

CHAPTER II

BACKGROUND AND LITERATURE SURVEY

2.1 Glycerol

Glycerol was discovered more than two centuries ago by Scheele (1742-1786), a Swedish chemist, when he heated a mixture of litharge (lead oxide) and olive oil. He extracted and isolated a sweet tasting liquid that he named "sweet oil". The French chemist Michel Eugene Chevreul (1786-1889) established the structure of fats as triesters made up three moles of mixed fatty acids and one mole of "sweet oil", which he renamed "glycerine" after the Greek word for "sweet". Glycerine is also referred to in many texts as "glycerol". Chemically, it is a tribasic alcohol and more correctly named 1,2,3-propane-triol. Its chemical structure is shown in figure 2.1.

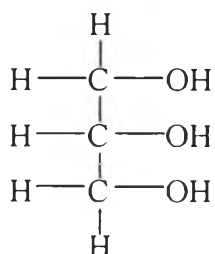


Figure 2.1 Chemical structure of glycerol.

Glycerol is a viscous, colorless and odorless with a sweet taste. It is hygroscopic, miscible with water and alcohol, but insoluble in ether, chlorinated solvents, hydrocarbons and oils. It is non-toxic and easily 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 is usually present as a tri-ester combined with such fatty acids as stearic, oleic, palmitic, and lauric acids. Generally, these are mixtures or

combinations of glycerol esters of several fatty acids. Vegetable oils such as soybean, palm kernel, sunflower, fat, coconut, and olive oil yield larger amounts of glycerol than animal fats such as lard and tallow.

The largest quantity of naturally occurring glycerol is obtained from four sources: soap manufacture, fatty acid production, fatty ester production, and propylene.

2.1.1 Soap Manufacture

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

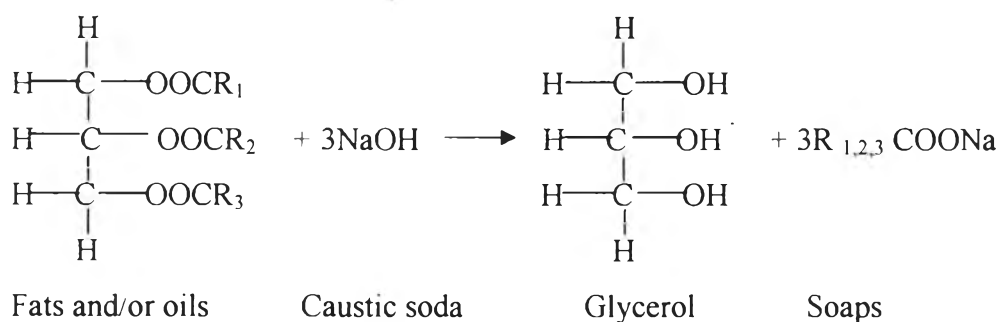


Figure 2.2 Production of soap.

2.1.2 Fatty Acid Production

Production of fatty acids by fat splitting (hydrolysis)

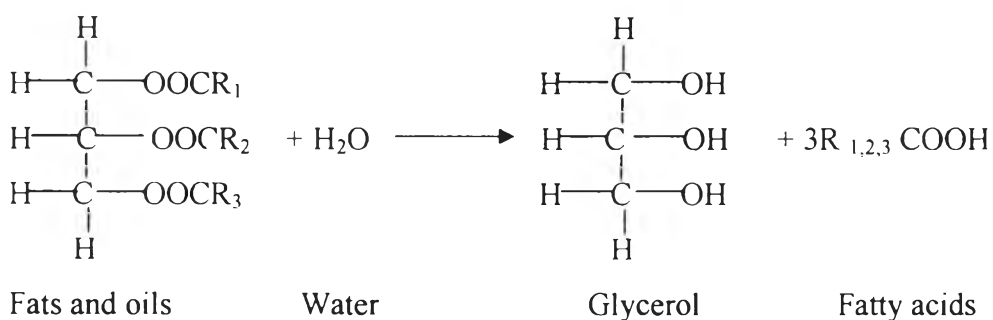


Figure 2.3 Production of fatty acids by fat splitting.

