



CHAPTER II LITERATURE REVIEW

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. However, the growth in biodiesel production is accompanied by increased glycerol supplies, an inevitable 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). The global annual production of biodiesel equals roughly 350,000 tonnes of crude glycerol; which has an expected annual growth of between 10 and 25 percent until 2010. Biodiesel production is the primary source of glycerol world-wide, and expected to account for 65% of glycerol production by 2010 (Henard, 2007).

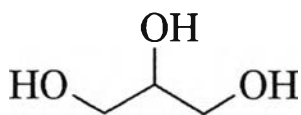


Figure 2.1 Chemical structure of glycerol.

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 in vegetable and animal fats. Ever since its discovery, the applications of glycerol has increased and today it is necessary chemical 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 ($\text{H}_3\text{C}-\text{HC}=\text{CH}_2$), a major by-product of petroleum cracking.

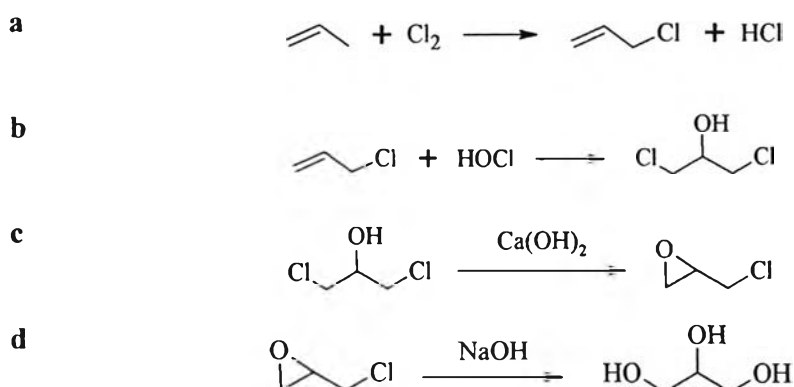


Figure 2.2 Reactive pathway for industrial production of glycerol from propene, a by-product of petro-cracking. European Oleochemicals and Allied Products Group (2007).

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 $\text{Ca}(\text{OH})_2$, 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 2.3 shows the predominant method of producing biodiesel industrially: transesterification of rapeseed oil at roughly atmospheric pressure and low temperature ($65\text{ }^\circ\text{C}$) in a batch process. Yields are normally above 98% (Engu'rdanos 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 COOC 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.

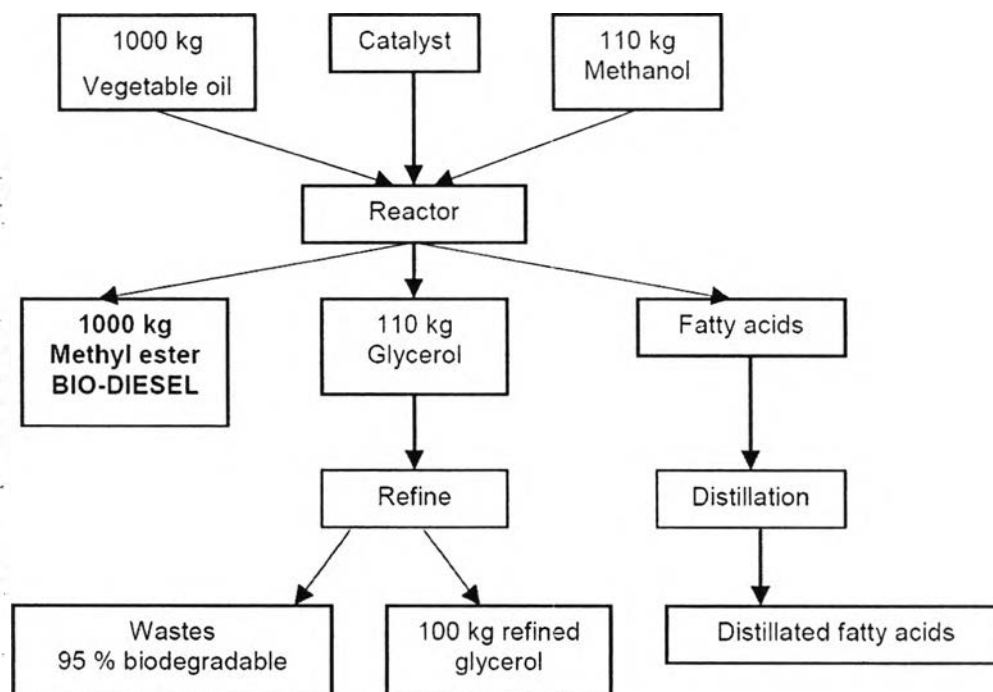


Figure 2.3 Production of biodiesel from renewable resources: each 1000 kg of biodiesel produced gives 100 kg of glycerol as by-product (Engu´ıdanos et al., 2002).

