CHAPTER II
BACKGROUND AND LITERATURE REVIEW

2.1 Background

The liquid bio-fuels, primarily bio-diesel and bio-alcohol, are transportation fuels, processed from agricultural crops and other renewable feedstock that can be used instead of fossil fuels in common internal combustion engines. Common renewable fuels include:

- Bio-alcohols.
- Bio-diesel.

Biodiesel is a renewable fuel produced from vegetable oil extracted from a variety of crops, such as soybean, sunflower seed, rapeseed, peanut, cottonseed, oil palm, etc. World production of biodiesel is approximately 3.5 million metric tonnes per annum, and growing rapidly (Foglia et al., 2006). This growth in biodiesel production, however, is accompanied by increased glycerol supplies, a major by-product of biodiesel production. This increase in availability of glycerol lowers its value and adversely impacts biodiesel economics. Accordingly, it is desirable to find new outlets for glycerol (Foglia et al., 2006).

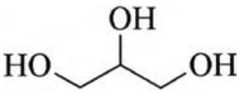


Figure 2.1 Chemical structure of glycerol, also commonly called glycerin.

Glycerol was discovered by the Swedish chemist C. W. Scheele in 1779 when he heated olive oil and lead oxide. Today, glycerol is a main component of all vegetable and animal fats. Ever since its discovery, the applications of glycerol has increased—today it is an indispensable chemical found in various products.

Glycerol has been obtained as a by-product of soap production or from the hydrolysis of fats and oils. This was also the main commercial supply of glycerol up until the Second World War With the rise of the petroleum industry, glycerol supply shifted to synthesis from propene ($H_3C{-}HC{=}CH_2$), a major by-product of petroleum cracking.

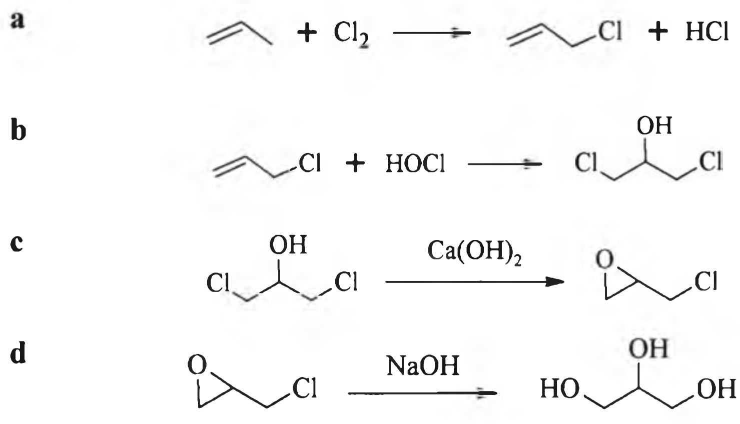


Figure 2.2 Reactive pathway for industrial production of glycerol from propene, a by-product of petro-cracking. European Oleochemicals and Allied Products Group (2007).

First the propene is chlorinated, producing hydrochloric acid and allyl chloride (Figure 2.2a). The allyl chloride is then hypochlorinated, making one mole of dichlorohydrin for each mole of allyl chloride (Figure 2.2b). The dichlorohydrin is treated with $Ca(OH)_2$, making an equimolar amount of epichlorohydrin, as well as calcium chloride and water (Figure 2.2c). In the last step, the epichlorohydrin is hydrolysed in the presence of a strong base, producing glycerol and sodium chloride (Figure 2.2d).

Currently the main supply of glycerol is as a by-product of biodiesel production, i.e, with a renewable resource as feedstock. Figure 2.2 shows the predominant method of producing biodiesel industrially: transesterification of rapeseed oil at roughly atmospheric pressure and low temperature (65 °C) in a batch process. Yields are normally above 98% (Enguídanos et al., 2002). The main product is rapeseed methyl ester, or RME, which can be mixed into petrodiesel in concentrations up to 20% with little or no modification of the diesel engine.

Figure 2.4 shows the chemical reaction of transesterification, in this case of a triglyceride (vegetable or animal fat). The alcohol (methanol) reacts with the triglyceride splitting each C=OOC bond, creating three alkyl esters (in this case methyl esters). The reaction between the alcohol and the glyceride is reversible; therefore the alcohol is added in excess to drive the reaction forward. The reaction is catalysed by either acid or base. Most industrial biodiesel production is base-catalysed, usually by a strong base like NaOH or KOH. Most vegetable oils could be used to produce alkyl esters using the depicted reaction, as long as their content of free fatty acids is low. Presence of free fatty acids will drive the reaction backwards.

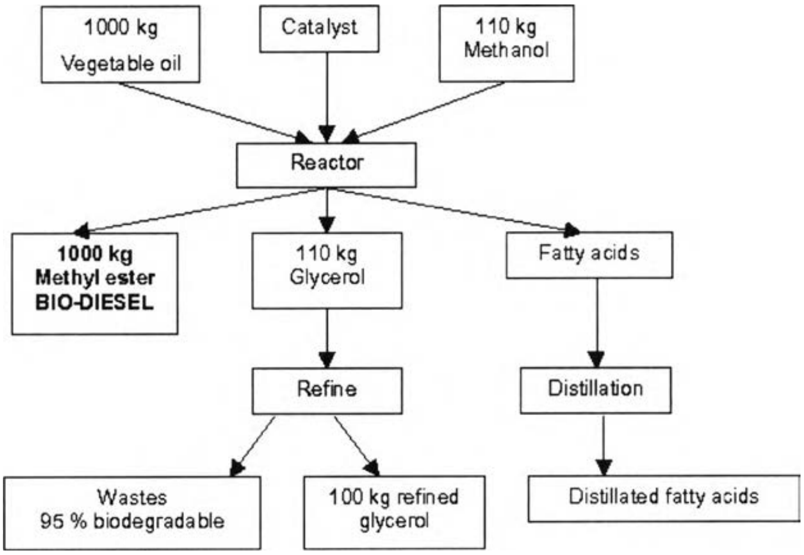


Figure 2.3 Production of biodiesel from renewable resources: each 1000 kg of biodiesel produced gives 100 kg of glycerol as by-product.

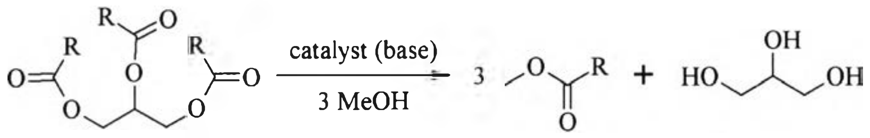


Figure 2.4 Transesterification of triglyceride to form methyl ester, the most common form of biodiesel. The R-groups of a single triglyceride need not be of the same length.

The crude glycerol glut produced in biodiesel synthesis is contaminated by process residues, such as metal salts, alcohol, water, and so forth. Earlier, this crude glycerol could be sold with a profit, but with rising biodiesel production, market price was only €50 per metric tonne in 2007 (The Glycerol Challenge Consortium, 2007)

The market price of refined glycerol was €450 per metric tonne — presenting a strong incentive for any producer of crude glycerol to refine their glycerol glut, since it earns them a premium of €400 per metric tonne. More importantly, the price of refined glycerol has been stable despite the increase in crude glycerol production. The challenge at hand is to refine the crude glycerol glut into something more valuable, instead of simply incarcerating it, which is commonly the case today.

This area is attracting much attention world-wide, and several large chemical companies are involved. Perstorp AB is Sweden's largest producer of RME, and subsequently a large producer of crude glycerol. Several approaches to utilize the glycerol glut have been proposed which involves refining it by means of vacuum distillation followed by fractional distillation, both which are common techniques, although rather expensive. Indeed, most industrial interest is directed towards utilizing glycerol as a building block for more valuable C_3 molecules.

A new industrial process has been proposed by both Dow and Solvay (Dow Epoxy, 2007; Solvay S. A., 2007) is in essence a reversal of the glycerol synthesis from propene (compare Figure 2.2). Solvay's process, called the Epicerol™ process, converts glycerol into epichlorohydrin. Obviously, an epoxide molecule is much more versatile as a building block than an alcohol. Epichlorohydrin is used to make epoxy resins, which have applications in the car, housing, boating and leisure industries; and also, curiously enough, as teabag paper reinforcement. Figure 2.4 shows the principal reactions of the Epicerol™ process. Since a few years back, most industrial production of glycerol from petroleum by-products has ceased, due to the rapid increase in glycerol from biodiesel production. The development of new industrial synthetic processes from glycerol is a natural step considering the current market conditions.