Some fatty acids obtained by fat splitting are neutralized to make soap, reduced to the corresponding fatty alcohol, or marketed as fatty acids.

2.1.3 Fatty Ester Production

In the manufacture of methyl esters, fats are esterified with methyl alcohol.

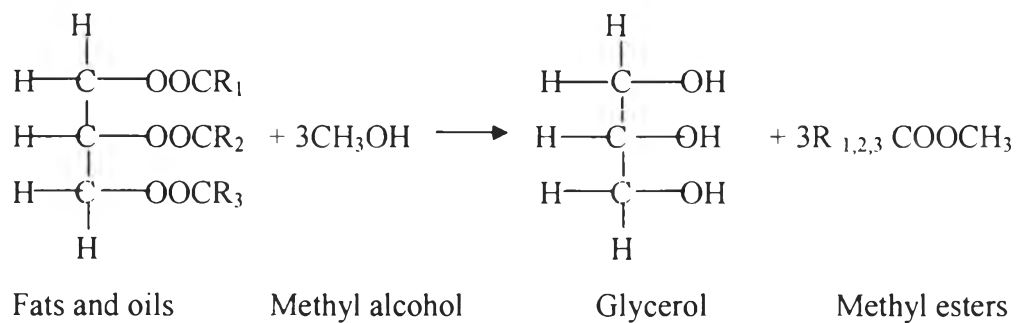


Figure 2.4 Production of fatty ester.

The methyl esters are reduced to the corresponding fatty alcohols, marketed as fatty esters, or used as an emission reducing component of diesel fuels.

2.1.4 Process for Synthesis Glycerol from Propylene

Process for synthesis glycerol from propylene via the following intermediates:

- Allyl chloride-epichlorohydrin
- Acrolein-allyl alcohol-glycidol
- Propylene oxide-allyl alcohol-glycidol

Although the acrolein and propylene oxide processes do not involve the use of chlorine, the epichlorohydrin route is the most favored industrially.

2.2 Uses and Fields of Application

As a matter of fact, glycerol is the main secondary product of oleochemistry (around 10 % by weight of natural oleochemicals production) and adds value to the competitiveness of oleochemical processes.

World production of glycerol is constantly increasing, which this rise is linked to the global increasing production of oleochemicals. In addition, the most important source of glycerol comes from oils and fats splitting destined to fatty acids and soaps.

Leffingwell and Lesser (1945) identified usages of glycerol. However, a gross classification can be shown with the help of a pie chart in Figure 2.5. Glycerol disappearance can be listed according to its applications in Table 2.1.

