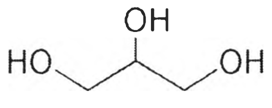
CHAPTER II
LITERATURE REVIEW

2.1 Glycerol

Glycerol and glycerin(e) are oftentimes used interchangeably, but glycerol is the preferred scientific terminology and refers to the pure trihydric alcohol, while glycerin(e) refers to the commercial products consisting of whatever grade or degree of purity (Kenar, 2007).Glycerol has been a well-known renewable chemical for more than two centuries. The Swedish chemist Carl Wilhelm Scheele discovered it in 1783 when treating natural oils with alkali materials. The name ``glycerol`` was given in 1811 by the chemist Michel Eugene Chevreul, who deduced this name from the Greek word ``glykos`` (= sweet) (Behr *et al.*, 2008).

The chemical structure for glycerol is $HOCH_2$-CHOH-CH_2OH as shown in Figure 1. Glycerol consists of a chain of three carbon atoms with each of the end carbon atoms bonded to two hydrogen atoms (C-H) and a hydroxyl group (-OH), and the central carbon atom is bonded to a hydrogen atom (C-H) and a hydroxyl group (-OH).

Glycerol is viscous, colorless, odorless, and sweet taste. It is clear hygroscopic liquid, non-toxic, easily biodegradable and pleasant taste which makes it an ideal ingredient in food, cosmetic, and pharmaceutical applications. Because glycerol has three hydroxyl groups (-OH), it is miscible in water and alcohols, but insoluble in ethers, chlorinated solvents, hydrocarbons, and oils.



Glycerol
1,2,3-propanetriol

$C_3H_8O_3$
MW: 92.09
mp: 17.8 °C
bp_{760}: 290 °C (decomp).
Density @ 20 °C = 1.2375
Flash point 176 °C

Figure 2.1 Chemical structure and some properties of glycerol (Kenar, 2007).

2.2 Reactions of Glycerol

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

2.2.1 Nitration of Glycerol

Nitration of glycerol is used to produce nitroglycerol, which is a common biological molecule from which triglycerides fats and oils are constructed, where all the -OH groups have been replaced by $-NO_2$ as structure is shown in Figure 2.2. The best manufacturing process was developed by Alfred Nobel in the 1860s. Nitroglycerol is an oily, colorless liquid, but also a high explosive that is so unstable that the slightest jolt, impact or friction can cause it to spontaneously detonate. Since the molecule contains oxygen, nitrogen, and carbon, when it explodes, a lot of energy is released as the atoms rearrange to form new molecules with strong and stable bonds.

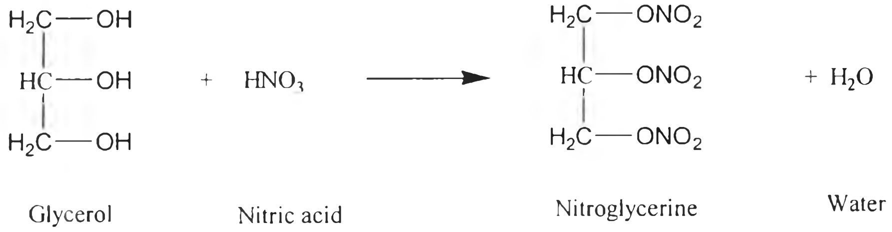


Figure 2.2 Production of nitroglycerin.

2.2.2 Esterification of Glycerol

The monoesters and diesters of glycerol occur naturally in fats that have become partially hydrolyzed. The triglycerides are primary components of naturally occurring fats and fatty oils. Monoglycerides and diglycerides are prepared by the direct condensation of a fatty acid or a fat (triglyceride) with glycerol, resulting in mixtures containing 40-60% monoglyceride, 30-45% diglycerides, and free glycerol. The example of monoglyceride is shown in Figure 2.3.

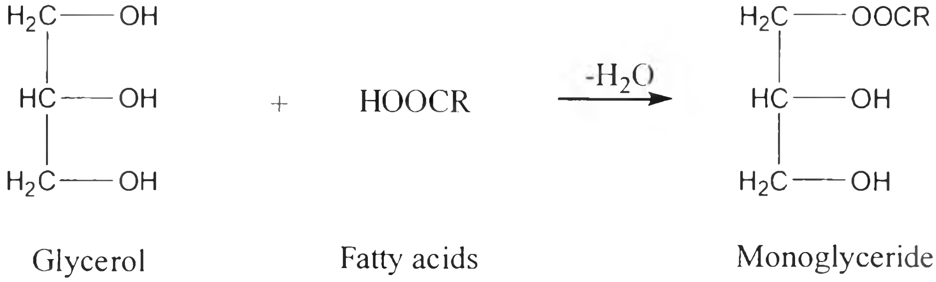


Figure 2.3 Production of monoglycerides.

A mixture of monoglycerides, diglycerides, and triglycerides is manufactured in large quantities for use in superglycerolated shortenings. Monoglycerides and diglycerides are important modifying agents in the manufacture of alkyd resins, detergents, and other surface-active agents.

2.2.3 Etherification of Glycerol

Etherification of glycerol and fatty alcohols occur in natural products. Some typical examples of naturally occurring fatty ethers of glycerol are the alpha glycerylmonoethers of stearyl, oleyl, and cetyl alcohol.

Glycerol reacts with ethylene oxide or propylene oxide to form polyether as shown in Figure 2.4. By adding the hydrophobic propoxy chain followed by the addition of hydrophilic ethoxyl chains or vice versa, "block copolymer" can be prepared. When the ethoxyl and propoxy chains are properly balanced, these block copolymers have surface-active properties. They also have been used as intermediates in the manufacture of some polymers.

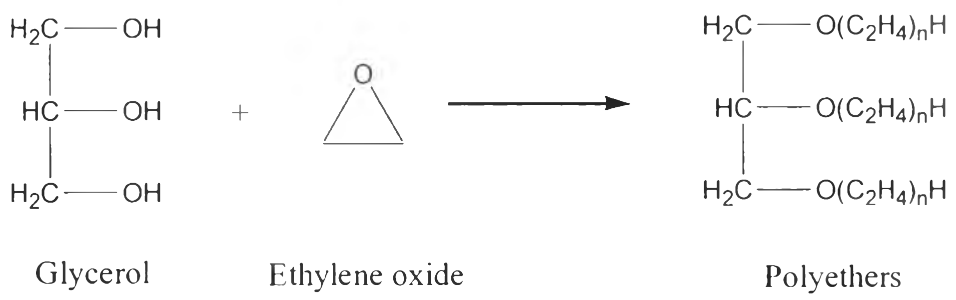


Figure 2.4 Production of polyethers.

2.2.4 Polymerization of Glycerol

Polymeric ethers are formed when glycerol reacts with itself to form polyglycerols via intermolecular dehydration as shown in Figure 2.5. Polyglycerol are produced commercially by heating glycerol at temperatures in the range of 473-548 K at normal or reduced pressure in the presence of alkaline catalysts such as sodium hydroxide, potassium hydroxide or sodium acetate. The reaction is usually carried out in an atmosphere of carbon dioxide or nitrogen.

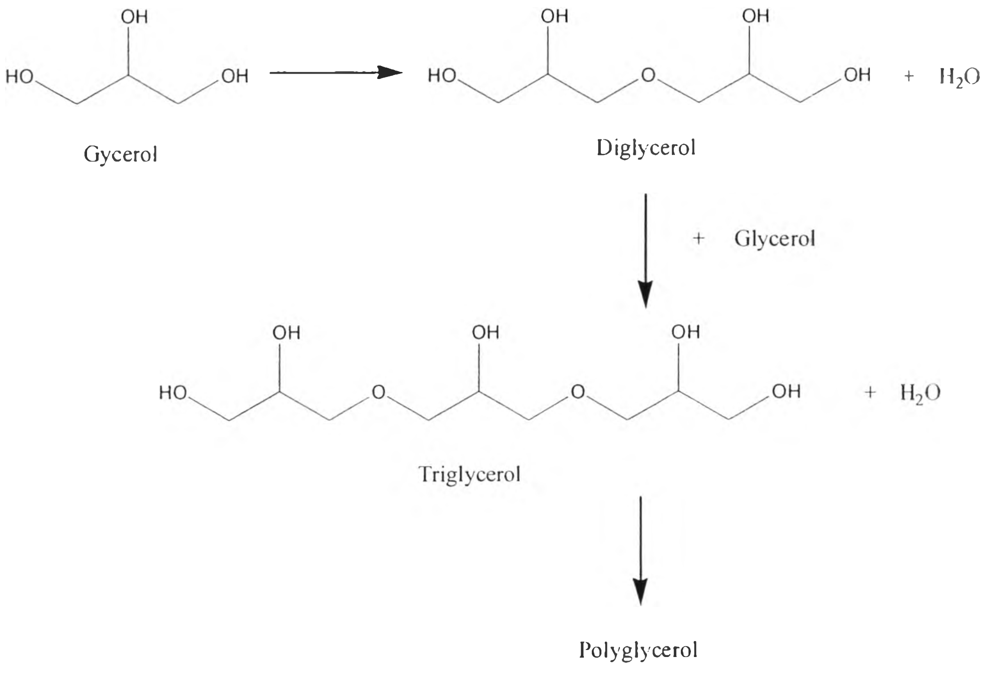


Figure 2.5 Schematic representation of the polymerization of glycerol to polyglycerols.