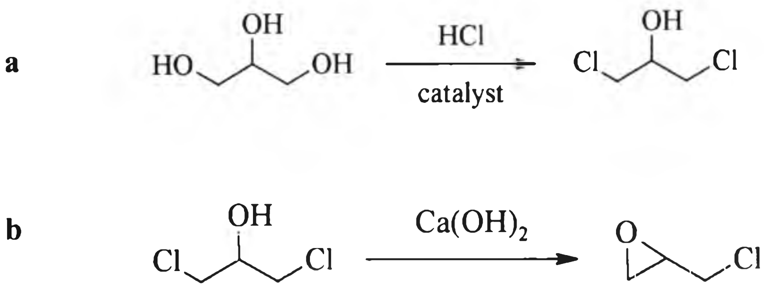


Figure 2.5 Making epichlorohydrin from renewable glycerol, as in Solvay's commercial Epicerol™ process. Solvay Chemicals, Inc. (2007).

No details on the catalyst which is used in the first step of the Epicerol™ process (Figure 2.4a) are available, other than it being a solid material. The catalysis is thus heterogeneous. The organic reactions involved (from glycerol to epichlorohydrin or the reverse) are well-known to organic chemists. The secret lies in the catalyst, which makes this process economically and industrially feasible.

2.2 Properties and Uses of Glycerol

Glycerol $C_3H_5(OH)_3$ has many common names such as glycerin, glycerine, glyceritol, glycyl alcohol, 1,2,3–propanetriol and 1,2,3–trihydroxypropane. Glycerol is a trihydric alcohol, having two primary and one secondary hydroxyl groups, which are its potential reaction sites and the basis for glycerol's usefulness as a chemical raw material. It has a molecular weight of 92.09, a density of 1.2375 (20 °C/ 4 °C), a melting point of 17.8 °C, a flash point of 176 °C and a boiling point of 290 °C accompanied by decomposition.

Glycerol's vast usage stems from its favorable properties. Glycerol is a transparent, viscous liquid, odorless, colorless, and sweet tasting (60% as sweet as sucrose) and of low toxicity. It is also strongly hygroscopic (in an exothermic reaction). It is completely soluble in water and alcohol, and insoluble in hydrocarbons (Li, 1998).

In fact, the uses of glycerol are so numerous, that we can by no means enumerate all of them. But allow me to present a few in the next paragraph, with several of the examples taken from an excellent essay by David (1996).

One can roughly divides the usage of glycerol into the areas of food additives, cosmetics and personal care, pharmacy, and industrial applications. Because of its hygroscopic properties, glycerol is used as moistening agent for baked goods. It is also added to candies and icings to prevent crystallization. Water/glycerol mixtures have been shown to prevent crystallization (Dashnau et al., 2006). Glycerol is used as a solvent for food colors and carrier for extracts and flavoring agents; because of its low volatility, it keeps the flavors from evaporating.

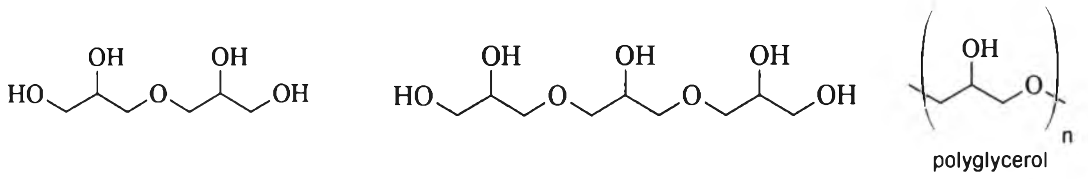
In pharmaceutical products, glycerol's emollient and demulcent properties makes it useful ingredient in salves, and its sweetness is used in tinctures to improve taste. In cosmetics glycerol is a major additive in lotions, creams and toothpaste, used mainly to impart smoothness.

Glycerol's uses in chemical industry cover a whole range of products and applications. Glycerol is the main starting material for nitroglycerine, which is used in the manufacture of dynamites and munitions. When reacted with dibasic acids, such as phthalic acid, it makes alkyd resins, an important class of chemicals used in coatings and paints. Glycerol is also used as a levitating agent to reduce the particle size of a powder on grinding. Glycerol is sprayed on pre-processed tobacco to prevent crumbling, due to its excellent humectant properties.

That was just a few of glycerol's many uses. In the next section we will look into the oligomers of glycerol, di- and triglycerol, and their possible advantages over glycerol.

2.3 Properties and Uses of Glycerol Oligomers

An oligomer is a short polymer, generally shorter than ten units. In this report, the term oligomer is used to describe glycerols up to and including pentaglycerol. The term "polyglycerols" is a general descriptor encompassing oligomers as well as higher polymers of glycerol.



a. Diglycerol b. Triglycerol c. polyglycerol

Figure 2.6 Structure formulas of diglycerol, triglycerol, and a general glycerol polymer. Note that the relative hydroxyl content, and thus hydrophilicity, decreases with chain length.

The viscosity of glycerol oligomers increases with chain length. The use of higher polyglycerols (higher or equal to heptaglycerol) is restricted in food applications (EU Commission, 1998), where the desired polylycerols are usually di- and triglycerol. A positive effect of increased chain length is decreased volatility, which reduces the evaporation of an added fragrance, e.g., in deodorants and mouthwashes (Solvay Chemicals, Inc., 2004). Other properties that follow chain length is increasing thermal stability and increasing refractive index. Additionally, the humectants property of glycerol is reduced as the chain length increases (since the hydrophilicity decreases).

Polyglycerols as such have a number of applications. Most notably, they are used in essentially all personal care applications, such as skin, oral or hair care products, as either additives or excipients. Also, polyglycerols can be used as reactants in the production of polyurethanes and polyesters (Solvay Chemicals, Inc., 2005).

Although the applications of polyglycerols as such are numerous, as evidenced in the preceding paragraphs, the polyglycerol esters find much more widespread application. In this reseach interated in lubricant application, a more detailed description of lubricant will be made in the next section.

2.4 Lubricant

The majority of lubricants are liquids. They may be classified according to their origin into two groups: mineral oils derived from petroleum (the majority) and synthetic oils. Most liquid lubricant contain additives to improve their natural properties, or impart nem properties to them, so that they have qualities suitable for their applications and their operability maybe prolonged. Liquid lubricants are used either as such or as water emulsions, where efficient cooling is required as well as lubricantion duty.

2.4.1 Mineral Oils

Mineral lubricanting oils having a variety of physical and chemical are now use. To obtain oils of the required properties, selection of the right crude petroleum source has to be combined with the right manufacturing procresses and the use of the right additives in the optimum proportions and dosages. Their properties depend on the number of carbon atoms in the average molecule, ie., on the size of the molecules expressed asrelative molecular mass (RMM- 250 or more), on the distillation range and on the hydrocarbon groups present. These are represented by straightn-chain and branched alkane, alkylcloalkanes, alkiylaromatics and alkylcycloaromatics. Compounds of sulphur, oxygen and nitrogen are also present.

2.4.2 Synthetic Oils

Although modern type of mineral oils reinforced by additives are capable of meeting a broad range of lubricatin and other requirements, their properties are in some cases significantly surpassed by those of synthetic oil, for example, where very low aor very high temperatures prevail, or under conditions where a wide operating temperature range or an conventional environment, e.g.g self-igintion hazard or exposure to ionising radiation, impose unsual requirement. Some types of synthetic oils are suitable for use in admixture with mineral oils - the so-celled "semisynthetic" oils - as well as additives for mineral oils. Synthetic oils now in use are gernerally chemical compounds of defined composition with defined functional groups, and may be broadly classified into: alkene polymers, alkylaromatics, chlorinated hydrocarbons, fluorinated hydrocarbons, polyalkylene glycols and polyalkylene ethers, alkyl esters of monocarboxylic aliphatic acids, alkyl esters of dicarboxylic aliphatic acids, alkyl and aryl ester of oxy-acids of phosphorus, alkyl and aryl ester of silicic acids, polsilxanes, and oils miscellaneus chemical families. The majority of synthetic oils can be improved by additives.