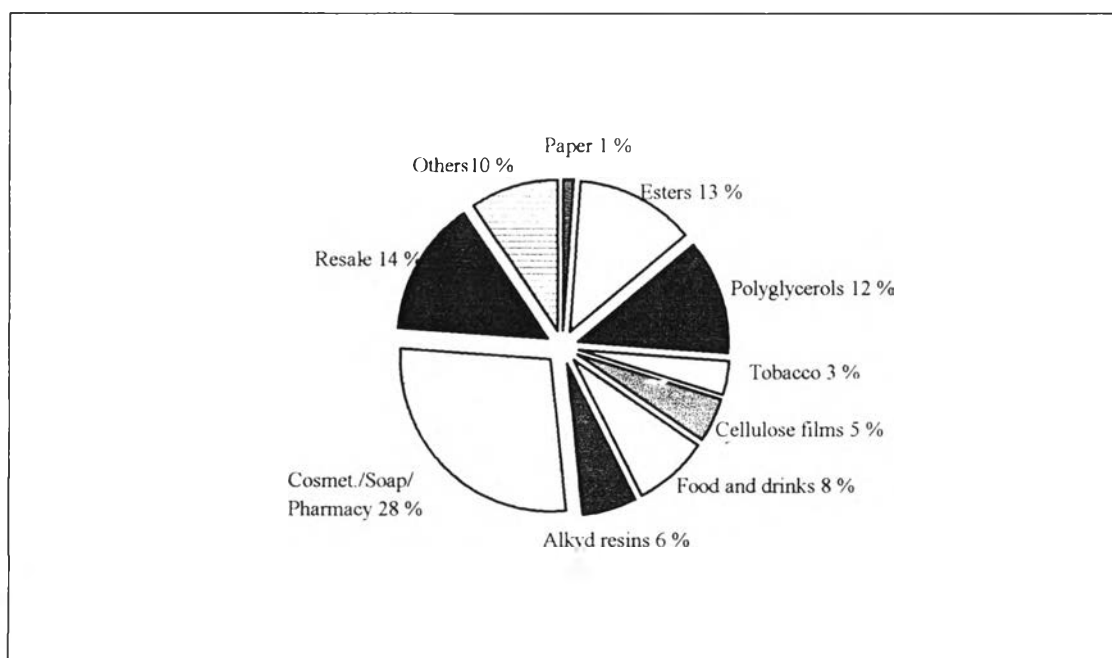


Figure 2.5 Distribution of glycerol uses (1995).

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 disappearance

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

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 glyceraldehyde, dihydroxyl acetone, and glyceric aldehyde. Reactions 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 mono- 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.

Mono- 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.

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

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 cetyl 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.

2.3.3 Polymerization of Glycerol

Polymeric ethers are formed when glycerol reacts with itself to form polyglycerols as shown in Figure 2.6.

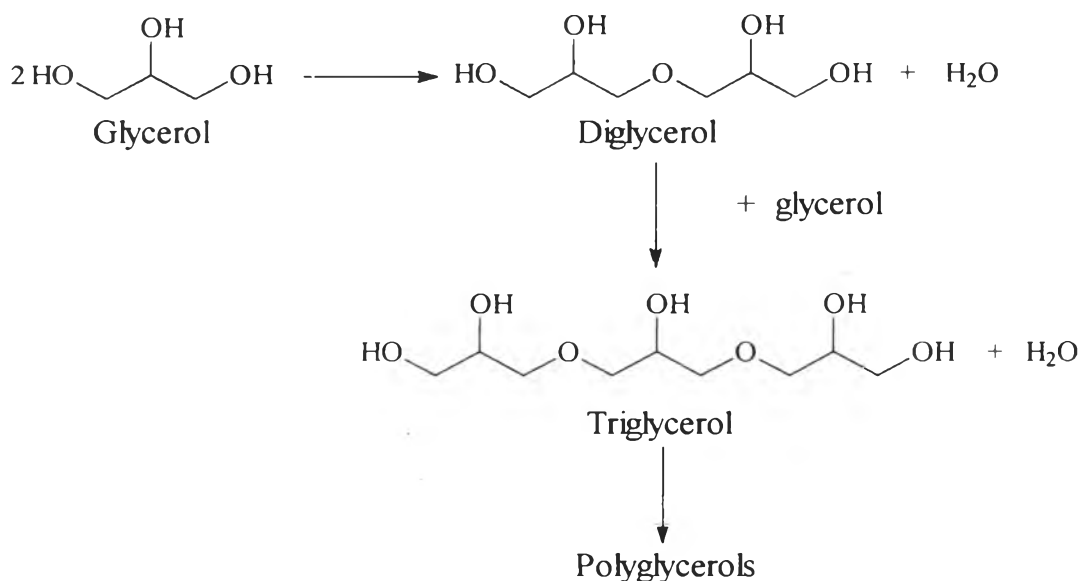


Figure 2.6 Schematic representation of the polymerization of glycerol to polyglycerols.

Polyglycerols have many properties of glycerol. For example, diglycerol is a viscous liquid about 25 times as viscous as glycerol. Polyglycerols offer greater flexibility and functionality than glycerol. Polyglycerols 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, much like glycerol, but have progressively higher molecular weights 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 hydroscopicity. 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.

2.3.4 Oxidation of Glycerol

Glycerol is quite stable in the presence of oxygen under normal conditions but it oxidizes in the presence of certain catalysts such as iron and copper. 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, glyceric acid, mesoxalic acid, and etc. Partial oxidation is usually hard to control; the oxidation products have been isolated, through more often they are prepared by indirect methods, rather than the controlled oxidation of glycerol.