Several properties of polyglycerols are quite similar to that of glycerol. However, diglycerol is a viscous liquid about 25 times as viscous as glycerol. Polyglycerols offer greater flexibility and functionality than glycerol. Polyglycerols up to and including dodecaglycerol (12 condensed glycerol molecule) have been prepared commercially. The polyglycerol with molecular weight higher than dodecaglycerol are solid. They are soluble in water, alcohol, and other polar solvents. They act as humectants, much like glycerol, but have progressively higher molecular weight and boiling points. The multiplicity of polyglycerol is not due to a single property, but rather to a unique combination of properties, such as broad compatibility, blandness, thickening agent, dispersing agent, lubricant, emollient, nontoxicity, biodegradable, stability, and hydroscopicity. These are the key physical properties that make polyglycerols an essential ingredient in cosmetic and food applications. Products based on polyglycerols are useful in surface-active agents emulsifiers, plasticizers, adhesives, lubricants, medical specialties, and dietetic foods.

2.2.5 Oxidation of Glycerol

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

Theoretically, glycerol can be oxidized to many oxidation products such as glyceraldehydes, dihydroxyl acetone as shown in Figure 2.6., glyceric acid, mesoalic acid, and etc. Partial oxidation is usually hard to control; the oxidation products have been isolated, through more often they are prepared by indirect methods, rather than controlled oxidation of glycerol.

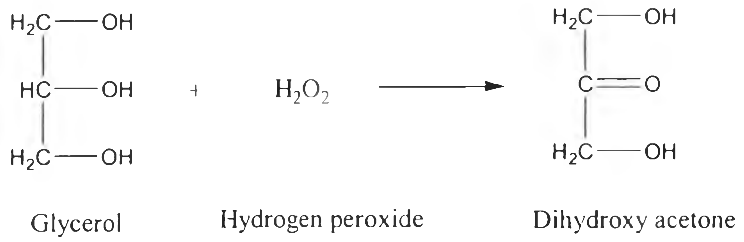


Figure 2.6 Production of dihydroxy acetone.

2.2.6 Dehydration of Glycerol

Dehydration of glycerol results in the formation of acrolein as shown in Figure 2.7, which is a clear liquid with a very pungent smell. Acrolein can be formed in trace quantities when glycerol is stored in inadequately protected metal containers and exposed to elevated temperatures, resulting in very noticeable, strong pungent off-odors.

Neher et al. (1995) described a process for production of acrolein by dehydration of glycerol in the liquid phase or in the gaseous phase by using an acidic solid catalyst. A glycerol-mixture with a glycerol content of 10 to 40 wt. % preferably between 10 and 25 wt. % was passed over the solid dehydration catalyst. Dehydration did indeed still occur if glycerol solution with a content above 40 wt. %. However, as the glycerol content rised, both the selectivity of the reaction and the service life of the catalyst were appreciably reduced. When performing the reaction in the liquid phase, it is convenient to dehydrate only to a glycerol conversion of approximately 15 to 25 % since selectivity decreases as conversion rises. Dehydration in the gaseous phase preferably proceeds in the temperature range between 543 K and 593 K while liquid phase dehydration preferably proceeds between 523 K and 573 K. An advantage of dehydration in the liquid phase over gaseous phase dehydration is lower energy consumption.

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

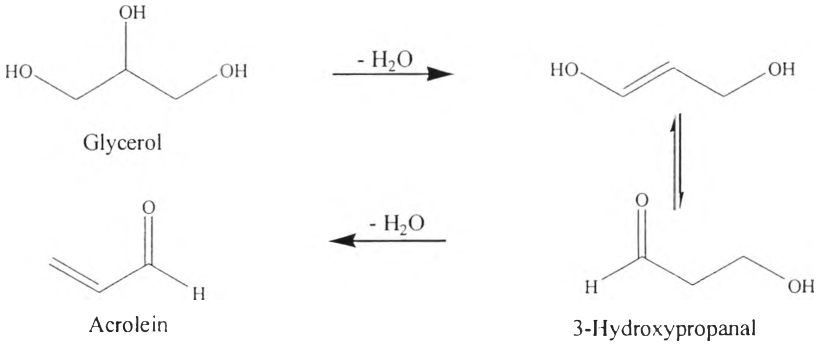


Figure 2.7 Acrolein formation by double dehydration of glycerol.

2.2.7 Hydrogenolysis of Glycerol

Hydrogenolysis is a term describing chemical reactions, in which hydrogen is used to break molecular bonds in a large organic molecule in order to provide smaller molecules. Hydrogenolysis reactions are usually conducted over a catalyst of some types, and at an elevated temperature (typically for carbohydrates, 373 to 573 K) and high hydrogen pressures (typically 70 to 300 atm). In glycols and carbohydrates, it is known that both C-C and C-O bonds can be broken by hydrogenolysis or hydrocracking, as it is sometimes called. In contrast to the case for hydrogenation of carbohydrates, the chemistry of hydrogenolysis of the sugar alcohols (alditols) is complex, not well understood, and variable with even small changes in the catalyst system or the process conditions particularly the reaction temperature. It is therefore difficult to describe the exact process chemistry taking place. In fact, there appears to be a chain or series of reactions, where primary reaction products are further hydrocracked to smaller molecule polyols and alcohols in secondary and tertiary reactions.

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

$$\underset{\text{Sorbitol}}{C_6H_{12}O_6} \quad + \quad \underset{\text{Hydrogen}}{2\,H_2} \quad \xrightarrow[\text{Heat}]{\text{Catalyst}} \quad \underset{\text{Glycerol}}{2\,C_3H_8O_3} \qquad (1)$$

$$\underset{\text{Sorbitol}}{C_6H_{12}O_6} \quad + \quad \underset{\text{Hydrogen}}{4\,H_2} \quad \xrightarrow[\text{Heat}]{\text{Catalyst}} \quad \underset{\text{Propylene gylcol}}{2\,C_3H_8O_2} \quad + \quad \underset{\text{Water}}{2\,H_2O} \qquad (2)$$

It has been shown conclusively that glycerol will be hydrocracked to propylene glycol, as in (3):

$$\underset{\text{Glycerol}}{C_3H_8O_3} + \underset{\text{Hydrogen}}{H_2} \xrightarrow[\text{Heat}]{\text{Catalyst}} \underset{\text{Propylene glycol}}{C_3H_8O_2} + \underset{\text{Water}}{2\,H_2O} \qquad (3)$$

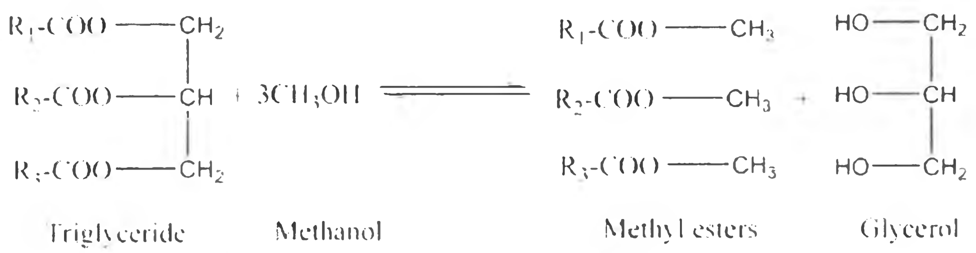
Smaller molecule compounds such as ethylene glycol, the propanediols, and the butanediols could be formed from various alditol cracking schemes, but it seems more likely that they are produced from glycerol hydrocracking under more severe process conditions (although the butanediols are more likely formed by a 4 - 2 split of the alditol carbon chain, together with EG or ethanol). In any case, it is typical for hydrogenolysis of sugar alcohols to produce several polyols and specialty chemical products.

