



CHAPTER II

BACKGROUND AND LITERATURE REVIEW

2.1 Glycerol

Glycerol was discovered more than two centuries ago by the Swedish chemist (Scheele, 1742). He heated a mixture of lead oxide (PbO) and olive oil, which renamed “sweet oil”. The French chemist (Chevreul, 1786) established the structure of fats as triesters made up three moles of mixed fatty acids and one mole of “sweet oil”, which renamed “glycerine”. Glycerol is the common name of the organic compound which consists of a chain of three carbon atoms with each of the end carbon atoms bonded to two hydrogen atoms (C-H) and a hydroxyl group (-OH), and the central carbon atom is bonded to a hydrogen atom (C-H) and a hydroxyl group (-OH). Glycerol have many common name such as glycerin, glycerine, glyceritol, glycy alcohol, 1,2,3-propanetriol, 1,2,3-trihydroxypropane. Its chemical formula is $C_3H_5(OH)_3$ and chemical structure is shown in Figure 2.1.

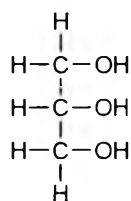


Figure 2.1 Chemical structure of glycerol.

Glycerol is a colorless, odorless, hygroscopic, and sweet-tasting viscous liquid. Glycerol is a sugar alcohol and has three hydrophilic alcoholic hydroxyl groups that are responsible for its solubility in water and alcohol, but insoluble in ether, chlorinated solvents, hydrocarbon and oils. Moreover, it is non-toxic and biodegradable. It has a pleasant taste and odor, which makes it an ideal ingredient in food and cosmetic application.

Glycerol occurs in combined form in all animal and vegetable fats and oils. It usually presents as a tri-ester combined with such fatty acids as stearic, oleic, palmitic, and lauric acids. Normally, glycerol from animal fats give better yield than vegetable oils.

Glycerol can be obtained from two main sources:

- Manufacture of glycerol from natural fats and oils
- Manufacture of glycerol from petrochemical and carbohydrate raw materials

2.1.1 Manufacture of Glycerol from Natural Fats and Oils:

2.1.1.1 Soap Manufacture

Soap is made from reaction of fats or oils with caustic soda.

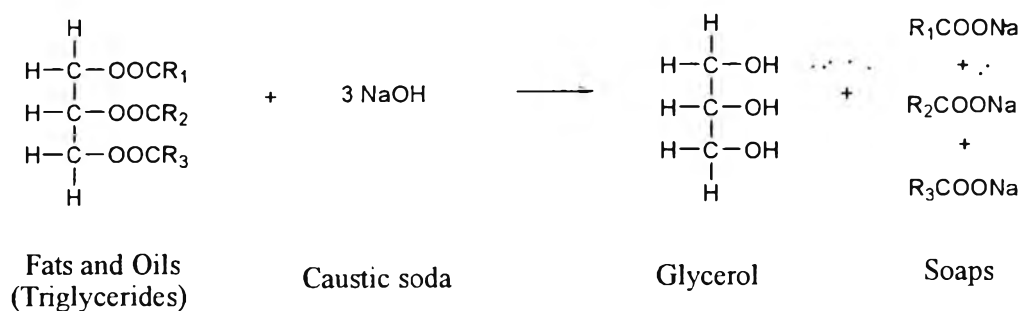


Figure 2.2 Reaction of soap manufacture.

2.1.1.2 Fatty Acid Production

Production of fatty acids by fat splitting (hydrolysis) is shown in Figure 2.3.

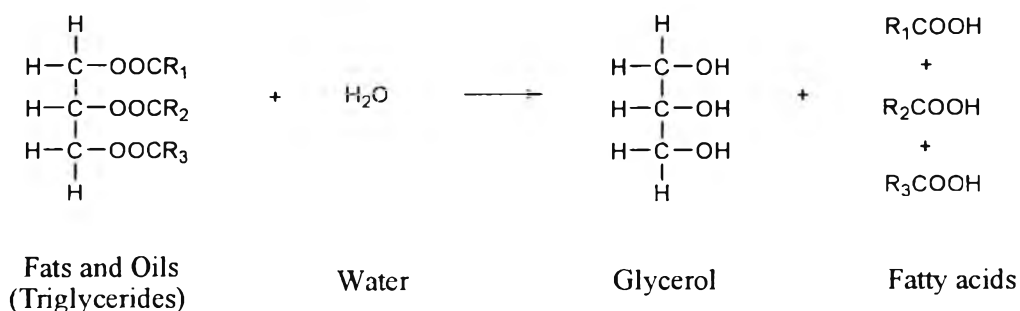


Figure 2.3 Reaction of fatty acid production.

2.1.1.3 Fatty acid methyl ester Production

Glycerol can be synthesized from vegetable oil via treatment with methanol (CH₃OH) and a catalytic base such as potassium hydroxide (KOH). Glycerol is produced as a by-product of biodiesel synthesis.

The purification of the lower glycerol phase involve neutralization, separation of unreacted methanol, dilution with wash liquid stream coming from methyl ester washing, splitting of soaps and final concentration up to 80%. Partially refined glycerol can be delivered as such to specialized distillers.

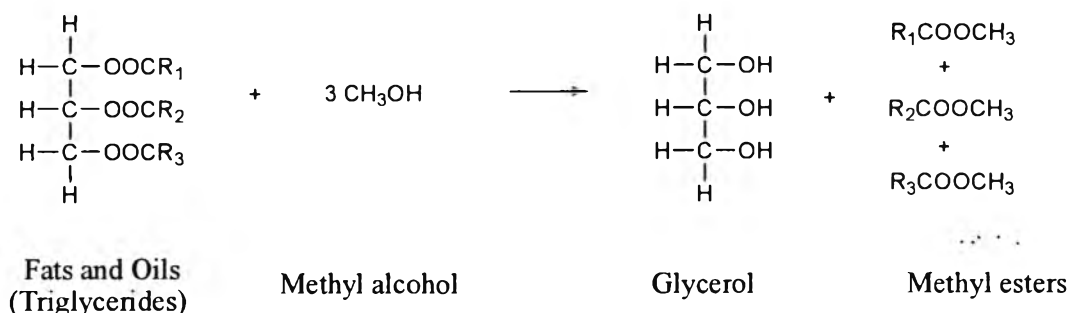


Figure 2.4 Reaction of fatty acid methyl ester Production.

2.1.2 Manufacture of Glycerol from Petrochemical and Carbohydrate Raw

Materials

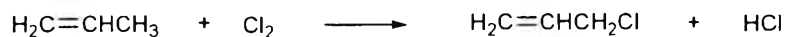
2.1.2.1 Process for Synthesis Glycerol from Petrochemical Raw Materials

Petrochemical Raw Materials such as propylene, allyl chloride, epichlorohydrin, glycerol chlorohydrins, acrolein, or allyl alcohol.

Process for synthesis glycerol from propylene via the following intermediates:

- The "Epichlorohydrin Route" Process Description

Chemical reactions:



Allyl chloride

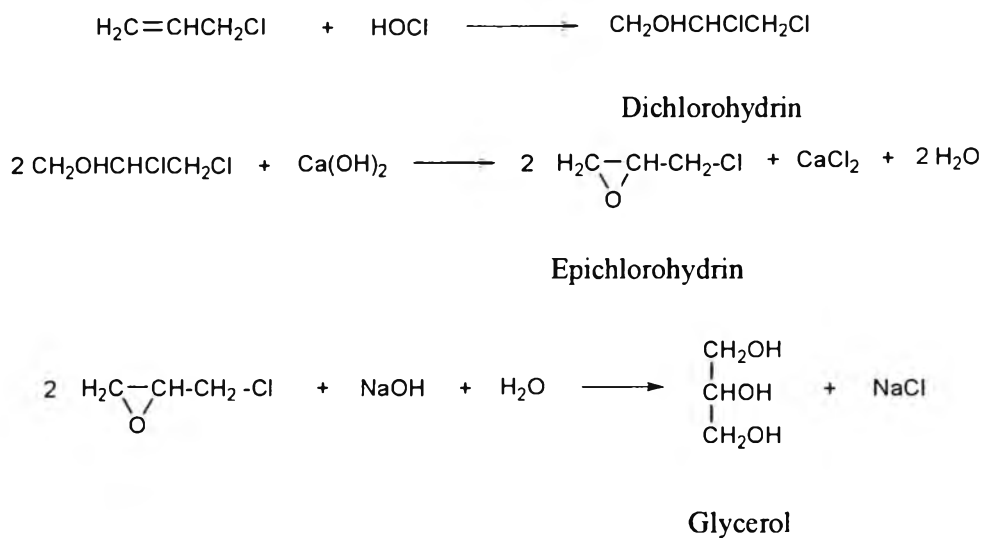


Figure 2.5 The “Epichlorohydrin Route” process description.