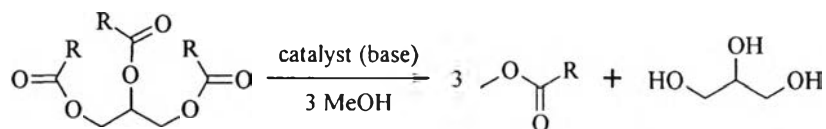


Figure 2.4 Transesterification of triglyceride to form methyl ester, the most common form of biodiesel. The R-groups of a single triglyceride need not be of the same length. If R=CH₃, the molecule is triacetin, the simplest possible fat.

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, current market price is only €50 per metric tonne.

The current market price of refined glycerol is €450/MT—presenting a strong motivation 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

2.1 General Aspects of Catalysis

Catalysts are employed in virtually all chemical reactions of industrial importance. Examples of such are petroleum cracking, fertilizer production, and methanol synthesis from CO and H₂. Perhaps the most well-known utility is as catalytic converters in automobiles all over the world. In short, catalysts make it possible to produce materials, or sustain reactions, that would otherwise have been unobtainable or prohibitively expensive.

In the following, starting from a common definition of a catalyst, the general properties of a catalyst will be described.

A catalyst is a substance that increases the rate at which a chemical reaction approaches equilibrium without itself becoming permanently involved in the reaction. (Richardson, 1989)

Thermodynamic equilibrium is unchanged, together with thermodynamic properties as G_r , H_r , and K_r . The catalyst affects the kinetics of the reaction by lowering the activation energy; which in turn is achieved by the catalysts ability to provide low-energetic pathways for the reaction, e.g., by providing a solid surface for the reaction to take place on. It is now necessary to introduce the term catalytic activity. Catalytic activity is intimately related to the fact that a catalyst only affects the kinetics. Catalytic activity is measured in moles per second (in the SI system). A catalyst will make a reaction reach equilibrium faster, just how fast is given by its activity.

A catalyst, in principle, promotes only one reaction, even if several reactions take place. A catalyst is thus able of improving not only activity but also selectivity. Since the catalyst is a chemical, reacting with reactants and products through chemisorption or complexing, its reactivity depends upon its own chemical structure. Thus, and this is very important in all fields of catalysis, a catalyst is selective. An ideal catalyst does not get permanently involved in the reaction it catalyses (again drawing from the definition). An ideal catalyst should in principle be able to continuously catalyse a reaction without ever needing replacement or regeneration. But in all real-life reactions, the catalyst loses its activity over time. It does get permanently involved in the reaction, sooner or later, and thus loses its catalytic activity. This is known as deactivation.

The main properties of a catalyst in an industrial application are, in no specific order:

- Activity.
- Selectivity.
- Deactivation.

The relative order of importance between these properties is not obvious. However, given that today's industry emphasize efficient utilization of feedstocks and energy, the relative order of importance is, according to Richardson (1989), selectivity > deactivation > activity.

An industrial catalyst is subject to mechanical, thermal and chemical stresses, which will eventually cause its deactivation. Mechanical stresses are caused by friction, which are in turn caused by mixing, stirring, or convection in the reactor. There can also be fouling of the catalyst, whereby reactor debris is deposited on the catalyst particles. This is especially relevant at industrial scale, but even in the laboratory setup fouling may have occurred caused by glass, rubber or packing materials in and around the reactor.

Thermal stress, on the other hand, weaken the catalyst so that it may undergo phase changes, surface changes or even particle sintering. At high enough temperatures catalyst components may vaporize, essentially destroying the catalyst. A catalyst is also subject to chemical stresses, chiefly poisoning and coking. Poisoning is slightly temperature dependent, and may be reversible or irreversible,

depending on poison and catalyst. There are three types of general poisoning reactions: (i) independent compounds present in the feed deactivate a catalyst site with a mechanism different from the main reaction, (ii) parallel reaction generates poison, or (iii) series reactions generate poison. A poison is any compound resulting in strong adsorption to the catalytic site, thereby blocking the access of the feed.