2.4.2.1 Synthetic Hydrocarbons

Synthetic hydrocarbons were developed simultaneously in Germany and the United States of America. It is known today, that all synthetic hydrocarbons –and the other economically important synthetic lubricating oils– can be synthesized starting with ethylene. Ethylene itself is one of the most important petrochemicals and today mainly produced in steam crackers

2.4.2.1.1 Polyalphaolefins

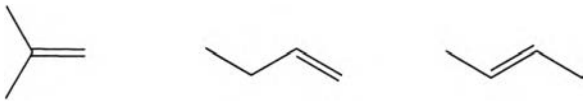
The term polyalphaolefin (PAO) is derived from the source of this class of base oil, usually α-decene or a mixture of α-olefins containing, in general, a minimum of six and a maximum of twelve carbon atoms. The oligomers are saturated, i.e. hydrogenated, and therefore belong to the aliphatic or branched paraffinic hydrocarbons. Linear α-olefins were first used for the synthesis of lubricating oil. Polyalphaolefins satisfy some of the requirements of ideal hydrocarbon lubricants that can be predicted from chemical structure considerations – ideal hydrocarbon lubricants should have straight chains, be completely saturated and crystallize at low temperatures. The viscosities of straight-chain alkanes do indeed increase with chain length; the same is true for their pour points and viscosity indexes (VI). At constant molecular mass branching leads to increased viscosity and a decrease in pour point and VI. The length and position of the side chains influence all three properties. When branching occurs in the middle of the main chain, pour points are lower. Long side chains improve viscosity–temperature (V–T) characteristics. Polyalphaolefins therefore have several advantages –narrow boiling ranges, very low pour points, viscosity index (VI) > 135 for all grades with kinematic viscosity > 4 $mm^2 s^{-1}$ at 100 °C. Their volatility is lower than that of all possible and equiviscous mineral oil grades and they contain only small quantities of unsaturated and polycyclic aromatic compounds and only traces of nitrogen, sulfur, or other impurities. Although in some oxidation tests without additives some mineral oils seem superior to polyalphaolefins, this is because of the presence of natural antioxidants in the mineral oils that have survived the refining proces. Their low polarity, on the other hand, leads to poorer solvency for very polar additives and can cause problems with seals. Therefore they tend to be used in combination with smaller amounts of (dicarboxylic acid) esters or solvent-refined mineral oils. Polyalphaolefins have been used traditionally in aerospace and lifetime applications, but today they are used in a wider variety of applications and have gained additional importance because of the increasing need for them in automotive lubricants.

2.4.2.1.2 Polyinternalolefins

Polyinternalolefins (PIO) are rather similar to polyalphaolefins. Both kinds of hydrocarbon are prepared by the oligomerization of linear olefins. The difference is that polyinternalolefins are made from cracked paraffinic base stocks. Internal olefins are more difficult to oligomerize and the resulting products have VIs 10 to 20 units lower than the VIs of equiviscous polyalphaolefins. Mixtures of polyalphaolefins with polyethylenes with kinematic viscosities from 100 to 2000 $mm^2 s^{-1}$ at 100 °C are available commercially. It can be expected that polyinternalolefins having these viscosities genuinely will be available in the future. While the cationic polymerization of ethylene with aluminium chloride yields oils with VIs up to 120 and molecular masses from 400 to 2000, the polymerization of propylene gives oils with lower VIs and poor thermal stability. Both kinds of lubricating oil have lost importance, but copolymers of both base materials are said to have the potential for gaining importance again.

2.4.2.1.3 Polybutenes

Polybutenes (PBs) are produced by the polymerization of a hydrocarbon stream that besides isobutene contains the other two butenes (butane-1 and butane-2) and the butanes. The main sources of the C-4 feedstock are naphtha steam crackers and refinery catalytic crackers. The Lewis acid-catalyzed process yields a copolymer with a backbone built mainly from isobutene units. The higher the molecular weight, the lower the content of other butenes, that is, the lower the molecular weight the more complex the structure. At the end of the carbon chain there remains one double bond. Therefore polybutenes are less resistant to oxidation than polyalphaolefins, polyinternalolefins, and alkylated aromatics–above 200 °C they begin to depolymerize and form gaseous products. Normally the end-group is cis- and trans-trisubstituted. It is possible to replace it by a disubstituted vinylidene group, that is more reactive. With maleic anhydride it yields polybutenylsuccinic anhydride derivatives, that are used as corrosion inhibitors and detergents.



a. isobutene b. butane-1 c. butene-2

Figure 2.7 Structure formulas of isobutene, butane-1, and butane-2.

Polybutenes with molecular masses from about 300 to 6000 are important as VI improvers. They are used as components in two-stroke oils, gear and hydraulic oils, metal working lubricants, greases, compressor lubricants, and wire-rope protectives. One of the options for future polybutene applications is the increased use as synergistic components in binary or ternary base oil systems.

2.4.2.1.4 Alkylated Aromatics

Alkylnaphthalenes as lubricants have been available in Germany since ca. 1930. Low-cost dialkylbenzenes are produced as by-products in the manufacture of linear and branched monoalkyl benzenes that themselves are feedstocks for the manufacture of detergents. The Friedel–Crafts alkylation of benzene with olefins tends to yield polyalkylated products, because of the reactivity of the primary product. With excess benzene, a suitable olefin, e.g. propene, and the right choice of a catalyst the reaction can be controlled and specialized alkyl benzenes can be synthesized. The structure of a typical alkylbenzene comprises six propene units (Figure 2.8). The properties of synthetic alkyl benzenes vary widely and are difficult to generalize.

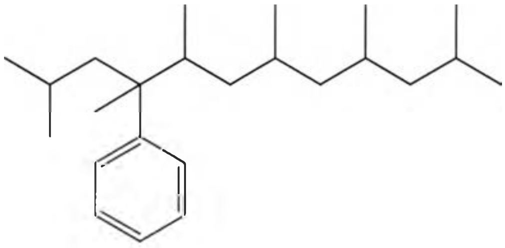


Figure 2.8 Structure of a typical alkylbenzene comprises six propene units.

Some of the properties of alkylated benzene can be explained by chemical structure considerations –ring formation leads to a larger increase in viscosity and decrease in VI values than alkyl substitution; side chains on a naphthenic ring have the opposite effect. A shift of cyclohexyl substituents from the end toward the middle of an alkyl chain has only a small effect on viscosity, but a strong negative effect on V–T; it also lowers the pour point; cyclopentane rings have a similar effect and alkylated aromatics have effects similar to those of equimolecular alkylnaphthenes but the products have lower viscosities and less favorable V–T dependence. Lower-cost dialkylbenzenes are used in a wide variety of industrial areas, e.g. in transformer oils, where high resistance to gas evolution is important. Tailored grades, especially the linear products, although having poorer properties than polyalphaolefins, because of their excellent solvency, their suitability for low temperatures, and their compatibility with elastomers still are an option. The most widespread use of these products is, however as refrigerator oils.

2.4.2.2 Halogenated Hydrocarbons

Chlorinated hydrocarbons are very stable and not combustible. They were once widely used as insulating oils, heat-transfer fluids, and hydraulic fluids, but this use has been discontinued because of the environmental problems they cause. Commercial liquid chlorofluorocarbons, all oligomers of chlorotrifluoroethylene contain between two and twelve units. They are suitable for use as lubricants mainly because of their extraordinary chemical stability, including against oxygen. Their low corrosivity, the good low-temperature characteristics of the low-viscosity grades and their lubricating properties are also advantageous. Disadvantages are their high volatility and their not ideal V-T dependence. The properties of the chlorofluorocarbons are a consequence of the larger volume of the chlorine and fluorine atoms, which hinders the flexibility of the molecule, of the reduced intermolecular cohesive forces, and of the different bond lengths. Their density naturally is relatively high, (between 1.7 and 2 g mL^{-1} at 40 °C). They are used as lubricants in oxygen compressors, in pumps for mineral acids, halogens, and oxygen, and in mills or mixers for strong oxidizing agents. They are also suitable lubricants for turbine pumps in rocket engines and as base oils for non-flammable hydraulic fluids. Although the halogenated hydrocarbons are comparable with perfluorinated polyethers with regard to their performance, but not as expensive, their future is unclear.