- The “*Nonhalogen Route*” from Propylene via Acrolein

Chemical reactions:

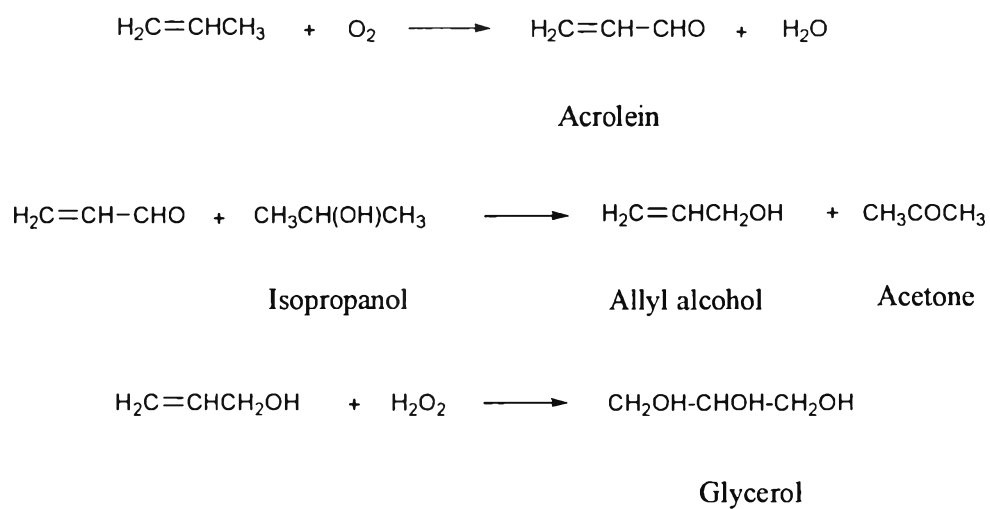


Figure 2.6 The nonhalogen route from propylene via acrolein.

- The “Propylene Oxide Route” to Glycerol (U.S. Defunct Chlorination of Allyl Alcohol Route)

Chemical reactions:

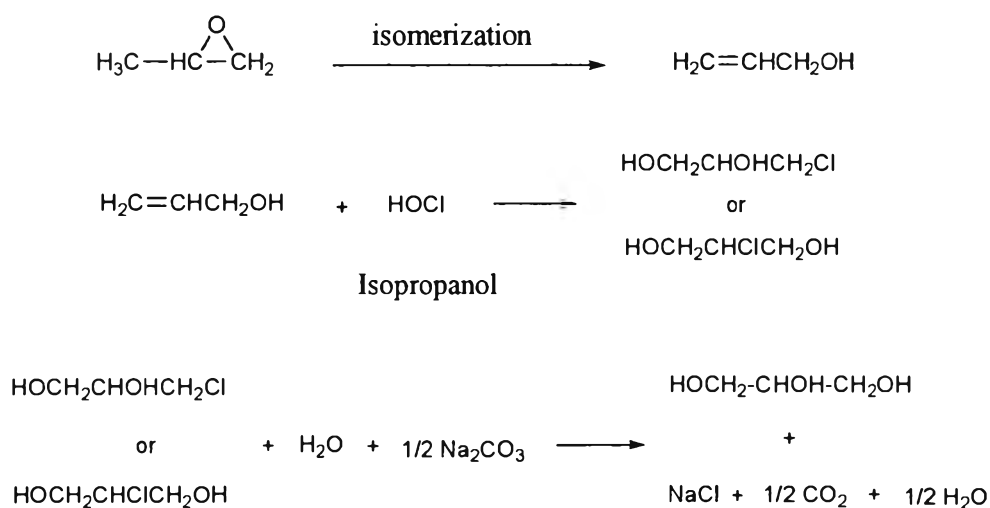


Figure 2.7 The propylene oxide route to glycerol.

- “Allied Chemical and Dye Corporation’s Route” from Allyl Alcohol by Epoxidation, Dehydration, and Further Hydroxylation

Chemical reactions:

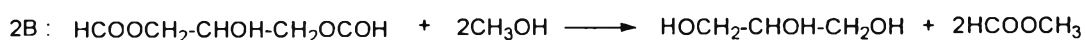
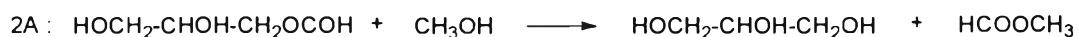
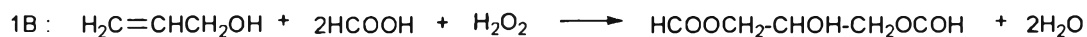
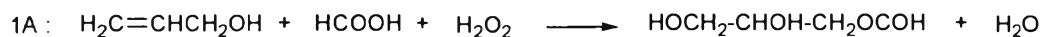


Figure 2.8 Allied chemical and dye corporation’s route from allyl alcohol by epoxidation, dehydration, and further hydroxylation.

- “Propylene Oxide Route” to Glycerol (U.S. Defunct Allyl Alcohol-Peracetic Acid Route)

Chemical reactions:

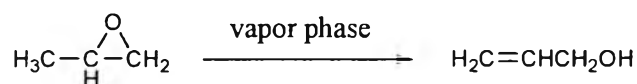


Figure 2.9 Propylene oxide route to glycerol.

2.1.2.2 Process for Synthesis Glycerol from Carbohydrate Raw Materials

- Hydrogenolysis of Various Carbohydrates
- Fermentation Technology for Glycerol Production

2.2 Uses and Applications of Glycerol

Glycerol production comes mainly from countries with significant oleochemical industries such as United States, Europe, Japan, and South-East Asia. The United States, Japan and more recently, China, are the major importers of glycerol while Europe and South-East Asia region are the dominant exporters of glycerol. Glycerol is most commonly used without modification, or very basic structural modifications, as an additive to materials. Its uses number in the thousands with large amounts being used in the manufacture of food and beverages, tobacco, pharmaceuticals, personal care products, urethane foams, and synthetic resins.

Navaol (2002) identified usages of glycerol. However, a gross classification can be shown with the help of a pie chart in Figure 2.10. Glycerol usage can be listed according to its application in Table 2.1

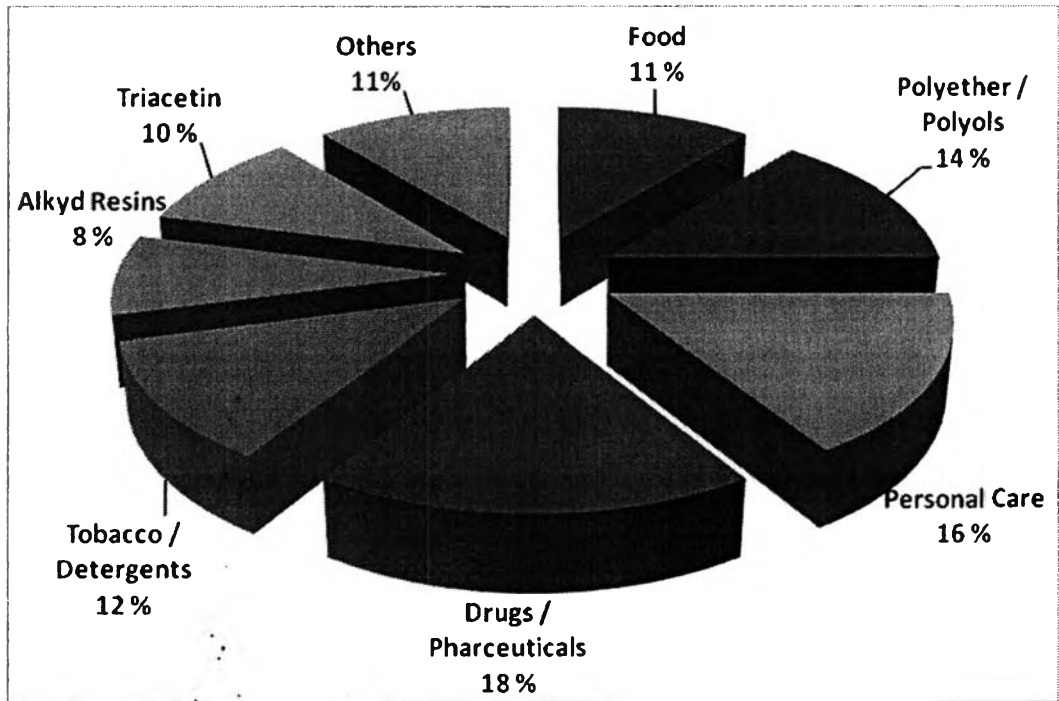


Figure 2.10 Distribution of glycerol uses (2002).