Usually, the field of catalysis as a whole is divided into three divisions: homogeneous, enzyme and heterogeneous catalysis (Thomas and Williams, 2005). In homogeneous catalysis the reactants and catalyst are in the same phase, most commonly as liquids. Advantages with homogeneous catalysis are high yields and high selectivity. Also, the techniques of organometallic chemistry are easily adopted for studying such reactions. Enzyme catalysis, or biocatalysis, is the field of studying the catalytic function of enzymes. Enzymes are tremendously active, as well as displaying a selectivity which surpasses anything man-made. The field of heterogeneous catalysis is where the current work belongs. A more detailed description of heterogeneous catalysis will be made in the next section.

2.2 Heterogeneous Basic Catalyst

In heterogeneous catalysis, the reactants and catalyst exist in different phases. Most commonly, solid catalysts are used with gaseous or liquid reactants. The main advantage of heterogeneous catalysis is its simplicity of use in industry. Theoretically it may be harder to grasp what is going on compared to homogeneous catalysis, but that is usually no problem as long as it works. First of all, a solid catalyst can be shaped into pellets, or rings, or spheres etc., and it can be used in slurries as well as fluid beds and so on. This versatility in application simplifies construction of new processes and leads to dependable operation. Compared to homogeneous catalysis, another important difference crystallizes: the products need no special separation step to remove residual catalyst. This is a major drawback of homogeneous catalysis. This is reflected in the fact that whereas homogeneous catalysis only finds limited industrial use, heterogeneous catalysis has numerous applications in industry.

Following the report (Hattori, H. 1995) by Pines et al., certain metal oxides with a single component were found to act as heterogenous basic catalysts in the absence of such alkali metals as Na and K. In the 1970s, Kokes et al. reported that hydrogen molecules were adsorbed oxide by acid-base interaction to form proton and hydride on the surface. They proved that the heterolytically dissociated hydrogens act as intermediates for alkene hydrogenation. In the same period, Hattori et al. reported that calcium oxides and magnesium oxide exhibited high activities for 1-butene isomerization if the catalysts were pretreated under proper conditions such as high temperature and high vacuum. The 1-butene isomerization over calcium oxide and magnesium oxide was recognized as a base-catalyzed reaction in which the reaction was initiated by abstraction of a proton from 1-butene by the basic site on the catalyst surfaces.

The catalytic activities of basic zeolites were reported also in early 1970s. Yashima et al. reported that side chain alkylation of toluene was catalyzed by alkali ion-exchanged X and Y type zeolites. The reaction is a typical base-catalyzed reaction, and the activity varied with the type of exchanged alkali cation and with type of zeolite, suggesting that the basic properties can be controlled by selecting the exchanged cation and the type of zeolite.

In addition to the above mentioned catalysts, a number of materials have been reported to act as heterogenous basic catalysts. The types of heterogenous basic catalysts are listed in table 2.1. Except for non-oxide catalysts, the basic sites are believed to be surface O atoms. Oxygen atoms existing on any materials may act as basic sites because any O atoms would be able to interact attractively with a proton. The material listed in table 2.1 act as a base toward most of the reagents, and therefore, are called heterogenous basic catalysts or solid base catalysts.

2.3 Properties and Uses of Glycerol

Glycerol has the chemical formula $C_3H_5(OH)_3$. It has many common name such as glycerin, glycerine, glyceritol, glycol alcohol, 1,2,3-propanetriol, 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.

Table 2.1 Types of heterogeneous basic catalysts

(1) single component metal oxides
alkalines earth oxides
alkali metal oxides
rare earth oxides
ThO ₂ , ZrO ₂ , ZnO, TiO ₂
(2) zeolites
alkali ion-exchanged zeolites
alkali ion-added zeolites
(3) supported alkali metal ions
alkali metal ions on alumina
alkali metal ions on silica
alkali metal on alkaline earth oxide
alkali metals and alkali metal hydroxids on alumina
(4) clay minerals
hydrotalcite
chrysotile
sepiolite
(5) non-oxide
KF supported on alumina
Lanthanide imide and nitride on zeolite

Glycerol's vast usage stems from its favorable properties. Glycerol is a transparent, viscous liquid. It is odor- and colorless. And it is 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.

One can roughly divide 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. 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 is about the oligomers of glycerol, di- and triglycerol, and their possible advantages over glycerol.

2.4 Properties and Uses of Polyglycerol

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.

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 polyglycerols 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).