2.3.5 Miscellaneous Reaction 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 2.7.

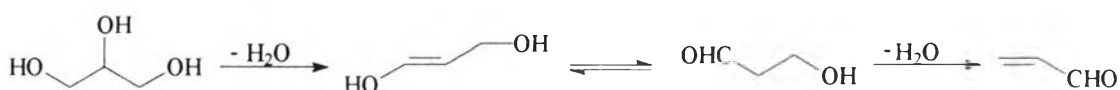


Figure 2.7 Acrolein formation by double dehydration of glycerol.

2.4 Polyglycerols

Polyglycerols have found extensive use in the food, cosmetic and pharmaceutical industry as surfactants, emulsifiers, 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 condition. 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 2.8. Polyglycerol esters function as emulsifiers, dispersants, solubilizers, thickeners, emollients, conditioners, and spreading agents. They are also used in the formulation of various cosmetic and personal care products.

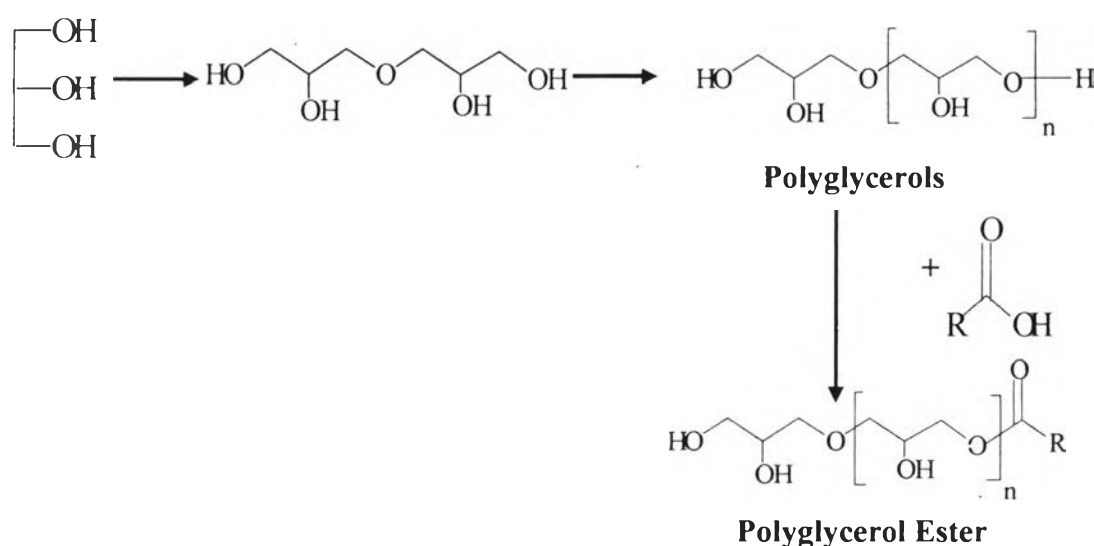


Figure 2.8 The formation of polyglycerol esters.

2.5 Synthesis of Polyglycerols

Polyglycerols were most often prepared by the polymerization of glycerol under alkaline 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 a water molecule. 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 system. 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 the name 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.

The polyglycerols were dense, viscous liquids and difficult to handle at ordinary temperatures when water free. In selecting equipment handled these polyols and their ester's, the effects of both viscosity and density must be taken into consideration. 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 blech 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 showed 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. Base-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 2.9.