The hydrogenolysis of glycerol is used to produce propylene glycol 1,3-propanediol, and other lower polyols at elevated temperatures and pressures in the presence of metal catalyst. However, the hydrogenolysis of glycerol has already been investigated by several groups since 1987, but the unsatisfactory selectivity has prevented use in industrial production.

2.3 Industrial Production of Glycerol

Glycerol can be found naturally in the form of fatty acid esters and also as important intermediates in the metabolism of living organisms. Traditionally, glycerol is obtained as a by-product in four different processes: soap manufacture, fatty acid production, fatty ester production, and microbial fermentation. It can also be synthesized from propylene oxide.

Glycerol can be obtained from biomass via hydrolysis or methanolysis of triglycerides. The reactions for the direct transformation of vegetable oils and animal fats into methyl esters and glycerol have been known for over a century. However, it is only recently, following more than 10 years of research and development, that the transesterification of triglycerides, using rapeseed, soybean, and sunflower oils, has gained significance for its role in the manufacture of high quality biodiesel fuel.



with R_1, R_2, R_3 = hydrocarbon chain from 15 to 21 carbon atoms

Figure 2.8 Overall reaction for production of biodiesel through vegetable oil methanolysis (Zhou *et al.*, 2008).

Glycerol is normally generated at the rate of 1 mol of glycerol for every 3 mol of methyl esters synthesized; approximately 10 wt. % of the total product.

In recent years, the rapid development of biodiesel production has formed large quantities of glycerol as a by-product. The glycerol market will likely to be saturated because of limited utilization of glycerol at the present time. Finding new applications for glycerol will increase the economy of the whole biodiesel production process.

The biodiesel industry generates a tremendous amount of crude glycerol. The crude glycerol that is produced as a by-product in the transesterification reaction to make biodiesel typically contains soap, methanol, water and transesterification homogenous catalysts such as sodium methylate, sodium hydroxide, and potassium hydroxide. In order to turn this crude glycerol into a usable state for existing or emerging uses, a purification process must take place. During this refinement process residual organic matter, water, salt, methanol, and odors are removed. The basic flow scheme of glycerol is shown in Figure 2.9.

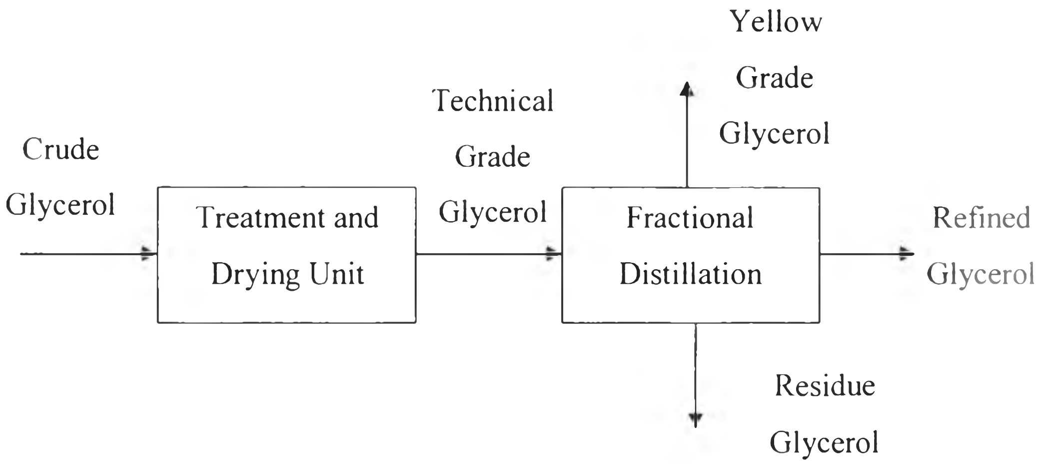


Figure 2.9 Basic flow scheme of glycerol refinement.

2.4 Glycerol Conversion into Valuable Chemicals

Using glycerol for the synthesis of value-added chemicals is of great industrial importance because, not only can glycerol be formed in large amounts during the biodiesel production, but also it is a nontoxic, edible, biosustainable and biodegradable compound.

In the past, most products were based on unmodified glycerol or simple modifications to glycerol molecules as the production of more complex chemical compounds were too costly. Now, the lower cost of glycerol can open many significant new markets in polymers, ethers, and other fine compounds. From a technical standpoint, glycerol's multifunctional structure and properties can be tailored by several different reaction pathways as shown in Figure 2.10. In the near future, the potential conversion of renewable resources into valuable commodity chemicals can facilitate the replacement of petroleum-based products. It is clear that a very large number of chemicals could be derived from glycerol. In this respect, catalysis represents a critical approach to green chemical technology in the activation and utilization of glycerol (Zhou *et al.*, 2008).

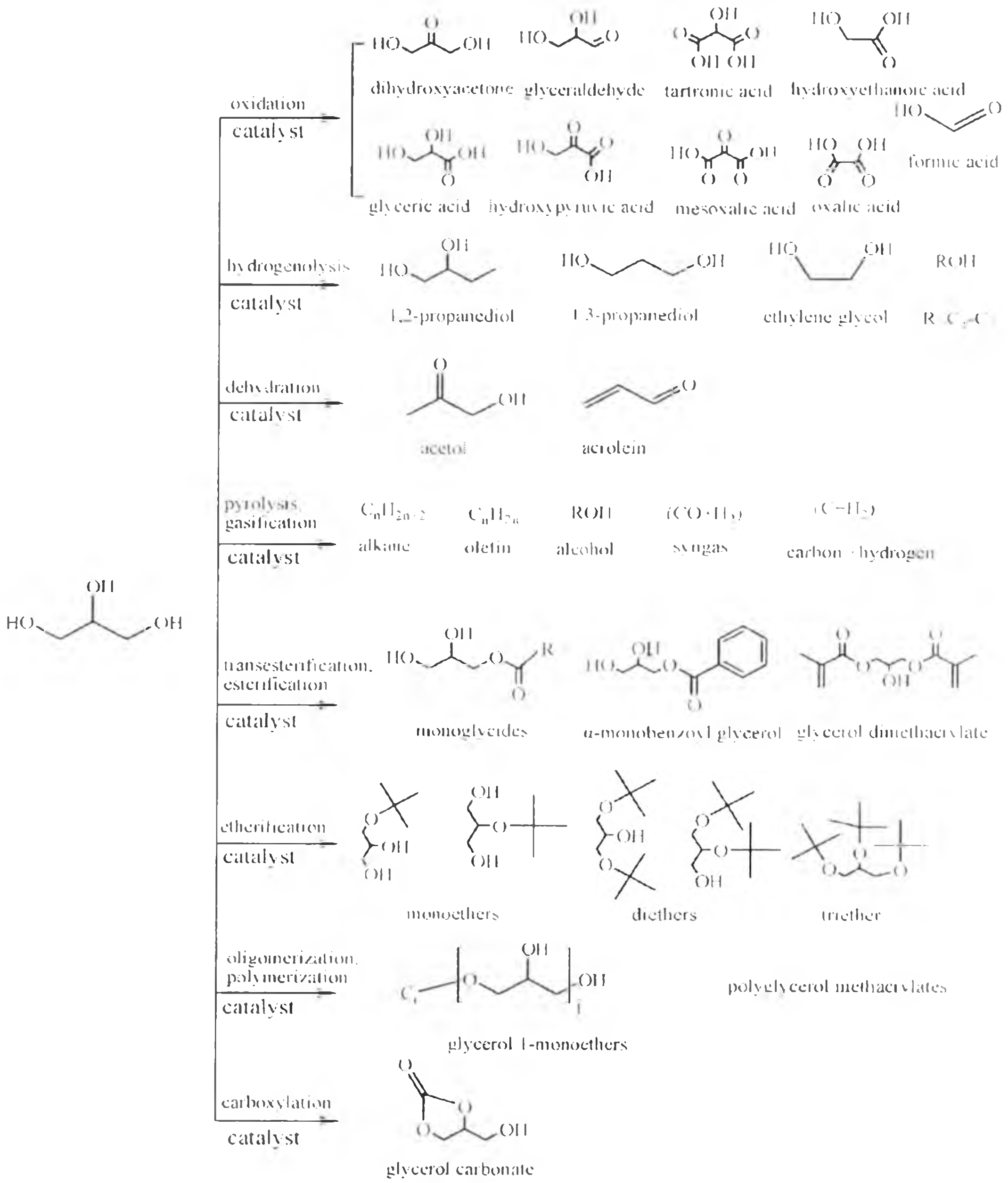


Figure 2.10 Processes of catalytic conversion of glycerol into useful chemicals (Zhou *et al.*, 2008).