Glycerol usages are similar to those of other generic designated polyols. Therefore, glycerol could increase its market share inside sectors traditionally occupied by other polyols: glycols, trimethylol propane, sorbitol, and pentaerythritol. From a simple and technical point of view, glycerol is able to displace these polyols in many applications such as tooth-paste, humectants, cosmetics, polyurethanes, alkyds and food.

Table 2.1 Glycerol consumption

Application	Consumption (tons)
Cosmet./Soap/Pharmacy	202,200
Alkyd resins	43,800
Food and Drinks	57,700
Polyglycerols	89,000
Tobacco	25,500
Cellulose films	35,000
Esters	93,400
Paper	7,300
Nitrates	2,900
Resale	103,700
Others	69,500
Total	730,000

Applications of Glycerol

Glycerol and its esters are mostly used in:

- Cosmetics and toiletries
- Pharmaceuticals
- Food and beverages
- Polyether polyols
- Alkyd resins (plastics) and cellophane
- Absolute alcohol
- Industrial applications

2.2.1 Cosmetics & Toiletries

The widest application of glycerol is in personal care products, where it performs a variety of functions like moisturization, conditioning, and solubilization. Glycerol is incorporated in toothpastes, mouthwashes, moisturizing creams and lotions, shaving foams, deodorants and lipsticks. Glycerol fatty acid esters are used as emulsifiers and conditioners in skin care and hair care products.

2.2.2 Pharmaceuticals

Glycerol can function as a moisturizer, plasticizer, solvent, laxative, and for the adjustment of viscosity and osmotic pressure. Glycerol is a component of many pharmaceutical formulations including gelatin capsules, syrups, creams, ointments, suppositories, and parenteral solutions. Glycerol Trinitrate is well known for the treatment of angina pectoris.

2.2.3 Food and Beverages

Glycerol and glycerol esters are approved food additives in several countries. They improve the quality of food products by preventing desiccation, improving texture and extending shelf life. They also enhance the compatibility of poorly miscible ingredients and optimize viscosity. Products that contain glycerol or its esters include fine bakery wares, bread, wine, gums, candy, fondants, ice-cream, margarine, meat and sausages, beverages, syrups, and flavor extracts. Moreover, glycerol is increasingly used in feeding animals.

2.2.4 Polyether Polyols

Glycerol is one of the major raw materials for the manufacture of polyols for flexible foams, and a lesser extent rigid polyurethane foams. Moreover, glycerol is the initiator which propylene oxide/ethylene oxide is added.

Sunder *et al.* (1999) studied polyether multiarm star-block copolymers that have been prepared by anionic ring-opening multibranching polymerization of glycidol, followed by anionic polymerization of propylene oxide. They present a convenient approach that permits to tailor the polarity of the hyperbranched polyglycerol without reducing the functionality and without variation of the basic polyether structure, thus without change of the relative chemical stability of the hyperbranched scaffold.

Mecking *et al.* (2000) studied conveniently preparation of stable solution of metal colloids in organic solvents which can be prepared by amphiphilic hyperbranched polymer. The metal cluster size is dependent upon the molecular

weight of the polymer. This preparation gives high activity and stability of the colloids in catalysis.

Frey *et al.* (2002) studied synthesis of hyperbranched polyglycerol and its derivatives represent a versatile and promising class of materials for future biomedical applications such as biodegradable and biocompatible polymers, advanced hydrogels, polymeric nanocapsules and nanoparticles, high loading polymeric supports for parallel synthesis and multivalent drugs, and selective core-shell architectures and cleavable nanocapsules,

Hebel *et al.* (2002) synthesis dendritic polyglycerol is well suited as a soluble polymeric support for boronic acids. This high-loading polyglycerol boronic esters can be used for homogeneous Suzuki cross-coupling reaction and allow for the simple purification of the biaryl products. To compare with normal homogeneous methods, a much easier and faster purification protocol results, which become significant when several reactions are performed simultaneously. In contrast to common solid-phase techniques, the separation of the soluble polymeric support is more time consuming, which makes this approach less suitable for high throughput. However, the separation strategies used here (precipitation and ultra filtration) allow the efficient workup on a preparative scale, which is not easily achieved with solid-phase resins.

Roller *et al.* (2004) studied dendritic polyglycerol as a high-loading support for parallel multistep synthesis of GABA lactam analogues. The key features of this parallel approach are the cyclative cleavage and simple separation techniques, such as dialysis, although dialysis is not yet the optimal method for quantitative retention of the polymeric support.

2.2.5 Alkyd Resins and Cellophane

Glycerol can be used in surface coatings and paints, used as a softener and plasticizer to impart flexibility, pliability and toughness. Besides, glycerol uses include meat casings, collagen casings (medical applications) and nonmeat packaging.

2.2.6 Others Industrial Applications

Glycerol and its derivatives are used in the following industrial applications:

- Antifreeze – Freezing point depressant
- Cigarette filters – Triacetin manufacturing
- Explosives – Dynamite is nitroglycerin mixed with an adsorbent material, which eliminates any risk of spontaneous explosion. nitroglycerin is obtained by direct nitration of high-purity glycerin
- Hydraulic fluids – Improved compression
- Tobacco – Moisturizer and softening agent
- Ignition of termite when combined with potassium permanganate
- Manufacture of paper as a plasticizer, Nitroglycerin, humectants and lubricant
- Used in lubricating, sizing and softening of yarn and fabric
- Used in de-/anti-icing fluids, as in verification of blood cells for storage in liquid nitrogen
- Patent applications have been filed for detergent softeners and surfactants based on glycerol (i.e., alkyl glyceryl ethers) instead of quaternary ammonium compounds.
- A way to preserve leaves is to submerge them in a solution of glycerol and water.

Use a mixture of one part glycerol to two parts water. Place the mixture in a flat pan, and totally submerge the leaves in a single layer in the liquid. You'll have to weigh them down to keep them submerged. In two to six days, they should have absorbed the liquid and be soft and pliable. Remove them from the pan and wipe off all the liquid with a soft cloth. Done correctly, the leaves will remain soft and pliable indefinitely.

- Addition to solutions of water and soap to increase that solution's ability to generate soap bubbles that will last a long time.
- Used in fog machine fluids
- Counteracts phenol burns

2.3 Derivatives of Glycerol

The glycerol molecule contained two primary and one secondary hydroxyl group. The three hydroxyl groups are on adjacent carbons. Because of the multiple hydroxyl groups and their positions on the carbon chain, glycerol has the potential to form more derivatives than an ordinary alcohol. Utilizing the reactivity of the hydroxyl groups, numerous derivatives can be prepared, including mono-, di-, and triesters and ether. Oxidation can lead to numerous derivatives, such as glyceraldehydes, dihydroxyl acetone, and glyceric aldehyde. Reaction involving hydroxyl groups at adjacent carbon atoms can result in breakage of the carbon-carbon bonds, as in the well-known analytical procedure with periodic acid, or by the condensation of two hydroxyl groups with another reagent, such as ketone, to form heterocyclic derivatives. Many of these reactions find applications in the production of industrially important materials.

2.3.1 Ester of Glycerol

The monoesters and diesters of glycerol occur naturally in fats that have become partially hydrolyzed. The triglycerides are primary components of naturally occurring fats and fatty oils.

Monoglycerides and diglycerides are prepared by the direct condensation of a fatty acid or a fat (triglyceride) with glycerol resulting in mixtures containing 40-60% monoglyceride, 30-45% diglycerides, and free glycerol. The example of monoglyceride is shown in Figure 2.11.

A mixture of monoglycerides, diglyceride, and triglycerides is manufactured in large quantities for use in superglycerinated shortenings. Monoglycerides and diglycerides are important modifying agents in the manufacture of alkyd resins, detergents, and other surface-active agents (Parolla and Draves, 1958).

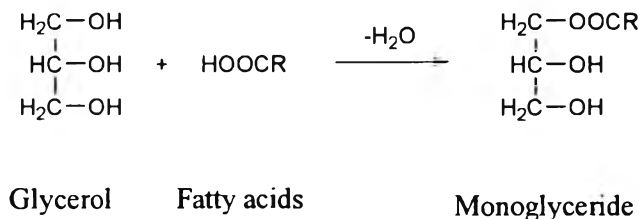


Figure 2.11 Reaction of monoglycerides production.