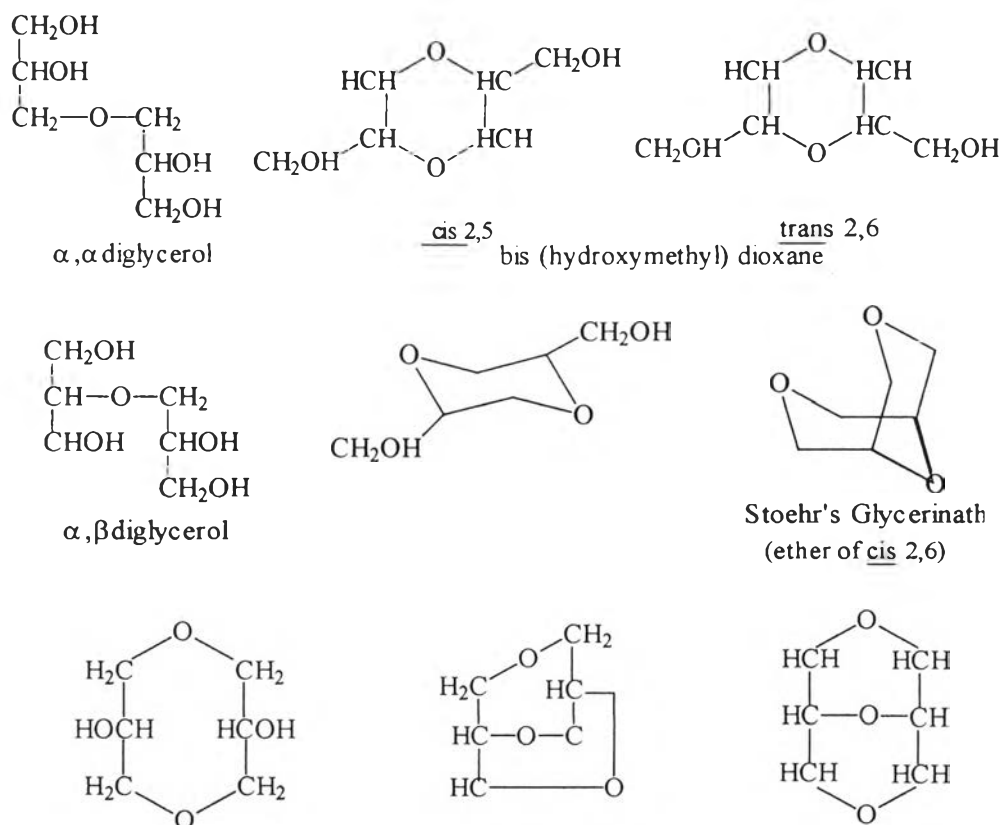


Figure 2.9 Structural configurations of diglycerol.

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 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 odour 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 of reaction was continuously taken off. The reaction was cooled rapidly and the mixture was treated with a bleaching agent. This process did not desire because high colored polyglycerols and a strong odor (pungent odor of acrolein) were obtained if the bleaching was not carried out.

Stühler (1985) studied the process for the preparation of polyglycerols by condensation of glycerol, which leded directly to products of good color quality and odour neutrality. The process was based on the condensation of glycerol at a temperature of 190 to 250°C in the present 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 object of the present invention was to provide 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 spend 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 Gardner color, a mild odor, and a bland taste. This polyglycerols were suitable for use as cosmetic and food additives. Therefore, there had been continuing efforted 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 added 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 were relatively poor in color quality.

Jakobson *et al.* (1990) studied process for the preparation of polyglycerols, which had low cyclic components. This process which 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, and 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 components 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. Which water was removed by distillation, the polyglycerols mixture were separated into diglycerol, higher polyglycerol and glycerol by fractional distillation.

A process which 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 which 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, isopropylidenglycerol 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.

2.6 Polymerization of Glycerol 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 of great interest for the synthesis of high-valuable products cheaper and more efficient than with 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 easy 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)

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.

Clacen *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 obtained show that impregnation method gives important activity, which must be correlated to important 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.

2.7 Analysis of Polyglycerols Product

Polyglycerols, obtained from polymerization of glycerol with catalysts, can be significantly contaminated with cyclic polyglycerols and acrolein due to incomplete polymerization reaction 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) and High Performance Liquid Chromatography (HPLC) 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 or quantitation.

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, glycerol and polyglycerol oligomers up to undecaglycerol and demonstrate its utility in monitoring the preparation of polyglycerols. Therefore, High Performance Liquid Chromatography (HPLC) appears to be a useful tool for monitoring the production of desired mixtures of polyglycerols and for analyzing polyglycerol esters through their polyglycerol moieties.