular weight (MW) bio-propylene oxide polyol production via alkoxylation of glycerol starter
- Glycerol-based 5000MW bio-propylene oxide polyol with 5 percent bio-ethylene oxide end cap production via alkoxylation of glycerol starter
- Glycerol-based 5000MW bio-propylene oxide polyol with 20 percent bio-ethylene oxide (Chain + End Cap) production via alkoxylation of glycerol starter
- Trimethylol propane based 3 000 MW bio-propylene oxide based polyol production via alkoxylation of trimethylolpropane starter
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- Acrylonitrile polymer production containing bio-propylene oxide polyol via acrylonitrile grafting to trifunctional polyol
- Phosphoric acid-based bio-propylene oxide polyol (250 OH NO., 672 MW) production via alkoxylation of phosphoric acid starter
- Sorbitol-based bio-propylene oxide polyol (460 OH NO., 732 MW) production via alkoxylation of sorbitol starter
- Sucrose-based bio-propylene oxide polyol (460 OH NO., 976 MW) production via alkoxylation of sucrose starter
- Toluenediamine-based bio-propylene oxide polyol (633 OH NO., 354 MW) production via alkoxylation of toluenediamine starter

All cost tables given in this report include a breakdown of the cost of production in terms of raw materials, utilities direct and allocated fixed costs, by unit consumption and per metric ton and annually, as well as contribution of depreciation to arrive at a cost estimate (a simple nominal return on capital is also included)

COMMERCIAL ANALYSIS

Ethylene glycol is a key raw material to the production of the large volume polyester polyethylene terephthalate (PET). PET is converted to staple and filament fibers used in textiles and industrial applications. PET resins are used to produce film and packaging materials with the major use being the fabrication of bottles for carbonated soft drinks. Other smaller, but growing applications include single serve milk, fruit/sports drinks, alcoholic beverages, especially beer, and health care products/cosmetics.

Ethylene glycol is also formulated into coolants, mainly used as antifreeze in the transportation market. This includes the use of antifreeze in the original equipment market (OEM) and in the aftermarket, often by individual vehicle owners, service stations, and lubrication shops. Other formulations of ethylene glycol are used as coolants and heat transfer agents in the industrial market and as aircraft and runway deicers. Ethylene glycol is used as a general-purpose solvent in a diverse application range.

- Ethylene glycol supply, demand and trade data is given and discussed for North America, Western Europe, and Asia Pacific. A list of plants in each region is given showing specific plant capacities, owning company, location and annual tonnage produced is given.

Propylene glycol has a broad spectrum of uses including unsaturated polyesters, functional fluids, foods/drugs/cosmetics, liquid detergents, plasticizers, paints and coatings, tobacco humectant, pet foods, etc. As can be seen in the figure below, the largest market segment is unsaturated polyesters, which are resins used in fiberglass-reinforced structures and surface coatings. Fiberglass-reinforced structures are used in the construction (tub/shower units), marine (boat hulls), and transportation (sheets) industries. Dicyclopentadiene-based resins offer competition.
Global Propylene Glycol Demand

- Functional Fluids: 21%
- Unsaturated Polyesters: 34%
- Others\(^{(1)}\): 16%
- Liquid Detergents: 11%
- Food/Drugs/Cosmetics: 18%

Total = 1.6 Million Metric Tons per Year

\(^{(1)}\) Includes pet foods, plasticizers, paints and coatings, tobacco humectant, etc.

- Global supply, demand, and trade for propylene glycol is given and discussed. A list of global plants is given showing specific plant capacities, owning company, location and annual tonnage produced is given.

- Polyether Polyols supply, demand and trade data is given and discussed for North America, Western Europe, and North-East Asia. A list of plants in each region is given showing specific plant capacities, owning company, location and annual tonnage produced is given.
Nexant, Inc.
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