The catalytic hydrogenolysis of glycerol to propanediols is one of the most attractive routes since it is a feasible and simple method that can convert the glycerol to high value-added products.

2.5 Selective Hydrogenolysis of Glycerol to Propanediols

Hydrogenolysis is a catalytic chemical reaction that breaks a chemical bond in an organic molecule with the simultaneous addition of a hydrogen atom to the resulting molecular fragments. Through the selective hydrogenolysis of glycerol in the presence of metallic catalysts and hydrogen, glycerol can be converted to 1.2-propanediol and 1,3-propanediol. which are useful final products. Therefore. catalytic hydrogenolysis of glycerol is another alternative route to increase the profitability of biodiesel production plants as the products of glycerol hydrogenolysis can easily replace the chemical compounds. which at present are industrially produced mainly by using non-renewable sources.

1,2-propanediol (1,2-PDO) or propylene glycol, is an important medium-value commodity chemical with a 4% annual growth in the market size. The current global market for 1.2-propanediol is roughly 2 million tonnes annually. It is used for manufacturing high-performance unsaturated polyesterresins,polyurethane foam systems. liquiddetergents, pharmaceuticals, cosmetics, tobacco humectants, flavors and fragrances, personal care, paints, animal feed,antifreeze, etc. Traditionally. it is produced by the hydration ofpropylene oxide derived from propylene by either thechlorohydrin process or the hydroperoxide process. Therehas been a rapid expansion of the market for 1,2-propanediol asantifreeze and de-icing agents because of the growing concernover the toxicity of ethylene glycol-based products to humansand animals(Zhou *et al.*, 2008). Recently. several major chemical producers, such as Dow. Cargill, Archer Daniels Midland, and Huntsman, have all announced plans to produce 1,2-propanediol from glycerol (Kenar, 2007).

1,3-propanediol (1.3-PDO) is also a high-value chemical that is an important compound in polymer production. 1,3-Propanediol is of interest as a reactant to preparecyclic compounds and as a monomer for various types of polyesters, polyurethanes, polyethers. Polyesters prepared from 1.3-propanediol and terephthalic acid produce polyesters, known commercially as SORONA® from DuPont, or CORTERRA® from Shell, which has unique properties in terms of chemical resistance, light stability, elastic recovery, and dyeability (Zhou *et al.*, 2008).There are two examples for thesynthesis of 1.3-propanediol based on petrochemicals: the firstone is the Shell process consisting of the hydroformylationof ethylene oxide to 3-hydroxypropanal followed by hydrogenationto 1,3-propanediol. The second is the Degussa-DuPont processbased on the hydration of acrolein to3-hydroxypropanal and further hydrogenation analogue to the Shell processas shown in Figure 2.11.

Problems in the conventional processes are the high pressureapplied in the hydroformylation and hydrogenation steps aswell as the use of aromatic solvents in the first and loss ofacrolein due to extraction processes in the second example.The yields are around 80% in the first and about 40% in thesecond process, so besides the demand of renewable sourceslike glycerol. there is also a huge interest in improving yieldsand overall selectivity of the processes applied. Therefore, thereaction from glycerol to 1,3-propanediol via heterogeneous,homogeneous or biocatalytic processes may become anattractive alternative (Behr *et al.*, 2008).

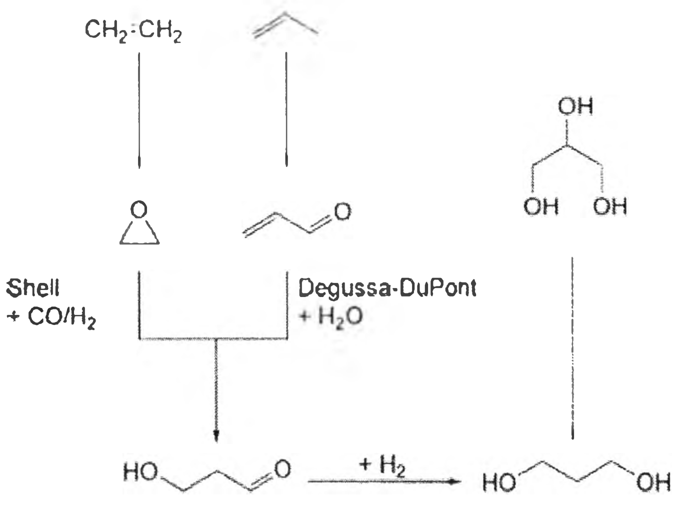


Figure 2.11 Different routes to 1,3-propanediol starting from ethene, propene or glycerol (Behr *et al.*, 2008).

In the petrochemical industry, it has been known that 1,3-propanediol is more valuable than 1,2-propanediol; however, the selective hydrogenolysis of glycerol to 1,3-propanediol is still unsatisfactory. On the other hand, the production of 1,2-propanediol becomes more potential since the method is one-step and simple (Miyazawa *et al.*, 2007). Therefore, the production of 1,2-propanediol from glycerol will be focused in this work.

2.6 Production of Propylene Glycol from Glycerol

The present industrial way for manufacturing 1,2-propanediol (propylene glycol) is the hydrolysis of propylene oxide with water (Figure 2.12). After the reaction step, the mixture must be stripped and distilled to separate the product from water and the higher substituted polyols. Although there are further processes such as the acetoxidation of propene followed by hydrolysis or the direct hydroxylation catalysed by osmium compounds, the classical route based on propyleneoxide is still widely used.

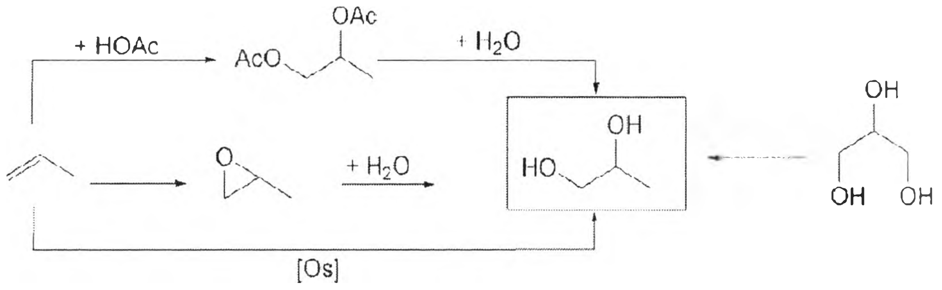


Figure 2.12 Comparison of the reaction routes to 1,2-propanediol starting from propene or glycerol (Behr *et al.*, 2008).

In particular, when 1,2-propanediol or its derivatives are applied in food, cosmetics or pharmaceutical products, the use of fossil raw materials is less favorable to the consumer acceptance, which leads to the demand of a renewable feedstock, such as glycerol. Glycerol can be converted to 1,2-propanediol using biocatalysts, homogeneous or heterogeneous catalysts, which are described in the following section.

2.6.1 Biocatalyst

A typical commercial example of technology switches with respect to catalyst and feedstock was demonstrated by a joint venture of the chemical company Ashland Inc. and the food processor Cargill. The aim of this project was the production of propylene glycol out of glycerol from the biodiesel industry at a factory in Europe. Cargill has already presented a process to obtain propylene glycol out of carbohydrates with *Escherichia coli* or *Thermoanaerobacteriumthermo-saccharolyticum* HG-8 (Behr *et al.*, 2008).

2.6.2 Homogeneous Catalyst

In general the hydrogenolysis of glycerol by homogeneous catalysts leads to a variety of by-products such as propanol or ethers and to a mixture of 1.2- and 1.3-propanediol. The amount of different products depends on the mechanism of the product formation. Earlier, Che *et al.* (1987) patented a one-step process for the catalytic hydrogenolysis of glycerol in water solution using syngas at 473 K and 32 MPa H_2 pressure in the presence of a homogeneous rhodium complex catalyst ($Rh(CO)_2(acac)$) and tungstic acid. During the reaction, 1,3-propanediol and 1,2-propanediol were produced with 20% and 23% yield, respectively.