2.3.2 Ether of Glycerol

Ethers of glycerol and fatty alcohols occur in natural products. Some typical examples of naturally occurring fatty ethers of glycerol are the alpha glyceryl monoethers of stearyl, oleyl, and acetyl alcohol (Baer *et al.*, 1947).

Glycerol reacts with ethylene oxide or propylene oxide to form polyether. By adding the hydrophobic propoxy chain followed by the addition of hydrophilic ethoxyl chains or vice versa “block copolymer” can be prepared. When the ethoxyl and propoxy chains are properly balanced, these block copolymers have surface-active properties. They also have been used as intermediates in the manufacture of some polymers.

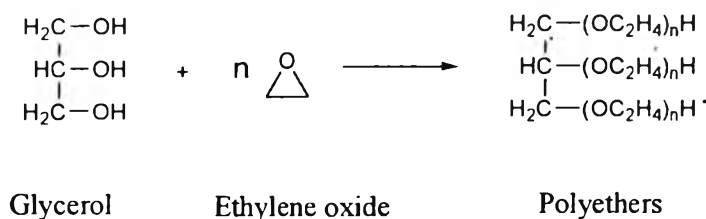


Figure 2.12 Reaction of polyethers production.

Sunder *et al.* (1999) studied the controlled synthesis of hyperbranched polyglycerols by ring-opening multibranching polymerization. In this study, they used glycidol as a monomer and 1,1,1-Tris(hydroxymethyl)propane (TMP) was used as initiator for the anionic polymerization carried out under slow addition conditions to minimize polymerization without initiator as well as cyclization. The main advantages of this preparation were controlled narrow molecular weight distribution.

2.3.3 Nitration of Glycerol

Nitration of glycerol is used to produce nitroglycerol, which is a common biological molecule from which triglycerides fats and oils are constructed, where all the $-OH$ groups have been replaced by $-NO_2$ as structure is shown in Figure 2.13. The best manufacturing process was developed by Alfred Nobel in the 1860s. Nitroglycerol is an oily, colorless liquid, but also a high explosive that is so unstable that the slightest jolt, impact or friction can cause it to spontaneously detonate. Since the molecule contains oxygen, nitrogen, and carbon, when it explodes, a lot of energy is released as the atoms rearrange to form new molecules with more strong and stable bonds.

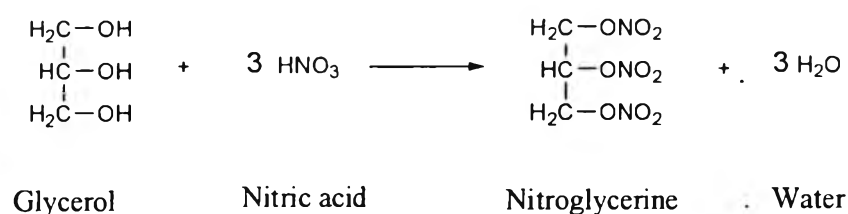


Figure 2.13 Reaction of nitroglycerine production.

2.3.4 Oxidation of Glycerol

Glycerol is quite stable in the presence of oxygen under normal conditions but it is oxidized in the presence of certain catalysts such as iron and copper. Moreover, glycerol is readily oxidized by a variety of chemical and microbiological oxidants, as well as electrolysis.

Theoretically, glycerol can be oxidized to many oxidation products such as glyceraldehydes, dihydroxyl acetone as shown in Figure 2.14., glyceric acid, mesoxalic acid, and etc. Partial oxidation is usually hard to control; the oxidation products have been isolated, though more often they are prepared by indirect methods, rather than the controlled oxidation of glycerol.

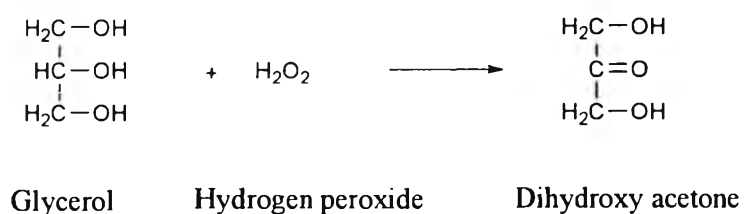


Figure 2.14 Reaction of dihydroxy acetone production.

2.3.5 Dehydration of Glycerol

Dehydration of glycerol results in the formation of acrolein, a clear liquid with a very pungent smell. Acrolein can be formed in trace quantities when glycerol is stored in inadequately protected metal containers and exposed to elevated temperatures, resulting in very noticeable, strong pungent off-odors as shown in Figure 2.15.

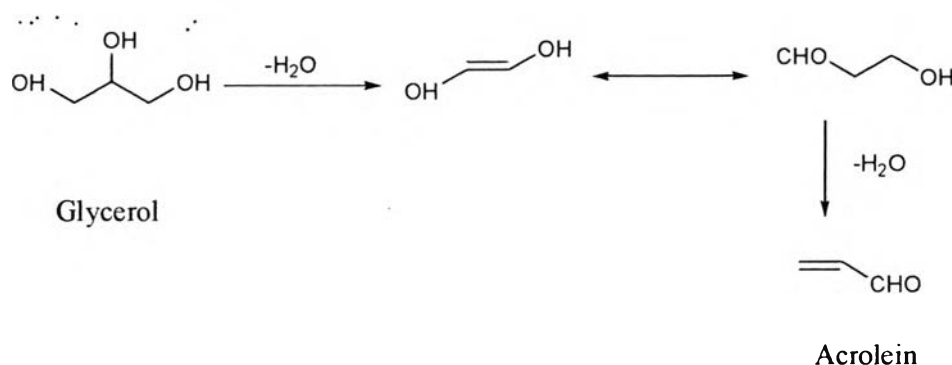


Figure 2.15 Acrolein formation by double dehydration of glycerol.

Neher *et al.* (1995) described a process for production of acrolein by dehydration of glycerol in the liquid phase or in the gaseous phase by using an acidic solid catalyst. A glycerol-mixture with a glycerol content of 10 to 40 wt% preferably between 10 and 25 wt% was passed over the solid dehydration catalyst. Dehydration did indeed still occur if glycerol concentration was above 40 wt%. However, as the glycerol content rises, both the selectivity of the reaction and the service life of the catalyst are appreciably reduced. When performing the reaction in the liquid phase, it is convenient to dehydrate only to conversion between 15 to 25% since selectivity

decreases as conversion rises. Dehydration in the gaseous phase preferably proceed in the temperature range between 270°C and 320°C while liquid phase dehydration preferably proceeds between 250°C and 300°C. An advantage of dehydration in the liquid phase over gaseous phase dehydration is lower energy consumption.

The aqueous acrolein solution may be directly used, for example, in the production of 1,3-propanediol by catalytic hydrogenation to 3-hydroxypropionaldehyde with subsequent catalytic hydrogenation.

2.3.6 Hydrogenolysis of Glycerol

Hydrogenolysis is a term describing chemical reactions, in which hydrogen is used to break molecular bonds in large organic molecules in order to provide smaller molecules. Hydrogenolysis reactions are usually conducted over a catalyst of some types, and at an elevated temperature and high hydrogen pressures.

Theoretically, the primary reaction is a hydrogen splitting of the alditol molecule at the center C-C bond to produce glycerol, or propylene glycol and water. However, there seems to be no proof that these reactions occur completely, since it is almost always the case that both glycerol and propylene glycol are produced in alditol hydrocracking. Following are the simple chemical equations for formation of glycerol and propylene glycol from sorbitol as shown in Figure 2.16.

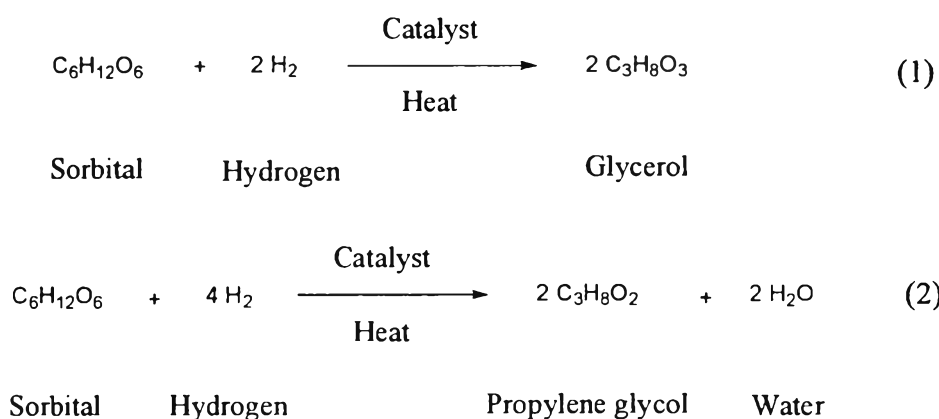


Figure 2.16 Chemical equations for formation of glycerol and propylene glycol from sorbitol.