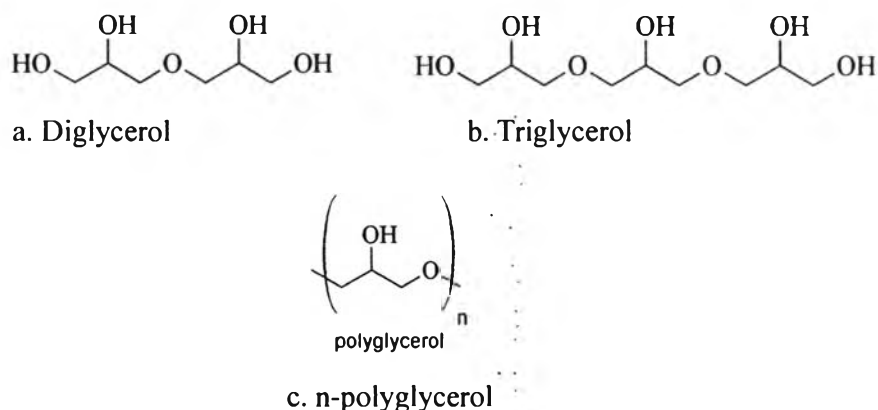


Figure 2.5 Structure formulas of diglycerol (a), triglycerol (b), and a general glycerol polymer (c). Note that the relative hydroxyl content, and thus hydrophilicity, decreases with chain length.

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.

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 (Wikipedia, 2007a).

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.

2.5 Etherification of Glycerol

The obvious way of polymerising glycerol is to simply add several glycerol molecules after each other, building arbitrarily long chains of polyglycerol. This kind of reaction is a condensation, or etherification, where one mole of water is created for every ether linkage formed. Simple as it may seem, condensation of glycerol may lead to a number of different products. Apart from getting linear polymer chains of varying lengths, one will get branched chains and to some extent also cyclic polyglycerols. If the condensation is done in the presence of air, one will also likely get acrolein, the simplest aldehyde. Acrolein is toxic and highly volatile, and used extensively as an intermediate in the chemical industry. To prevent formation of acrolein CO_2 or N_2 can be bubbled through the reaction mixture.

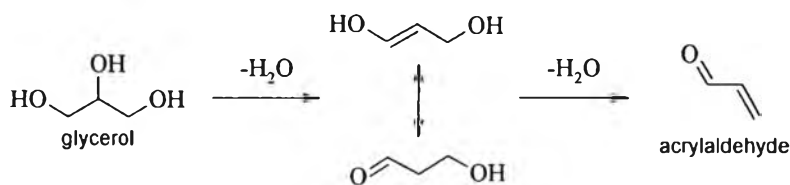


Figure 2.6 Dehydration of glycerol leading to formation of acrylaldehyde, or acrolein.

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, the process of polymerizing glycerol by homogeneous catalysis and outline its advantages and drawbacks will be described.

2.6 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 polymerising glycerol is to abandon the condensation route altogether.

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), 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 decrease.

2.7 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.

Seiden *et al.* (1976) studied process for preparing polyglycerol by heating glycerol under reduced pressure in the presence of sulfuric acid and glycerol ester. The condensation reaction was terminated by adding a neutralizing agent to the mixture. Unreacted glycerol and cyclic diglycerol were removed by distillation. This process was relatively complicated. Moreover, products are relatively poor in color quality.

Garti *et al.* (1981) found 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 because of lack of solubility.

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.

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).

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.

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 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.

Lemke (2002) 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.

Barrault *et al.* (2004) studied synthesis and modification of catalysts. The catalysts prepared by the impregnation method give the highest activity, but are subject to metal leaching. The reaction is carried out at 260°C at atmospheric pressure under N₂ 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 ones but they are less

stable, the impregnated catalysts can be reused without major modification of their selectivity to the (di-+tri-) glycerol.

Weckhuysen *et al.* (2008) studied the glycerol etherification reaction over alkaline earth metal oxides (BaO, SrO, CaO, and MgO) as heterogeneous catalysts with high activity. More specifically, they concentrated on exploring the catalytic potential of different CaO materials. As a result, depending on the preparation and treatment of the catalyst the material can defragment and form colloidal particles during the reaction. It was found that colloidal CaO particles of about 50–100 nm are spontaneously generated during reaction and their amount gradually increases with increasing reaction time. The glycerol conversion goes hand in hand with the amount of CaO colloidal particles in the reaction mixture. Catalytic testing of these CaO colloids, after isolation from the reaction medium, revealed a very high etherification activity, which may become of practical interest after finding a suitable way of immobilization since such supported colloidal systems would take advantage of both their hetero- and homogeneous nature.

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.

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.

2.8 Quantification of Polyglycerol

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-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.

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.