Schlaf*et al.* (2001) also described the catalytic hydrogenolysis of glycerol in sulfolane catalyzed by a homogeneous complex of ruthenium. Thereaction proceeded under milder conditions at 383 K and 5 MPa. But less than 5% yields of 1.2-PD and 1,3-PD were achieved. Recently, the Shell Oil Company developed a process that uses homogenous palladium complex in a water–sulfolane mixture containing methane sulfonic acid. After a 10 h reaction, 1-propanol, 1,2-propanediol and 1,3-propanediolwere detected in a ratio of 47 : 22 : 31 (Drent*et al.*, 2000).

2.6.3 Heterogeneous Catalyst

Carrying out over solid catalysts without the presence of dangerous solvents, it would become economically and environmentally attractive.

Montassier*et al.* (1991) carried out the hydrogenolysis of glycerol at 533 K and 30 MPa H_2 pressure in the presence of Raney Ni, Ru. Rh and Ir catalysts.

They found that mainly methane was produced, but when Raney Cu was used as a catalyst, 1,2-propanediol was the main reaction product. Raney Cu is known for its poor hydrogenolytic activity towards C–C bond but it is an efficient catalyst for C–O bond hydrogenation and dehydrogenation. A reaction mechanism for conversion of glycerol to 1.2-propanediol proposed by Montassier *et al.* is shown in Figure 2.13.

Chaminand*et al.* (2004) studied the hydrogenolysis of glycerol in the presence of heterogeneous catalysts. Aqueous solutions of glycerol were hydrogenolysed at 453 K and 8 MPa H_2 pressure for 90 hours. Among the various catalysts (Cu, Pd, Rh), supports (ZnO. C, Al_2O_3), solvents (H_2O, sulfolane, dioxane), and additive such as tungstic acid (H_2WO_4), the best selectivity (100%) to 1,2-propanediol was obtained when using CuO/ZnO catalysts. To improve the selectivity to 1,3-propanediol the reaction was conducted with rhodium catalysts with tungstic acid added to the reaction medium. The best result in terms of conversion and selectivity to 1.3-propanediol (1.3-PDO/1.2-PDO = 2) was obtained by operating in sulfolane. A general mechanism can be proposed to explain the influence of the different parameters on the activity and selectivity of the reaction (Figure 2.14).

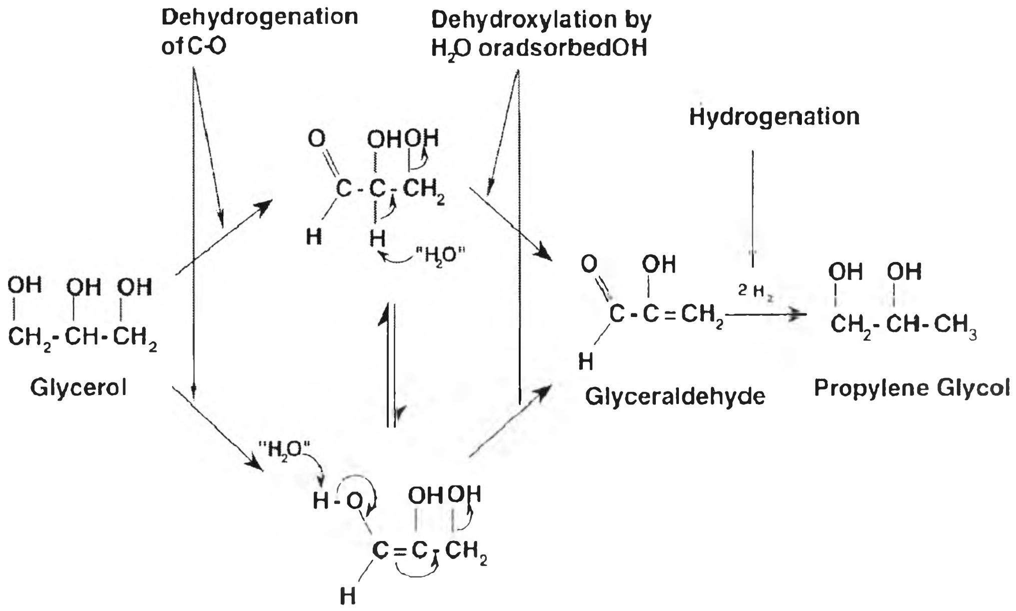


Figure 2.13 Reaction mechanism for conversion of glycerol to propylene glycol proposed by Montassier *et al.* (1991).

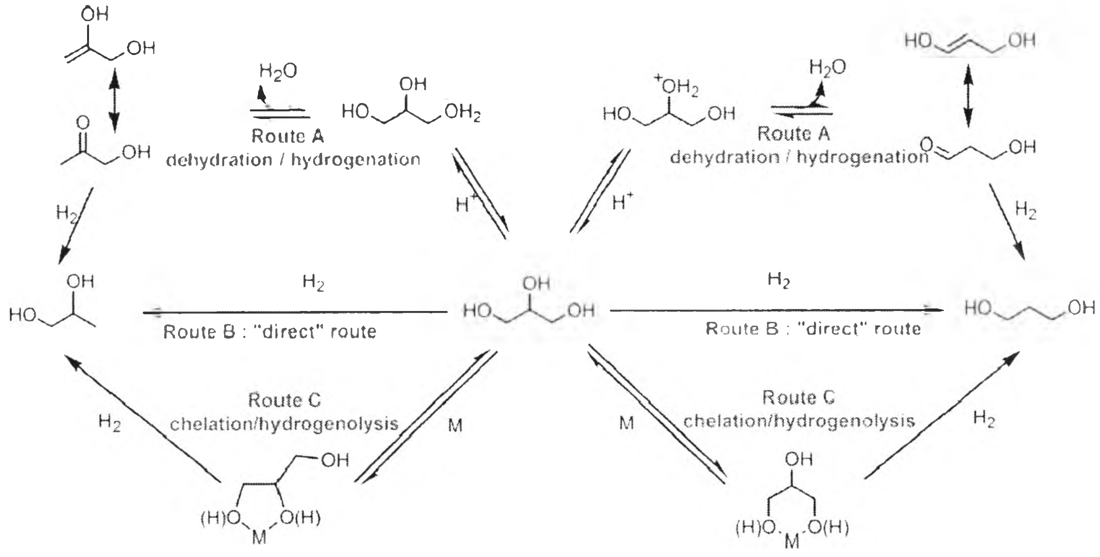


Figure 2.14 Possible reaction routes for catalytic hydrogenolysis of glycerol proposed by Chaminand*et al.* (2004).

The diols can be formed *via* several routes. The tungstic acid can favour the dehydration route (route A) *via* protonation of the hydroxyl groups and loss of water. The keto group formed as intermediate can be easily reduced under the reaction conditions. However, the use of alternative acid (HCl) yielded low conversion suggesting that the acidity of H_2WO_4 was not its dominant property for the considered reaction. Furthermore, the formation of a Rh–W catalyst cannot be excluded and can affect the selectivity and the activity of the hydrogenolysis. The addition of a second metal (Fe or Cu) in the reaction medium reduced the activity as if it poisoned the rhodium catalyst. Moreover, iron can be chelated by a diol and thus modifies the selectivity of the hydrogenolysis (route C).

Table 2.1 Summary of conversion of glycerol, yield and selectivity of propyleneglycol from glycerol over various metal catalysts (Dasari*et al.*, 2005)

Supplier	Description	Conversion	Yield	Selectivity
Johnson Matthey	5% Ru/C	43.7	17.5	40.0
Johnson Matthey	5% Ru/alumina	23.1	13.8	59.7
Degussa	5% Pd/C	5	3.6	72.0
Degussa	5% Pt/C	34.6	28.6	82.7
PMC Chemicals	10% Pd/C	8.9	4.3	48.3
PMC Chemicals	20% Pd/C	11.2	6.4	57.1
Grace Davision	Raney nickel	49.5	26.1	52.7
Grace Davision	Raney copper	48.9	33.8	69.1
Sud-Chemie	Copper	53	21.1	39.8
Sud-Chemie	Copper-chromite	54.8	46.6	85.0
Johnson Matthey	Ni/C	39.8	27.3	68.6
Alfa-Aesar	Ni/silica-alumina	45.1	29.1	64.5

Dasari*et al.* (2005) used the various types of commercial catalysts to study hydrogenolysis of a concentrated glycerol solution into propylene glycol under low pressure, as shown in Table 2.1. At temperatures above 473 K and hydrogen pressure of 1.4 MPa, the selectivity to propylene glycol decreased due to excessive hydrogenolysis of the propylene glycol. The yield of propylene glycol increased with decreasing water content. Copper-chromite catalyst was identified as the most effective catalyst, yielding 73% of propylene glycol at moderate reaction conditions of 473 K and 1.4 MPa. This result provides a very distinctive competitive advantage over traditional processes that use more severe reaction conditions.