2.4.2.3 Polyalkylene Glycols

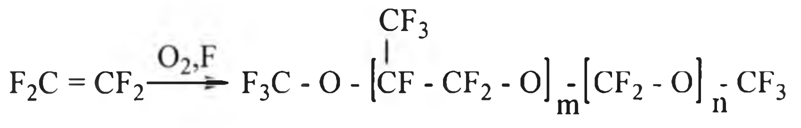
The first polyalkylene glycols suitable as lubricants were developed during World War II. Polyalkylene glycols are prepared by the reaction of epoxides, usually ethylene and propylene oxide, with compounds that contain active hydrogen, usually alcohols or water, in the presence of a basic catalyst. Variation of the ratio of the epoxides and the end groups leads to different products. Polymers with statistically distributed alkylene groups are made by use of a mixture of alkylene oxides. Separate addition leads to block copolymers. Because ethylene oxide is more reactive than propylene oxide, random copolymers tend to have the propylene oxide units at the chain ends. Polyalkylene glycols have at least one hydroxyl group at one end of the molecule, and can therefore be regarded as alcohols. The number of hydroxyl groups is increased by use of water or multifunctional starters. Miscibility with water increases with the number of ethylene oxide units. The solubility is a result of hydrogen-bonding of water with the free electron pairs of the oxygen. In solution the water-soluble grades are practically non-flammable. The hygroscopic character of the polyalkylene glycols is dependent on their hydroxyl group content–it decreases with increasing molecular weight and the number of ether bonds. The solubility in water decreases in the same way. That it also decreases with increasing temperature can be explained by a loss of hydrogen bonding. Solubility in hydrocarbons increases with the molecular weight. Polyalkylene glycols in general are soluble in aromatic hydrocarbons. The molecular weight and viscosity of polyalkylene glycols can be significantly influenced during production and be adjusted within narrow limits. The possibility of engineering products in this way distinguishes them from many other lubricants. Low molecular weight polyalkylene glycols containing more than 50% propylene oxide have pour points that go down to –65 °C. The lateral methyl groups are responsible for the disruption of crystallization. On the other hand pure high-molecular weight polyethylene glycols are wax-like solids with pour points near +4 °C. The kinematic viscosities range from 8 to 100 000 $mm^2 s^{-1}$ at 40 °C. With the change from diols to monoethers, ester ethers and diethers, at the same molecular weight, viscosities are reduced, particularly at low temperatures. In comparison with mineral oils, which give straight lines, the V–T diagrams of polyglycols show their viscosities are too high at both low and high temperatures. The VI values of polyalkylene glycols usually lie around 200. High-molecular-weight polyethylene glycols have VI values of up to 400. Prolonged heating of polyalkylene glycols to above 150 °C leads to depolymerization. The resulting aldehydes react further to give acids. It is an advantage that only soluble or volatile products are formed. Traces of alkali or alkaline earth metals promote the degradation. The decomposition can be prevented by addition of aminic antioxidants, to the extent that the oils can be used as heat-transfer fluids up to 250 °C. The polar nature of polyalkylene glycols gives the products strong affinity for metals, and so the lubricating film remains intact even at high surface pressure, a property useful in lubricants and metal cutting fluids. Easy removal by washing with water makes these suitable for applications that are difficult for other products. The toxicity of polyalkylene glycols is similar to that of glycerol for low-viscosity products and similar to that of isopropanol in more viscous products. This is of advantage in the food, pharmaceutical, tobacco, and cosmetics industries. Polyalkylene glycols lower the freezing point of water. High viscosity water-soluble products are shearstable liquid thickeners. Hydrophilic and hydrophobic fractions in block copolymers give them surfactant properties. The lubricating properties in mixed-friction areas and in rolling friction contacts can be improved by use of polyalkylene glycols with a broad molecular-weight range, for example; these can bridge the differences between water and the polyethers in terms of adhesion, viscosity, and volatility.

2.4.2.4 Polyethers

Alkylated aryl ethers, like alkyl ethers, have lower viscosities, lower VI values, lower pour points, and lower boiling points than the corresponding alkanes. Asymmetric substitution also reduces the pour point, but has an adverse effect on the V–T. Although such products have low viscosities, some have found use as components of lubricants used in the life sciences.

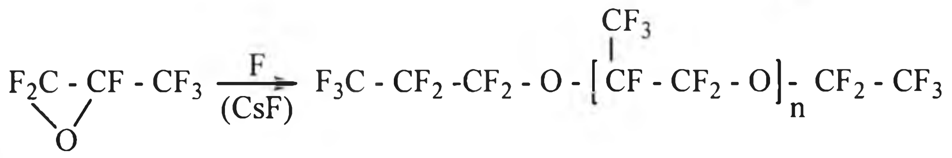
2.4.2.4.1 Perfluorinated Polyethers

Perfluoroalkylpolyethers (PFPE) as lubricants were probably first mentioned in 1965. The photochemical polymerization in the presence of oxygen, followed by fluorination with elemental fluorine leads to products of type A (Eq. 2.1), with tetrafluoroethylene. With hexafluoropropylene products of type B (Eq. 2.2), result. Anionic polymerization of hexafluoropropylene epoxide leads to products of type C (Eq. 2.3), and Lewis acid-catalyzed polymerization of 2,2,3,3-tetrafluorooxetane leads to products of type D (Eq. 2.4).

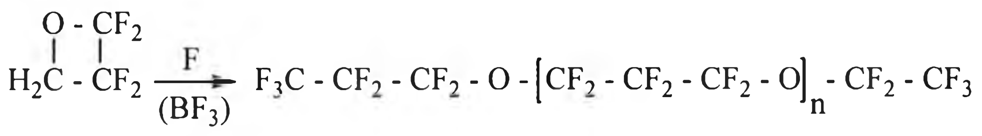


$$F_2C = CF_2 \xrightarrow{O_2,F} F_3C - O - [\overset{CF_3}{\overset{|}{CF}} - CF_2 - O]_m - [CF_2 - O]_n - CF_3 \qquad \text{Eq. 2.1}$$

$$F_2C = CF - CF_3 \xrightarrow{O_2,F} F_3C - O - [CF_3 - CF_2 - O]_m - [CF_2 - O]_n - CF_3 \qquad \text{Eq. 2.2}$$



$$F_2C - CF - CF_3 \xrightarrow[(CsF)]{F} F_3C - CF_2 - CF_2 - O - [\overset{CF_3}{\overset{|}{CF}} - CF_2 - O]_n - CF_2 - CF_3 \qquad \text{Eq. 2.3}$$

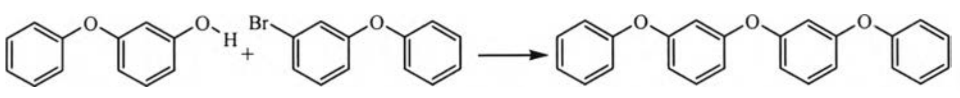


$$H_2C - CF_2 \xrightarrow[(BF_3)]{F} F_3C - CF_2 - CF_2 - O - [CF_2 - CF_2 - CF_2 - O]_n - CF_2 - CF_3 \qquad \text{Eq. 2.4}$$

The density of the PFPEs is nearly twice that of hydrocarbons. They are immiscible with most of the other base oils and non-flammable under nearly all practical conditions. The more common types A and B have a good to very good V-T and V-p dependence, and low pour points. The viscosity of linear PFPEs changes less with temperature and pressure than that of the non-linear variety, but has a non-negligible deviation from linearity, as has recently been reported. In air they are stable up to 400 °C. Trifluoromethyl groups that are adjacent to the ether bonds shield them from acid-catalyzed cleavage, but difluoroformyl groups contribute to a decrease in stability at higher temperatures. PFPEs are remarkably inert chemically, this is including elastomers. Their hydrolytic stability is excellent. Good radiation stability, that was stated earlier, has been doubted. The shear stability of PFPEs is better than that of other polymeric lubricants, but in the presence of steel and under boundary lubrication conditions PFPEs do not perform very well. The effect of humidity and their thermo-oxidative behavior have been investigated. It has been found that the performance can be improved with α,β-diketones. Perfluoropolyalkyl ethers have all the properties required by modern spacecraft: as lubricants and hydraulic fluids they resist to thermal and oxidative attack above 260 °C, possess good low-temperature flow characteristics, and are fire-resistant. They can also be used as power transmission and inert fluids and in transformers and generators as dielectrics with outstanding properties.