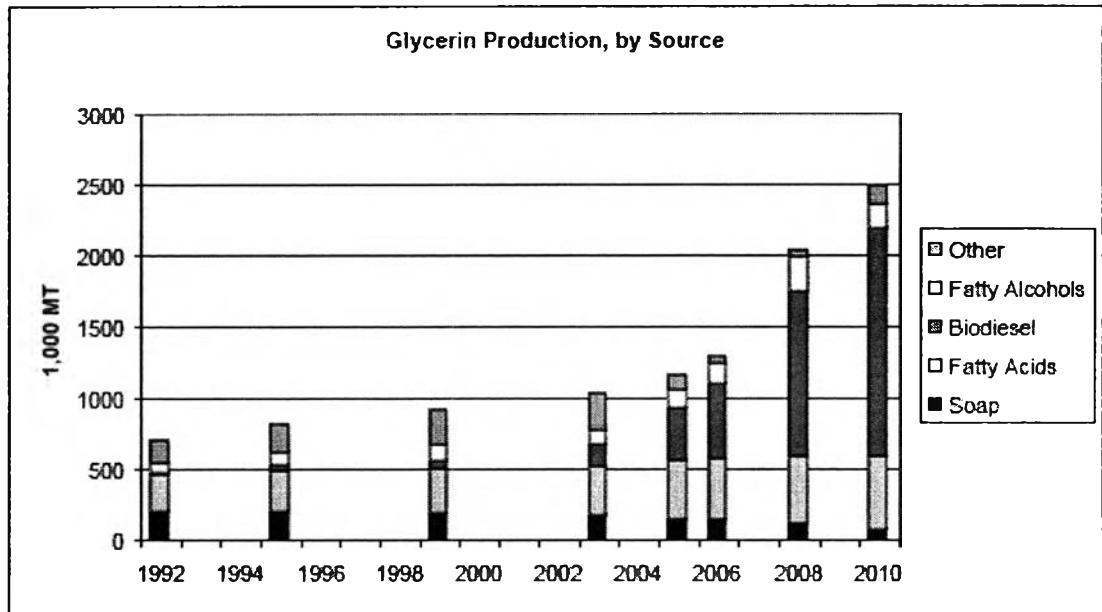
up to and including dodecaglycerol (12 condensed glycerol molecule) have been prepared commercially; the higher forms are solid. They are soluble in water, alcohol, and other polar solvents. They act as humectants but have progressively higher molecular weight and boiling points. The multiplicity of polyglycerol is not due to a single property, but rather to a unique combination of properties, such as broad compatibility, blandness, thickening agent, dispersing agent, lubricant, emollient, nontoxicity, biodegradable, stability and hygroscopicity. These are the key physical properties that make polyglycerols an almost essential ingredient in cosmetic and food applications. Products based on polyglycerols are useful in surface-active agents, emulsifiers, plasticizers, adhesives, lubricants, medical specialties, and dietetic foods.

Haag *et al.* (2000) introduced a new strategy to generate a polyglycerol pseudo-dendrimer, which also consists of dendritic and terminal units only, resembling the perfect glycerol dendrimer. The advantages of polyglycerol pseudo-dendrimer are obvious: (i) only three synthetic steps (polymerization, allylation, dihydroxylation) are required to tailor any molecular weight and low polydispersities, (ii) the synthesis can be carried out on a multigram scale, (iii) the capacity of 1,2-diols (terminal units) on the polymer is increased, and (iv) all reported advantages of the poly ether scaffold are preserved.

2.4 Glycerol Market

Glycerol is a by-product of the transesterification in which vegetable oil is processed to methyl ester. Every 10 kg of biodiesel produces 1 kg of glycerol.

From Figure 2.19, in 2006, biodiesel production became the primary source of glycerol supply in the world, accounting to 41 percent of total production, and is expected to grow to 65 percent in 2010. While glycerol production had grown roughly 4 percent per year until 2005, it is expected to grow by 10 to 25 percent annually from 2006 to 2010. Annual growth in consumption of glycerol (mainly by the cosmetic and pharmaceutical industries) is estimated at 3-4 percent, which is significantly below the expected growth trend in future production (Melinda, 2007).



Source: SOFIPROTEOL

Figure 2.19 Glycerol production.

In response, world glycerol prices have declined sharply. According to SOFIPROTEOL, spot prices for bulk glycerol in Europe and the United States have declined from 1700 euros per MT and 1 \$/lb, respectively, in 1995 to 450 euros per MT and 0.3 \$/lb in 2006.

Glycerol producers are exploring two new major markets: polyol substitution (e.g., in tooth paste) and animal feed, especially for the swine and poultry sectors.

2.5 Polyglycerols

Polyglycerols have found extensive use in the food, cosmetic and pharmaceutical industry as surfactants, emulsifier, lubricants gelling agents, humectants, adhesives, and textile fiber finishes. Polyglycerols is typically prepared by base-catalyzed polymerization of glycerol. A distribution of polymers is formed with the degree of polymerization ranging from 1 up to 20 or higher, dependent on the reaction conditions. Furthermore, polyglycerols are used as intermediates for

polyglycerol esters which find wide application as emulsifiers in food and personal care industries.

Polyglycerol esters are generally prepared in two-step reactions, alkaline polymerization of glycerol at elevated temperatures followed by an esterification reaction with fatty acids as shown in Figure 2.20. Polyglycerol esters function as emulsifiers, dispersants, solubilizers, thickeners, emollients, conditioners, and spreading agents. They are also used in the formation of various cosmetic and personal care products.

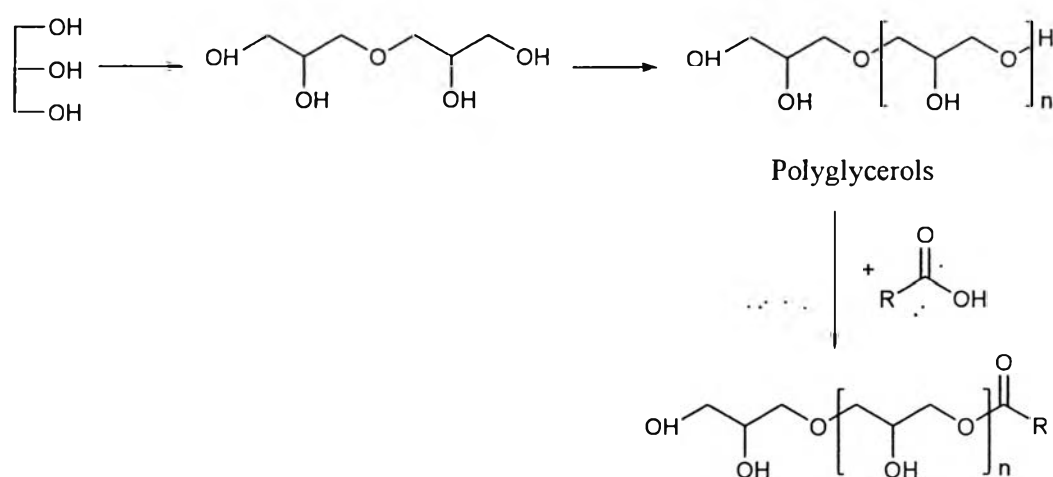


Figure 2.20 Formation of polyglycerol esters.

2.6 Synthesis of Polyglycerols

Polyglycerols were most often prepared by the polymerization of glycerol under alkali conditions at elevated temperatures. The condensation reaction involved the α -hydroxyl groups of two glycerol molecules that reacted to form ether linkage with the consequent expulsion of water molecules. The unreacted α -hydroxyl groups remained available to react with the hydroxyl groups of additional glycerol molecules or other polymerized molecules.

The reaction produced polymers, which were almost entirely linear. Care must be taken during the polymerization reaction to exclude air from the systems. Traces of oxygen led to the formation of acrolein as well as a dark product that

was not easily bleached. A search for a reducing agent to be present during the polymerization process in the vessel and to minimize formation of colored materials led us to add catalytic amounts of Al or Mg metals to the glycerol before heating. In addition, exclusion of air had been achieved by bubbling CO₂ or nitrogen during the condensation process (Garti *et al.*, 1981).