A new reaction pathway for converting glycerol to propylene glycol via an intermediate was validated by isolating the acetol intermediate. In a two-step reaction process,The first step carried out at atmospheric pressure involves the formation of 1-hydroxyacetone by the dehydrationreaction while the hydrogenation second step requires a hydrogen partial pressure, as shown in Figure 2.15.

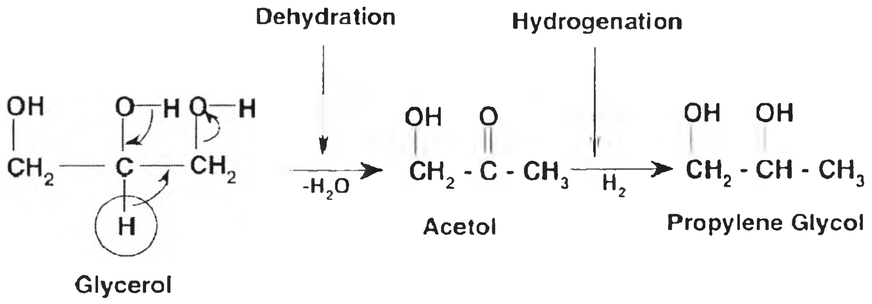


Figure 2.15 Proposed reaction mechanism for conversion of glycerol to propylene glycol (Dasari*et al.*, 2005).

Miyazawa *et al.* (2005, 2006) demonstrated that when active Ru, supported on carbon is used in combination with a cation exchange resin such as Amberlyst 15, it can exhibit higher activity in glycerol hydrogenolysis under mild reaction conditions (393 K and 4 MPa or 8MPa H_2) than other metal–acid bifunctional catalyst systems such as zeolites, sulfated zirconia, H_2WO_4, and liquid H_2SO_4. The Ru/C catalyst showed higher conversion than Rh/C. Pd/C, and Pt/C. However, the selectivity of cracking products was rather high over Ru/C, with the dehydration of glycerol to 1 hydroxyacetone being catalyzed by the acid catalysts. The subsequent hydrogenation of 1-hydroxyacetone on the metal catalysts gives 1,2-propanediol. Thus the addition of solid acid catalysts to Ru/C was effective in increasing the conversion and hydrogenolysis selectivity. A proposed reaction scheme for the hydrogenolysis of glycerol is shown in Figure 2.16.

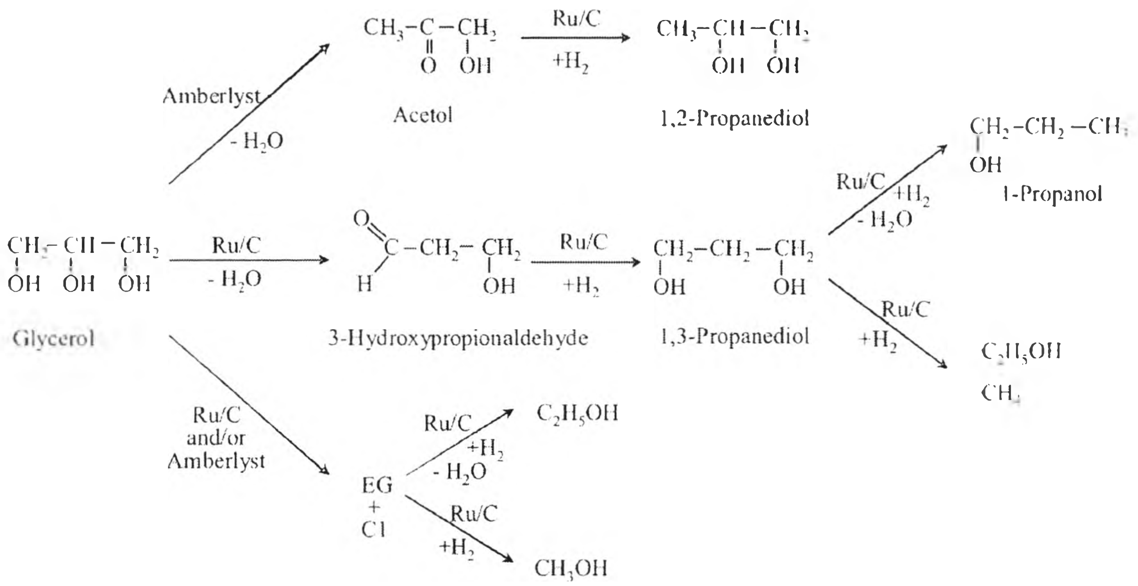


Figure 2.16 Reactionschemes of glycerol hydrogenolysis and degradation reactions (Miyazawa *et al.*, 2006).

During the hydrogenolysis reaction, the activity of the metal catalyst when combined with the cation exchang eresin can be related to that of 1-hydroxyacetone hydrogenation over the metal catalysts. In addition, the OH group on Ru/C can also catalyze the dehydration of glycerol to 3-hydroxypropionaldehyde, which ultimately can be converted into 1,3-propanediol and other degradation products through subsequent hydrogenation. From these results Ru/C + H_2SO_4 showed lower activity than combined Ru/C+Amberlyst, suggesting that the solid acid was more effective for the hydrogenolysis of glycerol.

Wang *et al.* (2007) studied the hydrogenolysis of glycerol to propylene glycol over Cu/ZnO catalysts at 473 K and 4.2 MPa H_2 pressure. Glycerol conversion and selectivity depend on Cu and ZnO particle sizes. Smaller ZnO and Cu domains led to higher conversion and propylene glycol selectivity, respectively. A high propylene glycol selectivity (83.6%) was achieved at 22.5% glycerol conversion with Cu/ZnO atomic ratio of 1. These catalysts possess acid and hydrogenation sites required for bifunctional glycerol reaction pathways. The pathways may involve glycerol dehydration to dehydrated intermediates on acid sites of ZnO surfaces, followed by hydrogenation of the intermediates on Cu surfaces, as shown in Figure 2.17, where the two proposed dehydrated intermediates were acetol (1-hydroxyacetone) and glycidol (3-hydroxy-1,2-epoxypropane).

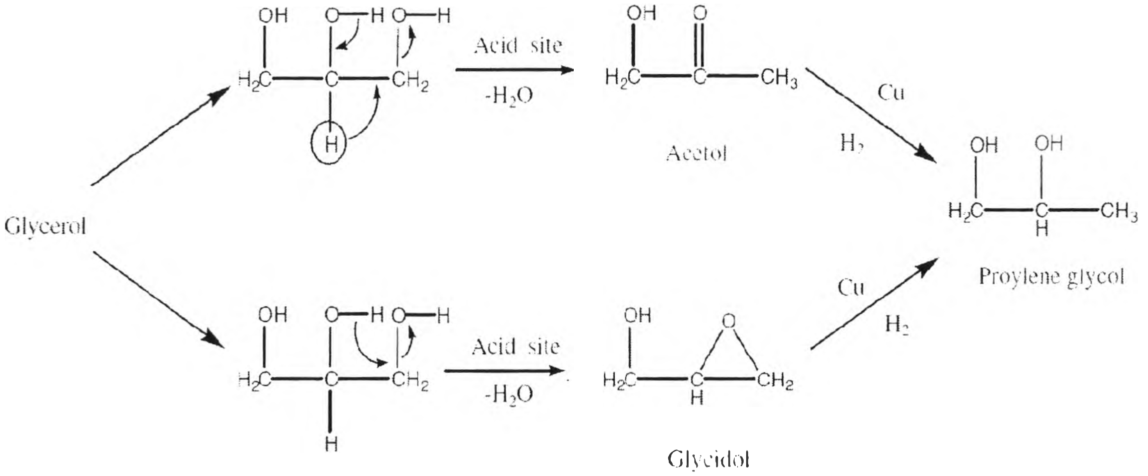


Figure 2.17 Proposed bifunctional glycerol hydrogenolysis reaction pathways (Wang *et al.*, 2007).