2.4.2.4.2 Polyphenyl Ethers

Polyphenyl ethers are the reaction products of phenols and halogenated aromatic compounds (Eq. 2.5). Abbreviated formulas are in use. They contain the substitution position and the number of phenyl rings and ether bonds:



Eq. 2.5

The aromatic groups increase the stability, but negatively affect the V–T dependence of these polyethers. Alkyl groups lower the high melting points. ***para*** Derivatives have lower volatilities; for ***ortho*** products the volatilities are higher. Spontaneous ignition occurs between 550 and 600 °C and alkyl substitution reduces this by ca. 50 °C. With the usual elastomers swelling occurs. The oxidation stability of polyphenyl ethers is only slightly lower than that of polyphenyls or tetraarylsilanes. Alkyl substituents reduce it. The thermal decomposition temperatures are up to 465 °C. Short-chain substituents reduce it to below 380 °C and with higher alkyl groups it drops to below 350 °C, that is, to temperatures typical for aliphatic hydrocarbons. Trifluoromethyl groups have a worse effect, the thermal decomposition temperature drops below 270 °C. Coke formation is low. It increases with alkyl substitution, particularly in the presence of methyl groups. Polyphenyl ethers are the most radiation-resistant lubricants. At low temperatures radiation affects the viscosity more pronouncedly than at high temperatures. It increases viscosity, acidity, evaporation loss, corrosivity, and coke formation, but reduces flash and ignition point. Between 200 and 300 °C the lubricating properties of polyphenyl ethers are reported to be comparable with those of mineral and ester oils and better than those of polysiloxanes and aromatic hydrocarbons. Alkylated polyphenyl ethers have better properties than the unsubstituted ethers. Polyphenyl ethers are suited as high-temperature or radiation-resistant hydraulic fluids and lubricants, and as lubricants for optical switches.

2.4.2.4.3 Polysiloxanes (Silicone Oils)

Polysiloxanes can be liquids or solids. Silicone oils suitable as lubricants are generally straight-chain polymers of the dimethylsiloxane and phenylmethylsiloxane series. The unique properties of silicone lubricating oils is their immiscibility with many organic fluids, the low temperature-dependence of their physical properties, and their physiological inertness. It is possible to make them with both very low pour points and high viscosity by increasing the asymmetry of the molecules, usually by partial replacement of the dimethylsilyl groups by phenylmethylsilyl groups. The density of silicone oils is in the region of that of water, those of dimethylsilicone oils are slightly below, those of phenylmethyl silicone oils slightly above. The extremely low viscosity–temperature coefficients (VTC) lower than 0.6 for low-viscosity dimethylsilicone oils are mainly due to the extraordinary flexibility of their Si–O chains. Low to medium viscosity silicone oils have Newtonian behavior up to high shear rates, but with increasing viscosity the apparent viscosity decreases with increasing shear rate, that is, pseudoplastic behaviour is observed. Compressibility and viscosity changes at high pressure depend strongly on the methyl-to-phenyl ratio of the silicone oils and are relatively large, again mainly because of the flexibility of their Si–O chains. The thermal decomposition of silicone oils begins at approx. 300 °C. In general the decomposition products are not corrosive, but they lower the viscosity of the oils. Up to 200 °C the oxidation stability of silicone oils is superior to that of hydrocarbons, esters, and polyalkylene glycols. The stability of phenylmethylsilicone grades, because of the resonance stabilization of the phenyl radicals, has been reported to exceed that of dimethylsilicone grades by up to 50 °C. The lubricating properties of phenylmethylsilicone oils are better than those of the dimethylsiloxanes; trifluoropropylmethylsilicone oils perform even better. Despite this they have been widely superseded by the perfluorinated polyethers. Silicone oils can be found in all kinds of industrial and military installations. Dimethylsilicone oils are used as lubricants for bearings and gears with rolling friction. In sliding friction their performance depends on the metal pairs, they are used, for example, as lubricants for bronze or brass on aluminum, copper, or zinc at low surface pressures and as lubricants for porous bronze bearings. Silicone oils are among the best lubricants for plastic bearings, but in precision instrument applications spreading should be prevented by use of an epilamization agent. They are suitable lubricants for rubber parts, also, and also serve as switch and transformer oils. Silicone oils with higher phenyl substitution are mainly used for the lubrication of turbines, ball bearings, and all kinds of instrument, especially at high temperatures. Their radiation stability is also remarkable. Silicone oils can be used as base oils for all kinds of lubricating greases, be it for sealing and damping applications, for reasons of chemical inertness, or for high performance low- and high-temperature applications.

2.4.2.5 Synthetic Esters

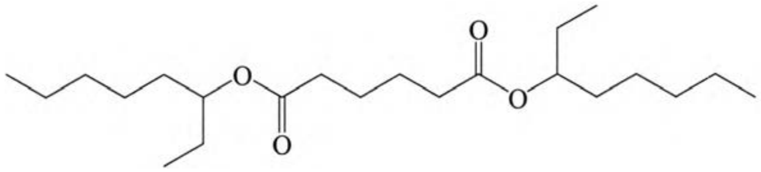
2.4.2.5.1 Esters of Carboxylic Acids

Synthetic ester lubricants for the jet age were developed in Germany during World War II. Hydrocarbon oils could not satisfy the demands on aircraft engine oils and alkyl esters of aliphatic carboxylic acids had favorable properties. Carboxylic groups, because of their strong dipole moments, reduce the volatility and increase the flash point of lubricating oils, and at the same time positively affect thermal stability, (the bonds of the COO group are thermally more stable than the C–C bond), solvency, lubricity, and biodegradability; on the other hand, they negatively affect the hydrolytic stability of a lubricant and the reactivity with metals or alloys that contain copper or lead.

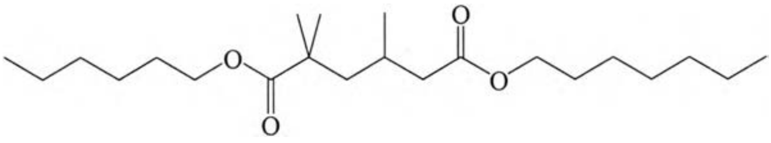
In principle all esters of carboxylic acids can be prepared in the same manner: (1) the carboxylic acid is reacted with excess alcohol in the presence of a catalyst, (mineral acids, ideally adsorbed on a solid, ion exchangers, Lewis acids, e.g. boron trifluoride, ideally as the etherate, and amphoteric hydroxides such as aluminium hydroxide can be used as catalysts); (2) to shift the equilibrium to the product side, the reaction water is removed during the process; and (3) the unreacted acid is neutralized with sodium carbonate or calcium hydroxideand then removed by filtration and the ester is distilled.

2.4.2.5.1.1 Dicarboxylic Acid Esters

Two types of ester molecule or their combinations have been found to be most suited as lubricant components: esters of branched primary alcohols with straight dicarboxylic acids (Figure 2.9 a); and esters of straight primary alcohols with branched dicarboxylic acids (Figure 2.9 b).



a. Di(2-ethylhexyl)adipate



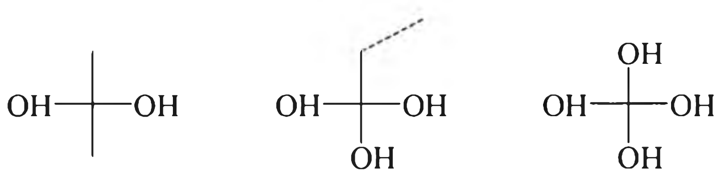
b. Diundecyl(2,2,4-trimethyl)adipatte

Figure 2.9 Structure formulas of di(2-ethylhexyl)adipate, and diundecyl(2,2,4-trimethyl)adipatte.