The polymerization reaction proceeded by chance and the molecular size distribution, which was expected to follow a normal distribution pattern. As a result, the commercial products did not contain pure molecular specie but a mixture of similar molecules having the average molecular weight of polyol. The most frequently manufacture polyglycerols were diglycerol, triglycerol, hexaglycerol, octaglycerol, and decaglycerol. Although higher polymers may be easily prepared, they were seldom manufactured since they were not permitted for use in foodstuffs.

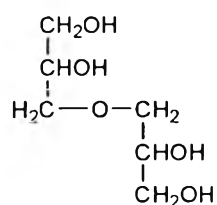
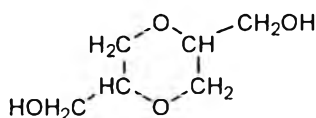
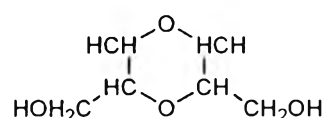
It was advisable to follow the progress of the reaction or degree of polymerization by determination of viscosity, refractive index, or hydroxyl value. They were used to control the desired degree of glycerol condensation. Polyglycerols range formed viscous liquids for the lower molecular weight and formed solid for the higher molecular weight. Viscosities and theoretical hydroxyl values, assuming no cyclization, were shown in Table 2.2.

Polyglycerols were dense, viscous liquids and difficult to handle at ordinary temperatures if they are free from water. In selected equipment handled these polyols and their ester, the effects of both viscosity and density must be taken into condensation. The reaction was terminated by cooling and acidulation reaction when the average molecular weight of the polymer had reached a predetermined value. Vacuum stripping reduced the unreacted polyglycerols; this also helped narrow the range of molecular weights in the resultant products. If the acrolein content of the polyol was high, it may be necessary to bleach the product. The polyglycerols may be bleached with special activated carbons, clays, ion exchange or chemical agents.

Table 2.2 Viscosities and hydroxyl values of polyglycerols

	MW	No. of OH groups	Viscosity CTKS @ 50°C	Hydroxyl Values
Glycerol	92	3	45	1830
Diglycerol	166	4	287	1352
Triglycerol	240	5	647	1169
Tetraglycerol	314	6	1067	1071
Pentaglycerol	388	7	1408	1012
Hexaglycerol	462	8	1671	970
Heptaglycerol	536	9	2053	941
Octaglycerol	610	10	2292	920
Nonaglycerol	684	11	2817	903
Decaglycerol	758	12	3199	880
Pentadecaglycerol	1128	13	4893	846

Previous works shows that the selectivity of the glycerol etherification was similar to a pseudo-polymerization and that a mixture of linear and cyclic polyglycerols was obtained especially in the presence of homogeneous catalyst. Summerbell *et al.* (1962) assigned definite structures to some of the polyglycerol derivatives. They demonstrated that diglycerol obtained by the acid-catalyzed condensation was cyclic polyglycerols (trans-2,5-bis-(hydroxymethyl)-p-dioxane). Based-catalyzed condensation yields predominantly linear polyglycerols such as α,α -diglycerol and α,β -diglycerol. Other metameric configuration are also possible such as cis-2,5-, cis-2,6-, and trans-2,6-bis (hydroxymethyl)-p-dioxane. These structures are shown in the figure 2.21.

 α,α diglycerolCis 2,5
bis (hydroxymethyl) dioxaneTrans 2,5
bis (hydroxymethyl) dioxane

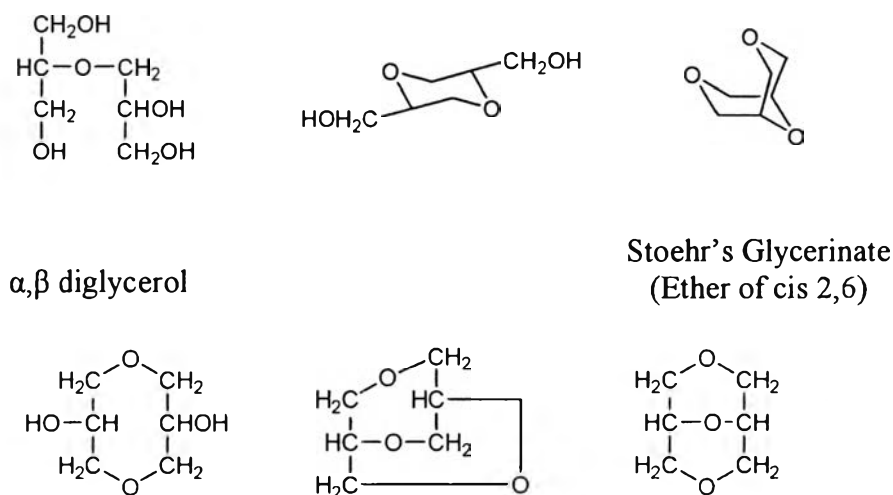


Figure 2.21 Structural configurations of diglycerol.

Normally, polyglycerols were produced commercially by heating glycerol at temperatures in the range of 200-275 °C at reduced pressure in the presence of an alkaline catalyst, such as sodium hydroxide, potassium hydroxide, or sodium carbonate. The reaction was usually carried out in an atmosphere of carbon dioxide or nitrogen. Proper processing conditions could greatly affect the quality, color, and odor of the resultant polyglycerol.

The manufacture of polyglycerols required drastic conditions, including high temperature and caustic media. Witcoff *et al.* (1950) studied the process of producing polyglycerols, which were free from the disadvantages attendant the high temperature polymerization process. They used etherifying agent was selected from the group consisting of glycerol-monohalohydrin and glycidol. Either of these etherifying agents reacted with the glycerol at low temperature. The product obtained di-, tri- and higher polyglycerol.

Polyglycerols were useful compounds, which used in many ways, for example for the preparation of surface-active substances, esters or oxyalkylated esters. These products were advantageously used as emulsifiers in the foodstuffs, cosmetic, detergent and pharmaceutical products. These intended used result in the requirement for good color quality and odor neutrality.

Babayan and Lehman (1972) suggested the preparation of polyglycerols with a good color quality. A procedure in which glycerol was reacted in the presence of alkaline catalysts such as sodium hydroxide, potassium hydroxide in the absence of water at a temperature of 100 to 300 °C. The water from reaction was continuously taken off. The reaction was cooled rapidly and the mixture was treated with a bleaching agent. This process was not desired because high colored polyglycerols and a strong odor (pungent odor of acrolein) were obtained if the bleaching was not carried out.

Stuhler (1985) studied the process for the preparation of polyglycerols by condensation of glycerol, which led directly to products of good color quality and odor neutrality. The process was based on the condensation of glycerol at a temperature of 190 to 250°C in the presence of catalysts. Catalysts were particular compounds containing phosphorous and alkali metal such as Na_2HPO_3 or NaH_2PO_2 . The polyglycerols are obtained with high color quality and odor neutrality by a simple reaction procedure, without a bleaching treatment.

One objective of the present invention was providing a process in which polyglycerols was obtained in good yields and low content of cyclic components. Cyclic polyglycerols caused degradation of product that affected the taste, performance and odor of product. Moreover, cyclic polyglycerols generally had a lower hydrophilic-lipophilic (HLB's) than linear polyglycerols. As a result, they typically acted as emulsion breakers rather than emulsion builders. Therefore, products spented costly and time consuming distillation step to remove cyclic polyglycerols. In the contrary, linear polyglycerols were more biodegradable and more soluble in water than cyclic polyglycerols. The linear polyglycerols had very desirable physical characteristics, including a clear appearance at melt, a desirable color, a mild odor, and a bland taste. This polyglycerols were suitable for use as cosmetic and food additives. Therefore, there had been continuing effort to find a method of preparing linear polyglycerols, which produced little cyclic polyglycerols.

Seiden *et al.* (1976) studied process for preparing polyglycerol by heating glycerol under reduced pressure in the presence of sulfuric acid and glycerol ester. The condensation reaction was terminated by adding a neutralizing agent to the

mixture. Unreacted glycerol and cyclic diglycerol were removed by distillation. This process was relatively complicated because it required maintenance of several specific reaction conditions. Moreover, products are relatively poor in color quality.

Jakobson *et al.* (1990) studied process for the preparation of polyglycerols, which had low cyclic components. In this study, glycerol, diglycerol or a higher polyglycerol reacted epichlorohydrin at elevated temperatures in the presence of base catalyst. The unseparated reaction obtained desalting the resultant reaction mixture, recovered glycerol, diglycerol and higher polyglycerols by fractional distillation.