The effect of support and catalyst reduction temperature on the catalytic performance of Ru catalysts in the hydrogenolysis of glycerol was investigated (Feng*et al.*, 2008). The support material affected the metal particle size and the reaction route. Among the tested catalysts, including Ru/SiO$_2$, Ru/NaY, Ru/γ–Al$_2$O$_3$, Ru/C, and Ru/TiO$_2$, the TiO$_2$ supported catalyst showed high activity giving the highest conversion of glycerol (90%); however, Ru/TiO$_2$ catalyst favored the production of ethylene glycol over 1,2-propanediol under the tested conditions (453 K, 5 MPa). In contrast, Ru/SiO$_2$ showed the lowest activity, but resulted in much higher selectivity to 1,2-propanediol than that of ethylene glycol. It was well consistent with the mean Ru particle size of the catalyst in the order of Ru/SiO$_2$ > Ru/NaY > Ru/γ-Al$_2$O$_3$ > Ru/C > Ru/TiO$_2$. This indicated that the hydrogenolysis of glycerol was more active on small metal particles. The reaction route involved a reversible dehydrogenation of glycerol to glyceraldehyde, followed by dehydration and/or retro-aldorization of glyceroldehyde to 2-hydroxyacrolein and/or glycolaldehyde, and finally, the two glycol precursors are hydrogenated to 1,2-

propanediol and ethylene glycol, respectively. Under the same reaction conditions, SiO_2 or $\gamma-Al_2O_3$ favored the dehydration route over the retro-aldolization route, leading to higher selectivity to 1,2-propanediol than that of ethylene glycol. In contrast, TiO_2 was in favor of the retro-aldolization route, resulting in higher selectivity to ethylene glycol. The reaction routes were shown in Figure 2.18.

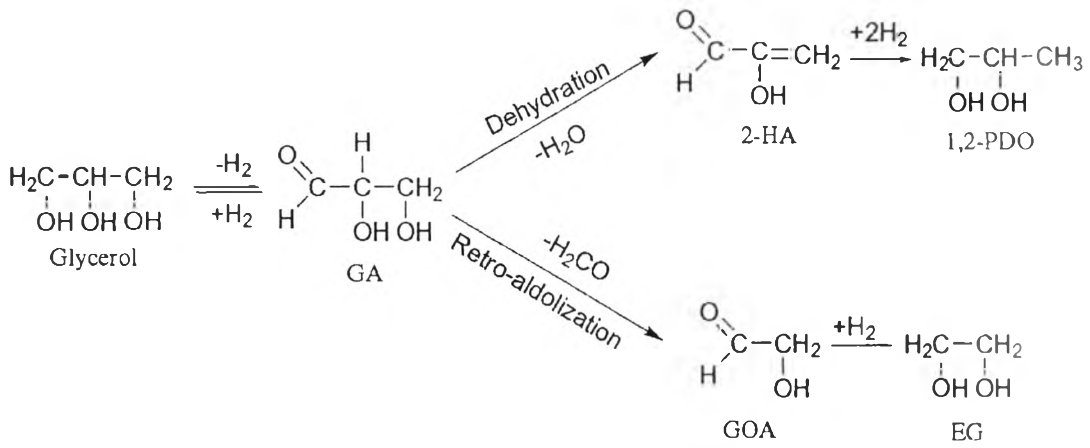


Figure 2.18 Reaction route for the hydrogenolysis of glycerol to glycols (Feng*et al.*, 2008).

The reaction activity of TiO_2-supported catalyst decreased with increasing catalyst reduction temperature, which was attributed to two reasons: (1) the growth in Ru particle size caused by heating treatment; and (2) the strong metal-support interaction (SMSI), which resulted in partial coverage of Ru metal particles by Ti_2O_3 species.

Sitthisa *et al.* (2007) investigated the dehydroxylation reaction at 523 K and 3.4 MPa H_2 pressure using 10% Cu/Al_2O_3 as a catalyst. The results showed that 100% conversion and 90% selectivity were obtained. However, the conversion dropped drastically after 6 h. Swangkotchakorn *et al.* (2008) introduced ZnO into Cu/Al_2O_3 catalyst and found that the addition of ZnO could prolong the stability of the catalyst by reducing the metal-support interaction to form aluminum copper, which may be the cause of catalyst deactivation. In addition, ZnO hindered the grain growth of CuO (El-Shobaky *et al.*, 1999), leading to higher dispersion of copper phase.

Chirddilok*et al.* (2009) reported that the Cu-ZnO/Al_2O_3 catalyst showed the best catalytic activity compared with Cu/Al_2O_3 and Cu/ZnO catalysts. The presence of ZnO facilitates the reduction of Cu to the lower temperature. This behavior was attributed to the highly dispersed CuO species present on the catalyst. The maximum activity was obtained for the catalyst calcined at 773 K. When compared with the catalyst prepared by co-precipitation, the stability of the impregnated catalyst was lower than the co-precipitated catalyst.The BET surface area indicated that the high performance of the catalyst can be ascribed to the higher surface area, and the better performance of the co-precipitated catalyst might be attributed to the presence of CuO highly dispersed in spinel-like matrix.

Panyad *et al.* (2011) concluded that the Cu–ZnO/Al_2O_3 catalyst prepared by the IWI method exhibited the highest catalytic activity and stability as compared to theones prepared by the SG and COP methods. The XRD, TPO and TPR results indicated that the causes of catalyst deactivation were the combination of coke formation and sintering of active copper metals. The Cu–ZnO/Al_2O_3 (SG) catalyst exhibited the lowest stability in terms of the highest Cu leaching. It was found that coke formation and sintering of Cu had more influence in suppressing the catalytic activity, compared to the Cu leaching.

2.7 Preparation of Supported Metal Catalysts

Supported metal oxide comprises a large class of catalytic materials used in numerous industrial processes. There are conventional approaches to preparing these materials. The methods that have found wide use (including industrial use) are impregnation and co-precipitation.

In the last two decades, the greatest progress has been made in the sol–gel preparation of dispersed single component and multi component systems by the hydrolysis of solutions of metal alkoxides and in the synthesis of new, so-called mesophase mesoporous materials (Pakhomov and Buyanov, 2005).

2.7.1 Impregnation

Impregnation is a preparation technique in which a solution of the precursor of the active phase is brought in contact with the support. Two methodologies exist. In dry impregnation, also referred to as "pore volume impregnation", just enough liquid (solution of the precursors) is used to fill the pore volume of the support. In wet impregnation, the support is dipped into an excess quantity of solution containing the precursor(s) of the impregnated phase. In dry impregnation, the solubility of the catalyst precursors and the pore volume of the support determine the maximum loading available each time of impregnation. If a high loading is needed, successive impregnations (and heat treatments) may be necessary. When several precursors are present simultaneously in the impregnation solution, the impregnation is called "co-impregnation" (Anderson and Garcia, 2005).

2.7.2 Precipitation

Co-precipitation differs from the other methods significantly. It is a method by which a solid is precipitated from a solution containing soluble precursors of both the support and surface oxides. Nucleation of the solid phase is initiated by mixing the solution with precipitating agent that either (1) change the solution pH and leads to precursor condensation to form oxide or hydroxides, or (2) " introduces additional ions into the system by which the solubility product for a certain precipitates is exceeded" (Schüth and Unger, 1997). Filtration and washing of counterions from the precipitate yield the final solid. The resultant architecture of the coprecipitated binary framework is more spatially distributed than a restrict supported metal oxide material prepared by the above methods. The distinct structure allows for better interaction between support and active species but also results in partial exclusion of the active species from the surface, rendering it inaccessible for catalysis. Surface density calculations for resulting materials thus overestimate actual value.

Inverse co-precipitation offers an improved alternative to co-precipitation. A limitation for co-precipitation is that the support and metal oxide precursors are unlikely to share similar solubilities (i.e., solubility products). Consequently, dropwise addition of a precipitating agent generates solids dominated by the more insoluble precursor during early stages and rich in the latter precursor at late stages. This gives rise to temporal-spatially inhomogeneous compositions. By contrast, inverse co-precipitation adds the precursor mixture dropwise to an excess of precipitating agent, this approach ensures that a strict ratio of precursors is maintained throughout the course of batchwise addition and leads to better co-precipitate homogeneity.