Esters of straight-chain dicarboxylic acids have better V–T characteristics than mineral oils, and higher VI values. The values decrease with increasing branching, but branching improves the low-temperature properties. Esters with little branching have the best properties, especially esters with methyl groups adjacent to the carboxyl group. When the esters contain tertiary hydrogen atoms, however, their stability toward oxidation is not improved. The sterically hindered esters have favorable thermal and hydrolytic stability. The hydrolytic stability has been further improved with the aid of carbodiimides. At low temperatures the viscosity of esters follows a time function and additives can have a negative effect on the viscosity and the pour point. With methacrylates as VI improvers values between 170 and 180 are reached. With complex esters as VI improvers degradation as a result of shear stress is less pronounced. Additives are mainly added to improve the EP performance, although the load-carrying capacity of esters in general is twice that of mineral oils. Dicarboxylic acid ester oils can improve the V–T characteristics of automotive engine oils without having a negative effect on the low-temperature viscosity or the Newtonian flow behavior. Such oils are suitable for diesel engines also. Esters have also gained importance as lubricity additives in greases and in polyalphaolefins as additives for the improvement of the compatibility with elastomers.

2.4.2.5.1.2 Polyol Esters

Since the 1940s neopentyl glycol ((2,2-dimethyl)-1,3-propandiol), trimethylolethane and -propane (1,1,1-tris(hydroxymethyl)ethane and –propane), and pentaerythritol (2,2-bis(hydroxymethyl)-1,3-propanediole) have been known as the alcoholic components of esters. Beside excellent thermal and oxidation stability, the esters have good V–T and lubricating properties and excellent viscosity characteristics at low temperatures. The reason is that the thermal stability of a primary OH group is greater than that of a secondary group, and the hydroxy derivatives of neopentane contain only primary hydroxy groups, and short side-chains in a hydrocarbon not only reduce its pour point, but tertiary C or H atoms at the same time facilitate the attack of oxygen; the polyols, however, have no tertiary H atoms and no H atoms in the b-position that could facilitate thermal cleavage.



(a) (b) (c)

Figure 2.10 Structure formulas : (a) neopentyl glycol, (b) trimethylolethane and -propane, and (c) pentaerythritol.

2.4.2.5.1.3 Complex Esters

Esters that contain straight or branched diols or polyalkylene glycols and straight or branched dicarboxylic acids as well as (mono)carboxylic acids and monofunctional alcohols have attracted interest. Usually first the diol is esterified with the dicarboxylic acid, then, depending on the desired product, the intermediate product is reacted with either a carboxylic acid or a monoalcohol. Two types of complex ester have become important:

ROH···HOOCrCOOH···HORrROH···HOOCrCOOH···HOR I
RCOOH···HORrROH···HOOCrCOOH···HORrROH···HOOCR II

The same scheme is valid when neopentane derived polyols or glycerol are involved.

That complex esters have higher molecular weights and higher viscosities than the common esters was one of the main reasons for their introduction. Esters of type II are superior to type I with regard to flash point, pour point, and low temperature viscosity. In type I polyalkylene glycols lead to lower pour points than aliphatic glycols. Medium molecular-weight oligomeric esters starting from (mainly vegetable) fatty acid triglycerides are of interest for environmentally friendly and high-performance applications, as are esters starting from adipic acid or sebacic acid and neopentyl glycol (type I), because their biodegradability and because their pour points are approximately the same as those of their monomers, although their viscosities are higher. High molecular weight complex esters of the type:

$$R\cdots(HOrOH\cdots HOOCrCOOH)_n\cdots R \tag{III}$$

have also been named polymer esters and find use mainly in applications where mineral oil and solvent resistance is required.

When alphaolefins and alkylmethacrylates are co-oligomerized another kind of polymer ester results and a third kind is based on polymers, that have been functionalized. With such products attempts have been made to combine the advantages of synthetic hydrocarbons and synthetic esters at a high viscosity level.

2.4.2.5.1.4 Fluorinated Carboxylic Acid Esters

Esters of fluorinated acids are readily hydrolyzed and the free acids have a strong oxidizing effect, therefore only esters with fluorinated alcohols can be used as lubricants. The thermal stability of fluorinated esters is better than that of the non-fluorinated analogs. The oxidation stability is also higher. Some types of rubber shrink in their presence and some antioxidants have a negative effect. Fluorinated esters were in the first place intended for high-temperature applications. It can be assumed that their use will be limited because of competition from the fluorinated polyethers. Esters containing sulfur as a part of the acidic or alcoholic component are known but have not gained any importance.

In the future, mixtures of all kinds of synthetic hydrocarbon and synthetic ester promise much improvement in all fields of application.

2.4.2.5.2 Phosphate Esters

Tertiary esters of phosphoric acid with alcohols or phenols were prepared as long as 150 years ago but were not introduced as antiwear additives before 1930. They have also gained importance as plasticizers, fire-resistant hydraulic fluids, compressor oils, and synthetic lubricants. They are usually divided into triaryl, trialkyl, and alkylaryl phosphates and are made by reaction of phosphoryl chloride with phenols or alcohols (Eq. 2.6). Their properties range from low-viscosity fluids to high-melting solids. With increasing molecular weight trialkyl phosphates change from water-soluble to insoluble liquids. The triaryl phosphates have higher viscosities and are insoluble in water. An aryl side-chain reduces the melting point. The properties of lkylaryl phosphates are between those of alkyl and aryl phosphates.

$$3\ ROH + POCl_3 \longrightarrow OP(OR)_3 + 3\ HCl \qquad \text{Eq. 2.6}$$

The hydrolytic stability varies between good and poor. Length and branching of the alkyl chain increase hydrolytic stability, tolyl substitution is superior to a phenyl. Alkylaryl phosphates are more susceptible to hydrolysis than trialkyl or triaryl phosphates. Phosphoric acid esters are less stable than carboxylic acid esters, but more stable than silicic or boric acid esters. Their hydrolytic stability can be increased with ion-exchange treatment and vacuum dehydration, hydrolysis of the phosphoric acid esters used as hydraulic fluids can be virtually eliminated.

The thermal stability of triaryl phosphates is better than that of the alkyl compounds. Branching of the alkyl radicals reduces the thermal stability, the effect becomes stronger with decreasing length. Trialkyl phosphates and alkyldiaryl compounds behave similarly. In general phosphoric acid esters are not corrosive. But thermal decomposition leads to the formation of phosphoric acid and this is a corrosion hazard. The high spontaneous ignition temperatures of up to 600 °C underline the good fire resistance of some products. Trialkyl and alkylaryl products have pour points down to –65 °C, when they contain VI improvers. The lubricating properties of the phosphoric acid esters are excellent, particularly on steel. They can be blended with almost all lubricants and additives. Their dissolving power is, on the other hand, responsible for their incompatibility with rubbers, varnishes, and plastics. Nylon, epoxy and phenol–formaldehyde resins are stable.

2.5 Polyglycerol Esters

Polyglycerol esters (PGE) are non-ionic surfactants. The polyglycerol part, usually made up of a linear di- or triglycerol, is connected to the fatty acid part with an ester linkage. The length and shape of the fatty acid may vary. An important property of polyglycerol esters and surfactants in general, is the hydrophilic-lipophilic balance (HLB). In the simplest method, the ratio is simply calculated as the molar mass of the hydrophilic part divided by the molecule's molar mass. The general behavior of a surfactant in a two-phase system can be predicted from the HLB.

PGEs are used in a whole range of applications. As emulsifiers in food and personal care products, as dispersants, thickeners or solubilizers in products like paints and inks, and as antifogging or antistatic agents in plastic films. Because of their approved use in food (not all PGEs are approved), polyglycerol ester is used as a lubricant for food handling equipment. All in all, polyglycerol esters and other polyglycerol derivatives are used in a whole range of consumer and industrial applications.

In general, the method to produce polyglycrol ester has two different steps: (1) polymerization of glycerol in the presence of a small amount of alkali (base catalyst), and (2) esterification of the resulting polyglrcerol. Figure 2.6 offers an overview of the process.