Subsequently, Jakobsen *et al.* (1991) studied a process was disclosed for preparation of polyglycerols (containing more than 50% by weight of diglycerol) which had low content of cyclic component by reacting chlorohydrins. In this reaction, α -monochlorohydrin reacted epichlorohydrin in the presence of acids. A medium product having an alkaline solution was added to the resulting unseparated reaction mixture. After the addition of water, the reaction mixture was desalinated via one of more cation exchangers and subsequent anion exchanger. Water was removed by distillation. The polyglycerols mixture was separated into diglycerol, higher polyglycerol and glycerol by fractional distillation.

A process that α -monochlorohydrin was reacted with epichlorohydrin at temperature 120°C in the presence of acids. This process gave the amount of tri-, tetra-, and higher polyglycerols as well as the amount of cyclic component. Moreover, a chlorine containing compounds were contaminated polyglycerols as a secondary product.

Jakobsen *et al.* (1993) improved process for the preparation of diglycerol and reduced the amount of cyclic polyglycerols. Furthermore, this process avoided the formation of chlorine containing organic compounds that were difficult to hydrolyze. In this process, isopropylidenedeglycerol reacted with α -monochlorohydrin in the presence of sodium hydroxide at sufficient temperatures. This process gave intermediate products, which reacted with acidic catalyst to yield product composition that comprised diglycerol and no cyclic compound.

Lemke (2003) discovered that if calcium hydroxide was used in place of potassium hydroxide or sodium hydroxide during polymerization of glycerol. The formation of cyclic polyglycerols was greatly reduced. Therefore, polyglycerols were prepared by mixing glycerol with calcium hydroxide catalyst. The reaction was performed at a temperature about 230°C in a pressure about 150 mmHg. The polyglycerols in high yield with minimal formation of cyclic polyglycerol were obtained.

Generally, polyglycerols are prepared by polymerization of glycerol at elevated temperature in the presence of homogeneous catalysts (sodium hydroxide or potassium hydroxide). But a disadvantage of the homogeneous catalysts was low selectivity. Moreover, the uses of homogeneous catalysts lead to several problems such as impurities, less selectivity, deterioration under high pressure and temperature, and subsequent catalyst separation. Then heterogeneous catalysts were interesting because they offer greatly simplify and economically impurities and catalysts removal from the products. Furthermore, the heterogeneous catalysts give high selectivity, reduces by-product, tolerate to high pressure and temperature, have long catalysts life and can be recycled or reused easily.

2.7 Polymerization of Glycerol by using Heterogeneous Catalysts

The synthesis of a desired polyglycerols by a chemical route was rather difficult and expensive. The use of solid catalysts in the transformation of renewable products such as glycerol was interesting for the synthesis of high-valuable products which was cheaper and more efficient than the classical methods. In addition, the uses of homogeneous catalysts lead to impurity of catalysts and undesired products after the reaction. Therefore, the products need process to separate impurities and catalysts. The use of heterogeneous catalysts would greatly simplify the removal of catalysts and impurities. A number of studies have been carried out on the heterogeneous catalytic system. The main advantages of using heterogeneous catalysts were high selectivity, reducing formation of by-product, and environmental

friendly. Moreover, the catalysts were easily separated from the oligomer products and the catalysts were regenerated.

Process of polymerizing glycerol in the presence of an acid zeolite gave high cyclic polyglycerols. Robert *et al.* (1998) studied catalysts in the polymerization of glycerol, glycidol, glycerol carbonate or isopropylidene glycerol. They found that polymers of glycerol with an appreciable percentage of linear polyglycerols were obtained if glycerol or glycerol derivatives were polymerized in the presence of rubidium fluoride or cesium fluoride impregnated on gamma alumina or zirconium oxide. In addition, glycerol, 2,2-dimethyl-1,3-dioxane-4-methanol, glycidol or glycerol carbonate was polymerized at 150 to 350°C in the presence of anionic clay material, preferably hydrotalcite as a catalyst. The products were obtained into preponderantly linear polyglycerols. (Eshuis *et al.*, 1998).

Harris *et al.* (1992) showed that the fraction of the diglycerol and diglycerol was below or equal to 65% over sodium zeolites and sodium silicate. They suggested that there was no shape selectivity effect over these catalysts and presumably the outer surface of the catalyst played an important role in the case of NaA zeolite sample.

In another work, Cottin *et al.* (1998) found that acid catalysts (benzene sulfonic, ion exchange resins) favor the dehydration of glycerol to acrolein while Na_2CO_3 was more active than a hydroxide or an oxide but the selectivity to diglycerol or triglycerol was very low. On the contrary the NaX and CsHY zeolites, which were less active at the beginning of the reaction, favor the formation of di- and triglycerol without any formation of acrolein. Indeed, the selectivity to diglycerol was higher than 90% over a CsHY or a NaX zeolite. In this particular case, it seemed that the pore size of the catalyst slightly increases the selectivity of the reaction, especially when glycerol conversion was less than 80%. Furthermore, they showed the effect of alkaline elements on the activity and selectivity; the best results were obtained with the most basic promoter. When using Cs-exchanged zeolite X a 70% glycerol conversion was obtained with high selectivity to di- (62%) and triglycerol (33%), and only a 4% of tetraglycerol. In contrast, medium-pore Cs-containing zeolites like ZSM-5 are less active and selective.

Barrault *et al.* (2002) demonstrated that solid and basic materials may replace the usual homogeneous catalyst with the same activity and selectivity but without formation of by-product and wastes. Moreover, in the presence of mesoporous solids with accurate pore size the glycerol was selectively transformed to linear di- and triglycerol; and a yield of more than 80% was obtained.

Clacén *et al.* (2002) studied the selective synthesis, from glycerol and without solvent, of polyglycerols having a low polymerization degree (di- and triglycerol) in the presence of solid mesoporous catalysts. The main part of this study consisted in the synthesis and impregnation of mesoporous solids with different basic elements in order to make them active, selective and stable for the target reaction. The catalytic results show that impregnation method gives significant activity, which must be correlated to active species incorporation. The selectivity of the modified mesoporous catalysts, the best value to di- and triglycerol are obtained over solids prepared by cesium impregnation. The re-use of these cesium impregnated catalysts did not affect the selectivity to the di- and triglycerol fraction. In the presence of lanthanum and magnesium containing catalysts, the glycerol dehydration to acrolein was very significant whereas this unwanted product was not formed when cesium was used as impregnation promoter.

Barrault *et al.* (2004) studied synthesis and modification of catalysts. The catalysts prepared by the impregnation method give the highest activity, but are subject to metal leaching. Mesoporous solids modified by cesium impregnation or exchange lead to the best selectivity and yield to (di-+tri-) glycerol. The most stable catalysts are the exchanged ones but though they are less stable, the impregnated catalysts can be reused without major modification of their selectivity to the (di-+tri) glycerol function.

2.8 Analysis of Polyglycerols

Polyglycerols, obtained from polymerization of glycerol with catalysts, can be significantly contained with cyclic polyglycerols and acrolein due to side reactions and insufficient purification of the product. Consequently, a sensitive and reliable analytical method is needed to monitor the purity of polyglycerols. Various chromatographic techniques such as Gas Liquid Chromatography (GLC), Gas Chromatography/Mass Spectroscopy (GC/MS), High Performance Liquid Chromatography (HPLC), Nuclear Magnetic Resonance (NMR), MALDI-TOF-MS, Gel Permeation Chromatography (GPC), VPO, DSC, Viscosimetry have been employed.

Sahararabundhe *et al.* (1967) applied Gas Liquid Chromatography (GLC) equipped with Flame Ionization Detector (FID) in determining the mono-, di-, tri-, penta-, and hexaglycerols in polyglycerols. However, this method is less convenient because of derivatization such as silylation before analysis is needed for the free hydroxyl groups in polyglycerols.

Robert *et al.* (1998) analyzed the polyglycerol mixtures by Gas Chromatography. The packed column was used 3% OV-1 on gaschrom Q. a linear programme was run from 100-300°C at a rate 10°C/minute. Structure of polyglycerols was analyzed by Gas Chromatography/Mass Spectrometry. The capillary CP-SII 5CB column was run from 50-270°C at rate 5°C/minute.

For both Gas Chromatography (GC) and Gas Chromatography/Mass Spectrometry (GC/MS), samples were analyzed as the silyl derivatives by reacting polyglycerols products with a mixture of hexamethyldisilazane, trimethylsilylchloride and pyridine prior to injection.