Tanaka *et al.* (2003) optimized a composition of Cu-ZnO/Al_2O_3 catalysts prepared by the impregnation method for water gas shift reaction (WGSR) coupled with CO oxidation in the reformed gas.The optimum composition of the impregnated catalyst for high WGSR activity was 5 wt. % Cu/5 wt.% ZnO/Al_2O_3. The optimum loading amounts of Cu and ZnO in the impregnated catalyst were smaller than those in the coprecipitated catalyst. Its catalytic activity above 473 K was comparable to that of the conventional coprecipitated Cu-ZnO/Al_2O_3 catalyst. However, the activity of the impregnated Cu-ZnO/Al_2O_3 catalysts was significantly lowered at 423 K, whereas no deactivation was observed for the co-precipitated catalyst at the same temperature. It was found that deactivation occurred over impregnated catalysts with H_2O and/or O_2 in the reaction gas; it prevented CO adsorption on the surface.

2.7.3 Sol–Gel Method

The sol–gel process involves first the formation of a sol followed by that of a gel. A sol, which is a liquid suspension of solid particles ranging in size from 1 nm to 1 micron, can be obtained by the hydrolysis and partial condensation of a precursor such as an inorganic salt or a metal alkoxide. The further condensation of sol particles into a three-dimensional network produces a gel, which is a material with a solid encapsulating a solvent. Alternatively, a gel can be produced by destabilizing a solution of preformed sols. In either case the materials are referred to aquasol (or aquagel) when water is used as a solvent, and alcosol (or alcogel) when alcohol is used. The encapsulated liquid can be removed from a gel by either evaporative drying or drying with supercritical extraction (supercritical drying for short). The resulting solid products are known as a xerogel and an aerogel, respectively. The four key steps in taking a precursor to a particular product from via sol–gel preparation: formation of a gel, aging of a gel, removal of solvent, and heat treatment are showed in Figure 2.19.

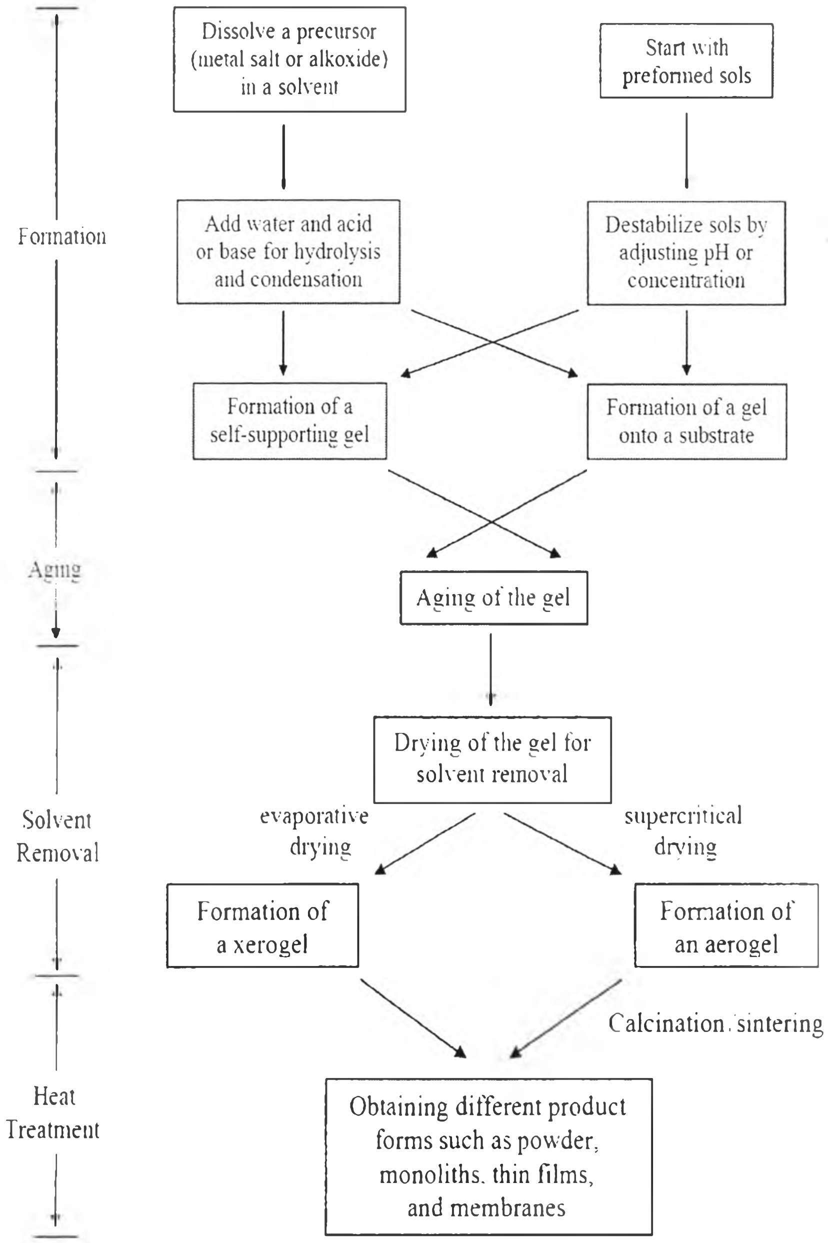


Figure 2.19 schematic diagrams showing the various steps of a sol–gel process (Ertl *et al.*, 1999).

The precursor in a sol–gel preparation can either be a metal salt/alkoxide dissolved in an appropriate solvent or a stable colloidal suspension of preformed sols. Metal alkoxides have been the most extensively used because they are commercially available in high purity and their solution chemistry has been documented. Alkoxides have the following advantages over inorganic precursors (Pakhomov and Buyanov, 2005):

(i) high purity of the precursor and final products;

(ii) reliable control of the process parameters determining the final structure of the alkogel and its properties;

(iii) uniformity of the chemical. physical, and morphological properties of the product;

(iv) mixing of the components at the molecular level;

(v) possibility of preparing samples at low temperatures;

(vi) possibility of introducing a variety of components in one step; and

(vii) possibility of controlling the reaction kinetics and stabilizing metastable systems.

Takeishi and Yamamoto (2007) patented the preparation method of copper alumina catalysts for dimethyl ether steam reforming (hydrogen production) by impregnation and sol–gel method. The results showed that. in an impregnation method in which a carrier made of alumina is impregnated in a catalyst metal solution to support a catalyst metal, a catalyst metal is supported only on the surface of a catalyst layer, showing poor dispersion. Furthermore, in the impregnation method. decrease in reforming ability is a caused sometimes by sintering of an active metal by heat. In contrast, the catalyst prepared by sol–gel method has a feature that catalyst metal is highly dispersed and is not easily sintered. Furthermore, by inclusion of Mn, Fe, or Zn. Copper being active in dimethyl ether steam reforming reaction can be increasingly dispersed and highly active Cu and Cu^+ can be kept stable. By this, an excellent reforming ability can be obtained even at low temperatures such as 473 K to 548 K, at which a reaction does not occur easily with a normal catalyst. A catalyst prepared by a sol–gel method can have a large pore diameter without reducing the specific surface area by inclusion of Mn, Fe, and/or Zn. Pores of 80 Å to 200 Å are most suitable for dimethyl ether reforming and can provide an excellent reforming ability even at low temperatures.

2.8 Types of Glycerol

Glycerol naturally occurs during the biodiesel production process and is specifically produced in the transesterification process. The glycerol produced at this stage is crude glycerol and is about 80% pure still containing contaminants like soap, methanol and water. In order to turn this crude glycerol into a usable state for existing or emerging uses, a purification process must take place. During this refinement process residual organic matter, water, salt, methanol, and odors are removed. There are many different types of glycerol grades ranging from crude glycerol, technical, yellow glycerol to refined glycerol.

2.9 Catalyst Deactivation

The mechanisms of catalyst deactivation can be grouped into six mechanisms of catalyst decay (Bartholomew, 2001). The causes of deactivation are basically three-fold: chemical, mechanical, and thermal. Each of the six basic mechanisms is defined in Table 2.2.

Table 2.2 Mechanisms of catalyst deactivation (Bartholomew, 2001)

Mechanism	Type	Brief definition/description
Poisoning	Chemical	Strong chemisorption of species on catalytic sites, thereby blocking sites for catalytic reaction
Fouling	Mechanical	Physical deposition of species from fluid phase onto the catalytic surface and in catalyst pores
Thermal degradation	Thermal	Thermally induced loss of catalytic surface area, support area, and active phase–support reactions
Vapor formation	Chemical	Reaction of gas with catalyst phase to produce volatile compound
Vapor–solid and solid–solid reactions	Chemical	Reaction of fluid, support, or promoter with catalytic phase to produce inactive phase
Attrition/crushing	Mechanical	Loss of catalytic material due to abrasion Loss of internal surface area due to mechanical-induced crushing of the catalyst particle