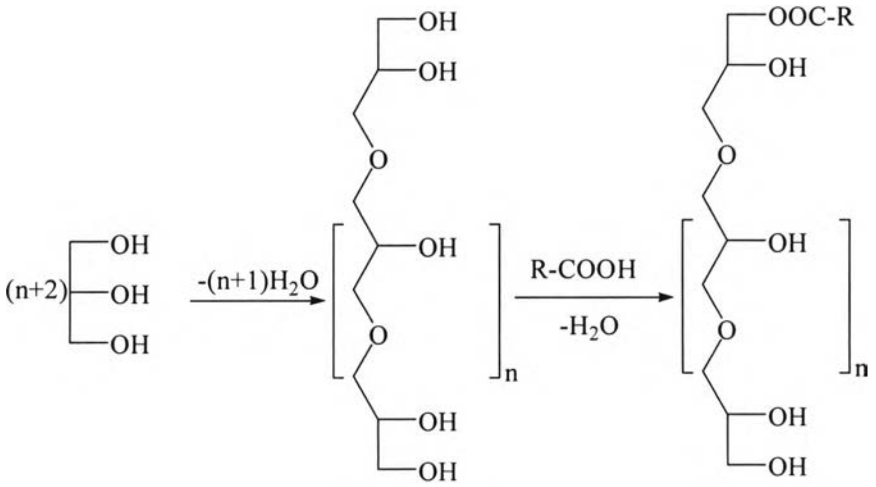


Figure 2.11 Method to produce polyglycerol ester.

2.5.1 Etherification of Glycerol

Etherification reaction of glycerol (Figure 2.7) is the reaction that the oligomers of glycerol in which the glycerol units are linked together via their α-hydroxyl groups to form ether bond toward linear or cyclic compounds 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. When a higher number of glycerol molecules are linked together, these compounds can be called polyglycerols. They were most often prepared under alkali conditions at elevated temperatures. However, care must be taken during the polymerization reaction to exclude air from the systems. Traces of oxygen leaded to the formation of acrolein as well as a dark product that was not easily bleached.

For the industrial production of polyglycerol by condensation of glycerol, glycerol is heated together with an alkaline catalyst at temperature 200°C to 275°C, under normal pressure or reduced pressure. Sodium hydroxide or sodium acetate is normally use as the catalyst. In typical process, approximately 0.3% of sodium hydroxide is added to glycerol and the reaction mixture is heated to a temperature around 230°C. The mixture is then slowly heated to 260°C–265°C, and kept at that temperature until the calculated quantity of water has distilled off. The time required for removal of the water changes slightly with the reaction conditions, although a reaction time of 11 hours for the production of diglycerol is typical. The reaction product obtained contains a number of different polyglycerols and also unreacted glycerol. It is contained diglycerol, triglycerol and higher oligomers of glycerol, according to its average composition which is characterized by the hydroxyl value or the quantity of water distilled off.

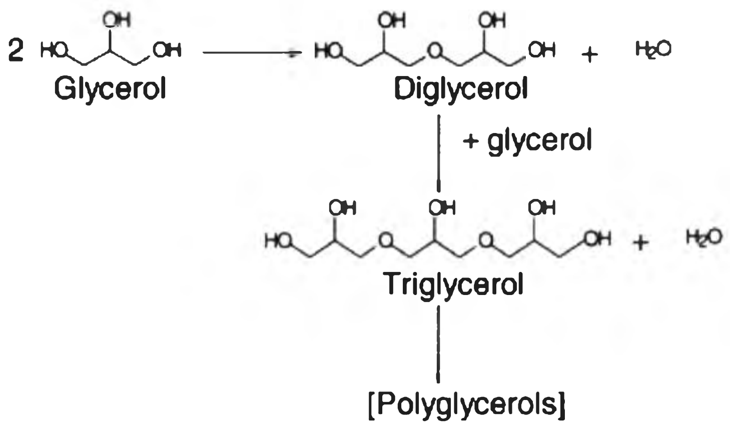


Figure 2.12 Schematic representation of the condensation of glycerol to polyglycerol.

Polymerization of glycerol is normally done with a specific linear polyglycerol as the intended product, most commonly, the linear di- and/or triglycerols. As the polyglycerol chain grows (by adding more glycerol units), the viscosity increases and the hydrophilicity decreases.

In the following section we will describe the process of polymerizing glycerol by homogeneous catalysis and outline its advantages and drawbacks.

2.5.1.1 Polymerization of Glycerol by Homogenous Catalysis

The obstacles encountered on polymerizing glycerol using condensation reactions are normally dealt with by reacting glycerol with epichlorohydrin in appropriate ratios to get the intended linear polyglycerol with high yields. This process is employed by Solvay, a large producer of polyglycerols (Solvay S. A., 2005). So the common solution to polymerizing glycerol is to abandon the condensation route altogether.

$$\text{glycerol} + \text{epichlorohydrin} \longrightarrow \text{polyglycerol}$$

The polymerisation reaction is followed by hydrolysis, neutralisation, and finally purification of the product (Solvay S. A., 2005). This process is also described in detail in a patent by Jakobson and Siemanowski (1990).

A drawback of this method of producing polyglycerols is the introduction of chlorinated reactants which inevitably lead to hydrochloric acid and other chlorinated by-products. Unfortunately, it seems there is no good way to polymerise glycerol homogeneously by simple condensation (etherification) without losing control of the final product's polyglycerol composition.

There is also a pretty old method (Seiden and Martin, 1976), which implements the following reaction:

$$\text{glycerol} \xrightarrow[\text{decreased pressure, 100-180°C}]{H_2SO_4\text{, glyceride}} \text{polyglycerol}$$

The polyglycerol composition is regulated by quenching the reaction at an appropriate time with a base that neutralises the catalyst (sulfuric acid). Then unreacted glycerol and cyclic diglycerol is removed by distillation.

An interesting fact noted by Seiden and Martin (1976) is that during the glycerol polymerisation process the initial rate of diglycerol formation is higher than that of the longer chain polymers. Further, the patent author claims, that "the diglycerol content reaches its maximum concentration when about 50 percent of the glycerol has been polymerised. From that point onwards, the rate of diglycerol formation is lower than the rate at which diglycerol is further polymerised. Accordingly, the concentration of diglycerol decreases." As it is, we can only take this fact for true under the conditions employed by this author. And those conditions are unfortunately rarely used today. Besides, the polyglycerol composition control offered by this method is unsatisfactory given present industrial standards.

2.5.1.2 Polymerization of glycerol by heterogeneous catalysis

This field is quite new, at least academically, and it has been hard to find publications describing this matter. Much of the research is probably kept secret for commercial reasons. but some work is public, and it has been done by one research group, as it seems. The articles of Clacens et al. (1998), Clacens et al. (2002) and Barrault et al. (2004) describe, in detail, the heterogeneous polymerization of glycerol, mainly by mesoporous materials but also by some zeolites (mainly ZSM-5).

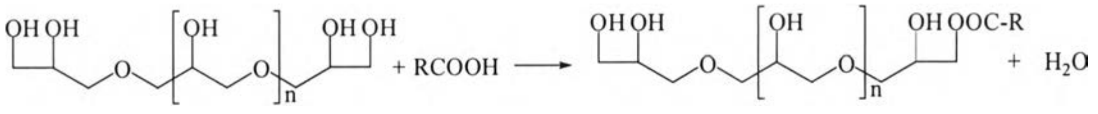
The experimental setup of the catalytic testing step in this project is largely based on that in the above-mentioned articles. In these articles, several impregnation metals are used, such as Cs, Mn, Al, Mg, and La. Additionally, these metals were also incorporated in the porous framework (at synthesis). Activity was found to be higher in the impregnated materials, probably partly due to catalysis taking place on soluble metal oxides.

To conclude this section, an industrial heterogeneous catalyst for the selective polymerization of glycerol is yet to be presented. This makes this field so much more exciting. Previous work revealed the homogenous catalysts were very active but not selective. On the other hand, heterogeneous catalysts such as zeolite, ion exchangers mesoporous molecular sieves or other basic materials were not so active but high selectivity to diglycerol obtained at different glycerol conversion which depends on the type of catalyst.