The High Performance Liquid Chromatography (HPLC) makes feasible direct analysis of polyglycerols products without derivatization. Artizetmuller *et al.* (1979) analyzed polyglycerols liberated from commercial polyglycerol ester using a silica (Lichrosorb Si 60) column and acetonitrile-water (85:15) as the mobile phase at room temperature. However, they did not study the separation of cyclic diglycerol and polyglycerols beyond hexaglycerol.

Kumar *et al.* (1984) used High Performance Liquid Chromatography equipped with refractive index detector to determine the composition of polyglycerols. They use a carbohydrate analysis column with acetonitrile-water (85:15) to separate and determine cyclic diglycerol and polyglycerol oligomers up to undecaglycerol and demonstrate its utility in monitoring the preparation of polyglycerols. Therefore, HPLC appears to be a useful equipment for monitoring the production of desired mixtures of polyglycerols and for analyzing polyglycerol esters through their polyglycerol moieties.

Sunder *et al.* (1999) used ^1H NMR and ^{13}C NMR spectra to assess the degree of branching (DB) for studying Controlled Synthesis of Hyperbranched Polyglycerols by Ring-Opening Multibranching Polymerization. Characterization was recorded in d_6 -methanol at concentrations of 250 g/L on a Bruker ARX 300 spectrometer, operating at 300 and 75.4 MHz, respectively. And then, they used MALDI-TOF-MS to characterize molecular weights of the polyols formed, which were performed with a Bruker Reflex II MALDI-TOF-MS (matrix-assisted laser desorption and ionization time-of-flight) mass spectrometer, equipped with a nitrogen laser delivering 3 ns laser pulses at 337 nm. A-Cyanohydroxycinnamic acid was used as matrix. Samples were prepared by dissolving the polymer in methanol at a concentration of 5 g/L. moreover, they used GPC to characterize molecular weights of the polyols formed. The polymers were dissolved in DMF at a concentration of 5 mg/mL. Measurements were performed with a Knauer microgel set C11 using DMF as an eluent at 45°C and a Polymer Laboratories Evaporative Mass Detector (EMD) 960 operating at 110°C. Poly (propylene oxides) 1000, 2000, 4000 (Aldrich), 8000, and 12000 (ARCO Chemical Co.) were used for calibration.

Barrault *et al.* (2004) and Clacens (2002) analyzed glycerol etherification by GPC after silylation. GPC equipped with an on-column injector, an FID, and a polar column (HT5) supplied by SGE (L = 25 m, ID = 0.22 mm, thickness of the film = 0.10 μm).

Sunder *et al.* (1999) used Vapor Pressure Osmometry (VPO) to measure the number average molecular weight of a polymer. In this characterization, VPO was carried out using a Knauer vapor pressure osmometer in methanol at 45°C in a

concentration range of 5-10 mg/mL. Benzil (Merck) was used for calibration. And then, they used Differential Scanning Calorimetry (DSC) to analyze physical properties. Measurements were carried out on a Perkin-Elmer 7 series thermal analysis system in the temperature range -100 to 20°C at heating rate of 16, 25, and 36 K/min. moreover, they used viscosimetry to analyze viscosity of polymer. Experiments were performed on a Schott AVS/6 Ubbelohde dilution viscosimeter at 20°C using a capillary with a diameter of 0.46 mm and methanol as solvent.

2.9 Solid Base Catalysts

Acid and base are paired concepts; a number of chemical interactions have been understood in terms of acid-base interaction. Among chemical reactions which involve acid-base interactions are acid-catalyzed and base-catalyzed reactions which are initiated by acid-base interactions followed by catalytic cycles. In acid-catalyzed reactions, reactants act as bases toward catalysts which act as acids. In base-catalyzed reactions, on the contrary, reactants act as acids toward catalysts which act as bases.

In homogeneous systems, a huge number of acid-catalyzed reactions and base-catalyzed reactions are known. In heterogeneous systems, a limited number of reactions are recognized as acid- or base-catalyzed reactions. In particular, base-catalyzed reactions have been studied to a lesser extent as compared to acid-catalyzed reactions in heterogeneous systems. Heterogeneous acid catalysis attracted much attention primarily because heterogeneous acidic catalysts act as catalysts in petroleum refinery and are known as a main catalyst in the cracking process which is the largest process among the industrial chemical processes. Extensive studies of heterogeneous cracking catalysts undertaken in the 1950s revealed that the essential nature of cracking catalysts are acidic, and generation of acidic sites on the solids was extensively studied. As a result, amorphous silica-alumina was utilized as a cracking catalyst, and then crystalline aluminosilicate (zeolite) was used afterward.

In contrast, numerous reactions such as isomerizations, alkylations, condensations, additions, and cyclizations are carried out industrially by using liquid bases catalysts. The replacement of liquid bases by cleaner catalytic alternatives is

quite necessary in the view of environmentally benign. Solid base catalysts are non-stoichiometric, non-corrosive and reusable, which can be a good alternative.

The first study of heterogeneous basic catalysts, which was pointed out by Hattori, was that Pines et al. studied sodium metal dispersed on alumina acted as an effective catalyst for double bond migration of alkenes in the 1950s. Since then, the studies of solid base catalysts have been continuous and progressed steadily. From a single metal oxide, such as MgO, to functionalized mesoporous materials, a variety of solid base catalysts have been developed and studied. Here, the solid base catalysts are divided into the types displayed in Table 2.3.

Table 2.3 Types of solid base catalysts

Type	Typical catalyst	Details of the catalyst
Single metal oxide	Alkaline earth oxide	MgO, CaO, SrO, BaO
	Rare earth oxide	La ₂ O ₃ , YbO ₂
	Transition metal oxide	ZrO ₂
Mixed oxide	Mg-Al mixed oxide	MgO-Al ₂ O ₃
	Mg-Ti mixed oxide	MgO-TiO ₂
Zeolite	Alkali ion-exchanged zeolite	Cs-exchanged zeolite X, Y
	Alkali metal or metal oxide occluded zeolite	Cs-occluded zeolite X, Y
Mesoporous material	Modified mesoporous material	MgO/SBA-15
	Functionalized mesoporous	MCM-41 functionalized with amino groups
	Mesoporous silicon oxynitride	-
Supported catalyst	compound: Na, K, KF, KNO ₃ , K ₂ O	KF/Al ₂ O ₃ , Na/NaOH/Al ₂ O ₃ ,
	Support: C, Al ₂ O ₃ , SiO ₂ , ZrO ₂ , MgO	Na/MgO
Clay and modified clay	Hydrotalcite, calcined and rehydrated hydrotalcite	Mg-Al hydrotalcites
	Chrysotile	-
	Sepiolite	Magnesium silicate
Oxynitride	Silicon oxynitride	SiON
	Aluminophosphate oxynitride	AlPON
	Zirconophosphate oxynitride	ZrPON
Other	Modified natural phosphate (NP)	Calcined NaNO ₃ /NP

Four reasons for recognizing certain materials as heterogeneous basic catalysts are as follows (Zhijian, 1997).

(1) Characterization of the surfaces indicates the existence of basic sites: Characterizations of the surfaces by various methods such as color change of the acid-base indicators adsorbed, surface reactions, adsorption of acidic molecules, and spectroscopy (W, IR, XPS, ESR, etc.) indicate that basic sites exist on the surfaces.

(2) There is a parallel relation between catalytic activity and the amount and/or strength of the basic sites: The catalytic activities correlate well with the amount of basic sites or with the strength of the basic sites measured by various methods. Also, the active sites are poisoned by acidic molecules such as HCl, H₂O, and CO₂.

(3) The material has similar activities to those of homogeneous basic catalysts for “base-catalyzed reactions” well-known in homogeneous systems: There are a number of reactions known as base-catalyzed reactions in homogeneous systems. Certain solid materials also catalyze these reactions to give the same products. The reaction mechanisms occurring on the surfaces are suggested to be essentially the same as those in homogeneous basic solutions.

(4) There are indications of anionic intermediates participating in the reactions: mechanistic studies of the reactions, product distributions, and spectroscopic observations of the species adsorbed on certain materials indicate that anionic intermediates are involved in the reactions.

Generation of Basic Sites

One of the reasons why the studies of heterogeneous basic catalysts are not as extensive as those of heterogeneous acidic catalysts seems to be the requirement for severe pretreatment conditions for active basic catalysts. The materials which are now known as strong basic materials used to be regarded as inert catalysts. In the long distant past, the catalysts were pretreated normally at relatively low temperatures of around 723 K. The surfaces should be covered with carbon dioxide, water, oxygen, etc. and showed no activities for base-catalyzed reactions. Generation of basic sites requires high-temperature pretreatment to remove carbon dioxide, water, and, in some cases, oxygen.