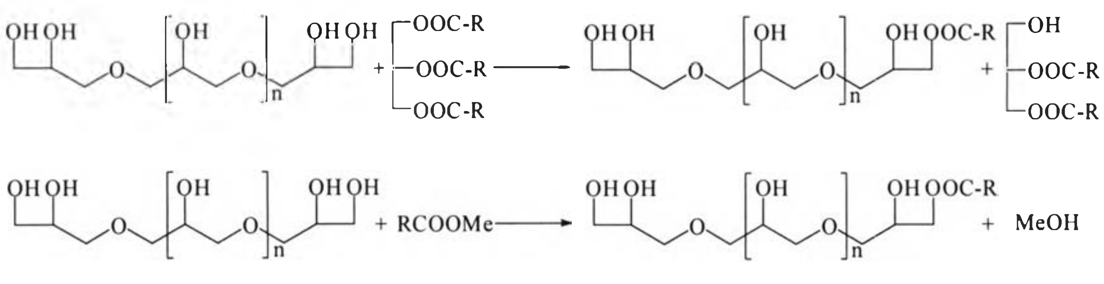
2.5.2 Polyglycerol Ester Synthesis

The production of fatty acid ester of polyglycerols has been usually achieved through (1) direct esterification of the polyol using either alkali or acid catalysts, (2) transesterification of the polyol with a triglyceride or a fatty acid methyl ester in the presence of a suitable alkaline catalyst or (3) addition polymerization of glycerdol to a fatty acid monoglyceride catalyzed by acids. These processes generally lead to the formation of mixtures in which the fatty acid chains are distributed among all available hydroxyl groups, whose proportions mainly depend on temperature and reagent molar ratio. Moreover, the molecular composition of the product is very difficult to determine and correlations between structure and performance cannot be established precisely.

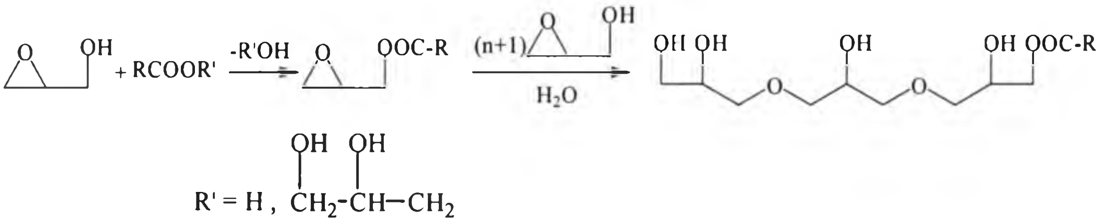
Direct esterification



Tranesterification



Addtion polymerization of glycidol



Seiden et al. (1976) studied process for preparing polyglycerol by heating glycerol under reduced pressure in the presence of sulfuric acid and low molecular weight glyceride. The condensation reaction was terminated by adding a neutralizing agent to the mixture. Unreacted glycerol and cyclic diglycerol were removed by distillation. The polyglycerol that was prepared can be esterified with fatty acid to provide polyglycerol fatty acid ester. However, this process was relatively complicated.

Garti *et al.* (1981) found that in the glycerol polymerization step that the carbonates are more active than hydroxides, despite the weaker base character of the former. This is attributed to the better solubility of carbonates in the glycerol and in the polymeric product at elevated temperatures. Oxides like MgO, CaO and ZnO are less active due to lower solubility. As for the esterification step, higher fatty acid/polyglycerol ratios (higher esterification) will need longer reaction time to complete the process. The color of the product is not affected by the esterification step but only by the polymerization step.

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

Barrault *et al.* (2002) demonstrated that solid and basic materials may replace the usual homogeneous catalyst with the same activity and selectivity 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 degree of polymerization (di- and triglycerol) in the presence of solid mesoporous catalysts. The main part of this study is 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 important activity, which must be correlated to important active species incorporation. The selectivity of the modified mesoporous catalysts to di- and triglycerol are obtained over solids prepared by cesium impregnation. The reuse 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.

Lemke (2002) provided processes for preparing polyglycerol and polyglycerol esters. These processes produce linear polyglycerols and polyglycerol esters in high yield. The process for preparing polyglycerols by reacting glycerol, polyglycerol, or mixture thereof in the presence of a calcium containing compound to form a solution containing polyglycerol. The reaction was performed at a temperature about 230°C in a pressure of about 150 mmHg. The polyglycerol ester was prepared by esterifying polyglycerol with one or more fatty acids in the presence of a calcium compound. The esterification process was performed at same temperature.

Barrault *et al.* (2004) studied synthesis and modification of catalysts. The catalysts prepared by the impregnation method gave the highest activity, but are subject to metal leaching. The reaction is carried out at 260°C at atmospheric pressure under N_2 in the presence of 2 wt% of catalyst. Mesoporous solids modified by cesium impregnation or exchange lead to the best selectivity and yield to (di-+tri-) glycerol (>90%). The most stable catalysts are the exchanged catalysts but they are less stable, the impregnated catalysts can be reused without major modification of their selectivity to the (di-+tri-) glycerol.

Ruppert *et al.* (2007) studied the selective etherification of glycerol to di- and tri-glycerol by using the alkaline earth metal oxide as heterogeneous catalyst and compared the result which obtained from homogeneous catalyst, Na_2CO_3. Glycerol conversion increased with increasing catalyst basicity; MgO<CaO<SrO<BaO. For all alkaline earth metal, at the start of the reaction mainly linear diglycerol was produced, whereas at higher conversion degrees branched diglycerol started to form. In different type of CaO materials were prepared. It was found these CaO-base materials not only differed in their surface area and number of basic sites, but also in their Lewis acid strength. Within these the CaO material possessing the strong Lewis acid sites has the highest catalyst when compared with BaO. Finally, the catalytic solids were stable under the experiment and the colloidal CaO particles of about 50-100 nm can be spontaneously generated during reaction. Catalytic testing of CaO colloids, after isolation from the reaction medium, revealed a very high etherification activity.

Petsriprasit *et al.* (2008) studied glycerol etherification catalyzed by alkaline earth oxides. The investigated catalysts (Na_2CO_3, NaOH, CaO, BaO, and MgO) showed different activities for the etherification of glycerol at 240 °C and with 2 wt% loading of each types of catalyst. Conversion of glycerol increases with increasing catalyst basicity: NaOH>Na_2CO_3>BaO>CaO>MgO. Temperature varied from 220 to 250 °C affected not only the rate of reaction but also the concentration of the formed diglycerol and other polyglycerols. The reaction temperature was not influence on the diglycerol selectivity. The kinetics of reaction of BaO and CaO were also investigated in order to find the reaction rate. The reaction order was found to be first order. The activation energies for the etherification of glycerol using BaO and CaO were 142.6 and 162.3 kJ/mol, respectively. CaO which has satisfied conversion and has commercial advantages was selected to study in pilot scale. The 20 kilogram pilot scale was studied under 2 wt% loading of CaO at 240°C condition.

2.6 Analysis of Polyglycerol and Polyglycerol Ester

Polyglycerols, obtained from polymerization of glycerol with catalysts, can significantly contain 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.

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–SI1 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 Performace 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 (HPLC) equipped with refractive index detector to determine the composition of polyglycerols. They use 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 tool for monitoring the production of desired mixtures of polyglycerols and for analyzing polyglycerol esters through their polyglycerol moieties.

Lafosse *et al.* (1999) used liquid chromatography with evaporative light scattering detection and mass spectrometry. A porous graphitic carbon and an aminopropyl-bond polymer were packed in the columns to separate and determine the isomeric diglycerols (*prim–prim*, *prim–sec* and *sec–sec*). The *prim–prim* isomeric diglycerols are separated on the porous graphite carbon packed column with pure water as mobile phase. On the aminopropyl–bond polymer packed column with acetonitrile–water (90:10) as mobile phase, the *prim–sec* and *sec–sec* isomeric diglycerols are also separated. The amounts of other compounds were identified by LC–MS.

Garti *et al.* (1983) analyzed the sorbitan esters of several fatty acids by high performance liquid chromatography (HPLC) equipped with UV detector, operated at 220 nm. The separations were achieved on 25 cm × 4.6 mm id stainless steel columns prepacked with 10 μm Lichrosorb RP–18 with isopropanol–water (88:12) as mobile phase. The samples were dissolved in 85% isopropanol and 15% water.